III-2

Materials Sciences



BL6U



Angle-resolved Photoelectron Spectroscopic Study of TiSe₂ using a Newly Developed Software for the Momentum Microscope Apparatus

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1T-TiSe₂ is one of the transition metal dicalchogenides (TMDC). Among TMDCs, TiSe₂ is quite interesting because it exhibits a unique charge-density-wave transition at T_c of ~200K into the (2x2x2) 3D superstructure despite the quasi-2D character of the TMDC. Currently, for the investigation of TiSe₂, we are developing a new software for the analysis and presentation of the data obtained with a new momentum microscope apparatus. In this report, we demonstrate some of ARPES results of the TiSe₂ at the room temperature taken using the new software.

The software is written with the Python language with the help of some open-source libraries and additional software; e.g., "PyQtgraph", "Mayavi", "OpenCV", "vtk", "Paraview". The software can be operated in multiple OS's; such as Windows-10, Mac-OS, and Linux. Fig.1 (a) shows the stereogram picture of the ARPES volume map of TiSe₂ taken at hv=80eV. In fact, the stereogram is created by using "Paraview"

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which is well-known free software for a scientific visualization. We only prepare the input file for "Paraview" by transforming the ARPES data into the "vtk" format, which is standard as the 3D format. The usage of this sort of well-established software and format gives us advantages in many aspects including cutting the development time, and a convenience for an additional transformation, etc. Figures 1(b)-(d) are intensity maps in the 2D-cut indicated by the black lines in Fig. 1(a). These maps can be easily provided, thanks to our new program together with the "PyQtGraph" library, at any lines in the volume. The two momentum distribution curves and an energy distribution curve are also automatically created (not shown here).

We are progressing the investigation of the TiSe₂ by using the momentum microscope with the help of the new software.

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Fig. 1. ARPES volume maps of $TiSe_2$ at room temperature. The photon energy used is 80 eV. (a) : stereogram of the whole volume map, (b)-(d): intensity maps in 2D-cut along the black lines shown in (a).

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Crystallinity Evaluation of Gd₃Al₂Ga₃O₁₂:Ce Crystals Grown by Cz and µ-PD Methods Using Gamma-ray-induced Positron Annihilation Lifetime Spectroscopy and High-Resolution UV Absorption Spectroscopy

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The Czochralski (Cz) method is well-known to be a conventional technique to grow crystals from hightemperature melt [1]. The Cz method enables us to obtain large size crystals of high quality. Because the growth rate is not so high, it generally takes time to grow crystals. The micro-pulling down (µ-PD) method is a melt-growth technique similarity to the Cz method [2]. There are a number of advantages for the u-PD method: (i) The growth rate is relatively high, (ii) the effective doping of impurities is possible, and (iii) the crystal shape is controllable. The µ-PD method is suitable for the screening test in the development of functional crystalline materials. In comparison between the Cz and µ-PD methods, it has generally been believed that the crystallinity of Cz grown crystals are better than that of μ -PD grown crystals. However, to our knowledge, no comparison on crystallinity between the Cz and µ-PD methods has not yet been carried out. In the present study, we have investigated the existence of vacancy type defects and the local structures of Gd atoms in Cz and μ -PD grown Gd₃Al₂Ga₃O₁₂:Ce (GAGG:Ce) crystals by gamma-rayinduced positron annihilation lifetime spectroscopy (GiPALS), and UV and absorption spectroscopy, respectively. GiPALS experiment was performed at the BL1U. High resolution UV absorption spectroscopy were conducted at the BL7B, respectively.

The results of GiPALS analysis are shown in Table I. The data for the Cz crystal were reported [3]. The lifetimes for the μ -PD crystal are longer than those for the Cz crystal. The bulk lifetime was calculated to be 167 ps for GAGG [4]. This value was the same as the bulk lifetime for the Cz crystal, but did not agree with that (=200 ps) for the μ -PD crystal. It is likely that the μ -PD crystal includes cation vacancies of high concentration, compared to the Cz crystal. The defect lifetime for the μ -PD crystal is longer than that for the Cz crystal, indicating that vacancy clusters are formed in the μ -PD crystal.

A number of peaks are observed in UV absorption spectra for GAGG:Ce crystals [5]. These peaks were assigned to the ${}^{8}S_{7/2} \rightarrow {}^{6}P_{7/2}$, ${}^{6}P_{5/2}$ and ${}^{6}P_{3/2}$ transitions in the (4f)⁷ configuration of a Gd³⁺ ion. Because the peak position and full-width-half-maximum (FWHM) are sensitive for the local structure of Gd atoms, they can

be used as a simple probe to see the change in environment around the Gd atoms. The ${}^{8}S_{7/2} \rightarrow {}^{6}P_{3/2}$ peak consisted of two subpeaks resulting from the Stark effect [6]. The peak positions and FWHM were evaluated by curve-fit analysis assuming the sum of two Lorentz functions. The results are listed in Table II. No differences are found between the Cz and μ -PD crystals. Detailed structural studies based on a single crystal X-ray diffraction (XRD) measurement will be performed to obtain more sophisticated information on the structure of the GAGG:Ce crystals.

Table I: Lifetimes and relative intensities determined by GiPALS analysis for the Cz and μ -PD crystals.

	Lifetime (ps)	Relative intensity (%)
$C_{7}[3]$	161 ± 1.5	92.4 ± 3.7
CZ	304 ± 19	7.6 ± 3.7
	198 ± 1.1	98.45 ± 0.21
μ-PD	625 ± 36	1.55 ± 0.21

Table II: Peak positions and FWHM of the Gd^{3+ 8}S_{7/2} \rightarrow ⁶P_{3/2} absorption peak for the Cz and µ-PD crystals.

r = 3/2							
	Peak position (nm)	FWHM (nm)					
C-	301.43	0.20					
CZ	301.65	0.21					
	301.42	0.19					
μ-ΡD	301.64	0.18					

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BL1U

Vacancy-Type Defect in Mg₂Sn Crystals Studied by Gamma-Ray-Induced Positron Annihilation Lifetime Spectroscopy

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Thermoelectric (TE) materials attract much attention because they can directly convert waste heat into electricity. Exploration of TE materials is significant to secure energy resources in future. Intermetallic compounds are one of the promising candidates that can be applied to TE materials. Magnesium stannate (Mg₂Sn) has been studied for the TE application. The control of point defects such as vacancies and interstitials is crucial for this purpose, because they influence the carrier concentration and thermal conductivity included in the expression of the dimensionless figure of merit. Recently, an analysis of point defects was performed to reveal the relationship between point defects and TE properties [1]. Primary point defects in Mg₂Sn were Mg vacancies at the 8c site (V_{Mg}) and Mg interstitials at the 4b site (Mg_i), which generated valence holes and conduction electrons, respectively, by ionization of acceptors and donors. Saito *et al.* succeeded in observing the existence of V_{Mg} defects by a transmission electron microscope (TEM), and confirmed by an inductively coupled plasma mass spectroscopy. Furthermore, they demonstrated that the TE properties of Mg₂Sn are optimized by adjusting the fraction of V_{Mg}. It is therefore meaningful to evaluate the fraction of V_{Mg} quantitatively. In the present study, we have measured gamma-ray-induced positron annihilation lifetime spectroscopy (GiPALS) spectra of Mg₂Sn crystals grown under various conditions. Experiment was performed at the beamline 1U in UVSOR synchrotron facility. Details of GiPALS experiment were described in Ref. [2].

Figure 1 shows the GiPALS spectrum of the Mg₂Sn crystal grown from high-temperature melt under an Ar atmosphere of 0.6 atm. The data was obtained at room temperature. The GiPALS spectrum is of an exponential decay component with the lifetime of 255 ps. We performed a first-principles calculation using the ABINIT [3,4], to determine the positron annihilation lifetime at the bulk state (bulk lifetime) which means the crystal lattice without vacancy-type defects. The bulk lifetime was calculated 257 ps. This value is in good agreement with the lifetime determined from an curve fit analysis of the GiPALS spectrum. It is likely to assign this component to the positron annihilation at the bulk state.

In Ref. [1], the fraction of V_{Mg} was estimated 5.6 % by single crystal x-ray diffraction (SC-XRD). The

average size of V_{Mg} defects was also estimated 11 nm. Figure 1 revealed that only a bulk component appears in the GiPALS spectrum. This result does not mean that V_{Mg} defects are not included in the Mg₂Sn crystal investigated here, because GiPALS is silent for the existence of vacancies with the radii larger than a few nm [5]. The missing of defect components in the GiPALS spectrum is consistent with the result of SC-XRD analysis.



Fig. 1. GiPALS spectrum of a Mg₂Sn crystal, measured at room temperature.

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In-situ Observation of Oxygen Vacancy in CeO₂ Using Gamma-ray Induced Positron Annihilation Spectroscopy

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CeO₂ has been extensively studied as a heterogeneous catalyst for automotive exhaust gas purification, CO oxidation, and VOC oxidation reactions. Such catalytic activity of CeO₂ is due to the redox property of Ce⁴⁺/Ce³⁺ and the associated formation of oxygen vacancies. Recently, it is reported that the existence of oxygen vacancies, especially oxygen vacancy clusters of CeO₂ surface is a key role for the oxidation reactions with molecular oxygen as an oxidant. The gaseous oxygen can be adsorbed and activated on the oxygen vacancy clusters of CeO₂ surface, resulting in the formation of active oxygen species and high catalytic activity [1].

On the other hand, positron annihilation spectroscopy (PAS) is a well-known method to detect lattice defects with high sensitivity. Among positron annihilation spectroscopy, gamma-ray induced positron annihilation spectroscopy (Gi-PAS) is an ultimate method to have the following features. 1) Since positrons could be generate inside a sample and observe their annihilation process, making it possible to perform measurements under harsh conditions such as high temperatures and/or high pressures. 2) In addition, the positron lifetime spectrum does not include the source component, which allows for detailed discussion of a positron lifetime [2].

In this study, we performed in-situ observation of oxygen vacancies in CeO_2 at a high temperature using Gi-PAS.

We have set up a gamma-ray spectroscopy system at the laser-Compton scattering (LCS) beamline of BL1U at UVSOR-III [3], and measured the lifetime of the annihilation gamma-rays at room temperature and $300 \,^{\circ}$ C using BaF₂ scintillation detector. We used the software Lifetime9 (LT9) to analyze the spectra.

Figure 1 shows the positron annihilation lifetime spectra of CeO₂ measured at room temperature and 300 °C. The positron annihilation lifetime and relative intensity analyzed using LT9 are also listed in Table 1. The lifetime of the positron annihilation is able to give information about the size, type and relative concentration of defects/vacancies. The positron annihilation lifetime spectra of CeO₂ at room temperature and 300 °C yielded two distinct lifetime components, τ_1 and τ_2 with relative intensities I_1 ($I_1 = 100 - I_2$) and I_2 . At both temperatures, the lifetimes (τ_1 and τ_2) were almost the same, however the relative intensities (I_1 and I_2) were different: I_2 for 300 °C was larger than that for room temperature. Wang *et al.*

reported that molecular oxygen adsorbed on the oxygen vacancy clusters of CeO₂ surface desorbed at around 150 °C and lattice oxygen atoms of CeO₂ surfaces desorbed at around 450 °C [4]. Taking into this consideration, the result obtained in this study, i.e., the larger I_2 at 300 °C, is considered to be due to the desorption of oxygen molecules adsorbed on the oxygen vacancy clusters on the CeO₂ surface. In the next fiscal year, we will investigate the temperature and atmosphere dependence about the behavior of the oxygen vacancies of CeO₂ surface in detail.



Fig. 1. Positron annihilation lifetime spectra of CeO_2 measured at room temperature and 300 °C

Table 1 Positron annihilation lifetime and relative intensity of CeO₂.

	5	=		
	Temp.	τ_1 (ps)	τ_2 (ps)	I_2 (%)
	R.T.	206.5 ± 1.7	489.0 ± 14	17.1 ± 3.0
	300 °C	204.0 ± 3.3	490.0 ± 8.8	25.5 ± 1.0
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Existence of Shallow Donor in Mg₂Si Crystals Revealed by Terahertz Absorption Spectroscopy

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Magnesium silicide (Mg₂Si) is known to be a semiconductor which has the fundamental absorption of an indirect transition type. The fundamental absorption edge locates at around 0.6 eV. Because Mg2Si can responds to the infrared (IR) light with photon energies above 0.61 eV, this material is expected to be a plausible candidate for the application of an IR photodetector. Mg₂Si shows n-type conductivity without incorporating impurities. This is because an interstitial Mg atom at the 4b site works as an intrinsic donor [1]. Electrical properties of Mg₂Si crystals have been reported so far [2]. The existence of shallow donors with the activation energy of 8-9 meV was suggested in Mg2Si crystals with the carrier density of 1015 cm-3 order. Although the Mg₂Si crystals were grown from high purity Mg and Si sources, they contained various impurities. Thus, it still remains unclear whether such shallow donors are associated with interstitial Mg atoms. Terahertz absorption spectroscopy is an experimental technique to explore the existence of shallow donors in solids. Practically, the existence of shallow donors in Si crystals has been found so far [3]. In the present study, we have carried out terahertz absorption spectroscopy for undoped Mg₂Si crystals to find the existence of shallow donors.

Mg₂Si crystals were grown from high-temperature melt in Ar atmosphere by a vertical Bridgeman furnace. Experiment was performed at the beamline BL1B. The carrier concentration of the sample used in this work was determined to be 4.3×1015 cm-3 by a Hall-effect measurement. The terahertz absorption spectra of an undoped Mg₂Si crystal is shown in Fig. 1. The data were obtained at 5 K. Two prominent peaks appear at 58 and 66 cm⁻¹. These peaks were weakened under irradiation with 800 nm photons from a Ti:Sa laser. Furthermore, the two peaks were weakened with increasing temperature, and disappeared around 20 K. The temperature dependence of the two peaks was analyzed by assuming a simple model that a donor creates a conduction electron. The activation energy for the donor originating in the two peaks was 7-8 meV, in good agreement with that determined from the temperature dependence of the carrier concentration [2]. It is therefore reasonable to assign the origin of the two peaks to shallow donors in Mg₂Si. The weakening of the two peaks by photoirradiation result is explained as photoionization of shallow donors. Now, we are

investigating experimentally and theoretically whether such shallow donors are formed by interstitial Mg atoms.



Fig. 1 Terahertz absorption spectra of an undoped Mg₂Si crystal, measured at 5 K under non-irradiation (blue) and irradiation (red) with 800 nm photons from a Ti:Sa laser.

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Electron-Irradiation Effects on Germanium

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Polycrystalline germanium (poly-Ge) is attractive as a material for three-dimensional integrated circuits owing to its high mobilities for both electrons and holes and its lower melting temperature than Si at approximately 450 °C. However, a large number of holes are generated in poly-Ge film because of crystal defects; hence, identification of the origin of the acceptors in poly-Ge is an important consideration.

As Ge has a high dielectric constant, the energy levels of the acceptors are expected to be shallow in Ge, similar to other group-III impurities; hence, the BL1B line of UVSOR is suitable for detecting defects attributable to the acceptors. In our previous research, we used electron irradiation (e-irradiation) to introduce vacancies and self-interstitials in bulk p-type [Indium (In)-doped] Ge samples of 2.0 mm thickness and 12 Ω ·cm resistivity; we observed that e-irradiation introduces donors that are eliminated at temperatures of 400 °C [1]. However, the main peaks (lines C and D [2. 3]) of the In acceptor were saturated owing to the high In concentration. Thus, we used the satellite peak referred to as line G to obtain the above results [1].

In the present work, we used low-In-content bulk Ge samples (33 $\Omega \cdot cm$) and high e-irradiation of 4.5 MeV and 6×10^{15} cm⁻². Following this, the samples were annealed at 100, 200, 300, and 400 °C for 30 min in a conventional furnace system to evaluate the changes to the spectra. The optical transmission spectra were measured at liquid He temperature using BL1B.

Figure 1 shows the spectra of as-grown and asirradiated samples, along with samples annealed at 100, 200, 300, and 400 °C. The intensities of the lines corresponding to the In acceptor (lines C and D) decreased after e-irradiation, but began recovering to those of the as-grown sample when the annealing temperature increased to 400 °C. Figure 2 shows the variations in the peak intensities of lines C and G, which were normalized by those of as-grown Ge. Variation in the intensity of line G was obtained from the experimental results of Ref. [1], which indicates that e-irradiation introduces donor defects but eliminates at 400 °C.

In general, it is believed that e-irradiation introduces simple structural defects, such as vacancies, selfinterstitials, and their aggregates. However, acceptors are generated in poly-Ge thin films crystallized at 500 °C. The difference in thermal stability between the e-irradiation-induced defects and acceptors in poly-Ge indicates that the acceptors in poly-Ge films are not simple defects, such as those introduced by eirradiation.

In summary, the optical transmission spectra of eirradiated Ge were measured at liquid He temperatures, and it was observed that e-irradiation generates donors that are eliminated at temperatures of 400 °C. The difference in thermal stability between the e-irradiation defects and acceptors in poly-Ge thin films clearly indicates that the origins of these two types of defects are different.



Fig. 1. Transmission spectra of e-irradiated p-type Ge



Fig. 2. Annealing dependencies of lines C and G. The plot of line G was obtained from Ref. [1].

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Formation of Catalytically Active MoC_x Species during Methane Dehydroaromatization over Mo-V Co-Modified H-MFI Zeolites

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A Molybdenum-modified H-MFI zeolite (Mo/ H-MFI) catalyst is a typical GTL (Gas To Liquid) catalyst for methane dehydroaromatization. The reaction socalled MTB (Methane To Benzene) one is valuable for direct conversion from natural gases to useful petroleum compounds. Over the Mo/H-MFI catalysts, definite deactivation due to coke deposition has been a serious problem for enhancement of MTB reactivity, and thus, clarification of the deactivation process over the catalysts is one of the important points. A cause of the deactivation is based on coke deposition on strong acid sites over H-MFI and structural deactivation on carbonized Mo species. Thus, clarification of active Mo sites with high and durable activity for methane dehydrogenation is one of the most important subjects. In the present study, Mo L_{III}-edge XANES is applied to characterize the active Mo-carbide species on Mo/H-MFI and Mo-V co-modified H-MFI.

Mo(5wt%)/H-MFI and Mo-V/H-MFI (Mo/V=10) catalysts were prepared by impregnation of H-MFI, and followed by drying overnight and calcination at 773 K. The methane dehydroaromatization reactivity was evaluated at 1023 K as described in a previous report.[1, 2] Mo L_{III}-edge XANES spectra were obtained in BL2A of UVSOR-IMS in a total-electron yield mode using InSb double-crystal monochromator. REX-2000 (Rigaku) software were used for normalization of each XANES spectra.

For L-edge XANES spectra over Mo/H-MFI catalysts (on time course of the MTB reaction) as shown in Fig. 1, the active Mo species in both Mo/H-MFI and Mo/-V/H-MFI are due to more deeply carbonized species than α -Mo₂C. It suggests the formation of MoC_x (x > 0.5) as an important species for high MTB reactily. By Mo-V co-modification on H-MFI, the carbonization to form active MoC_x species became faster. It indicates the formation of easily reduced Mo sites to form deeply carbonized species. For 185 minutes on the MTB reaction (during the deactivation), excess carbonization was inhibited by V co-modification as exhibited in the edge energy shown in Table 1. The result is likely to relate to a suppression effect of deactivation.

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Fig. 1. Mo L_{III}-edge XANES spectra of Mo/H-MFI (Si/Al₂=28) and Mo-V/H-MFI (Mo/V=10) catalysts after methane dehydroaromatization at 1023 K for 30 – 185 min. The references, α -Mo₂C and Mo metal, are also shown in each figure.

Table 1. Edge energy values obtained by 1st derivatives of $L_{\rm III}$ -edge XANES shown in Fig. 1.

Mo/H-MFI(28))	Mo-V/H-MFI	(Mo/V=10)
Time on	Edge Energy	Time on	Edge Energy
Stream / min.	/ eV	Stream / min.	/ eV
30	2521.36	30	2520.96
55	2520.86	55	2520.86
185	2520.48	185	2520.60
α-Mo ₂ C	2520.96	α-Mo₂C	2520.96
Mo Metal	2520.22	Mo Metal	2520.22

Local Environment of Heat Treated Ag-Doped PHI-Type Zeolite

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Zeolites are crystalline aluminosilicates which have nano-sized cavities in their crystal structures. Zeolite frameworks were classified into over 250 types by the international zeolite associations. [1] They have cation-exchange abilities due to their unique crystal structures. Ag-doped zeolites have attracted many researchers as rare-earth free phosphors. [2] They were prepared by ion-exchange in Ag⁺ aqueous solution and subsequent heat-treatments. In these processes, Ag nano-clusters were formed in zeolitic cavities and behave as luminescent center. In addition, some Agdoped zeolites are not stable at high temperature and become amorphous phases. [3]

In the present study, we investigated local environments of heat-treated Ag-doped PHI-type zeolite (Ag-PHI) using X-ray absorption near edge structure (XANES).

Ag-PHI samples were synthesized by ion-exchange and subsequent heat treatments. PHI-type zeolite was prepared by a hydrothermal method. The starting material was soaked in 0.1 mol/L of Ag(NO₃)₂ aqueous solution for 1 h under dark condition. The samples were washed by ion-exchanged water and dried at 50 °C in air. Then, they were heated at 450 °C and 700 °C for 4 h.

XANES spectra were collected by the partial fluorescent yield method using a silicon drift detector at BL2A in UVSOR. Fluorescence X-ray spectra were deconvoluted using gauss functions, which was reported elsewhere. [4] X-ray beam was monochromated by KTP double crystals for Al-K and InSb ones for Si-K and Ag- L_3 .

X-ray diffraction (XRD) patterns of the Ag-PHI heated at 450 °C have same features to the starting material. On the other hand, the samples heated at 700 °C gave amorphous pattern. No Ag compound were observed. It is noted that Ag nano-particles were not observed by scanning electron microscope either.

Al-*K* and Si-*K* XANES were measured in order to investigate the structure of the amorphous samples. The samples heated at 700 °C have the similar features to those of PHI-type zeolite and Ag-PHI heated at 450 °C. The features were different from those of typical glasses. These results indicated that samples heated at 700 °C were not a mere glass, but partially collapsed zeolite.

Figure 1 shows Ag- L_3 XANES of the Ag-PHI samples. The samples heated at 450 °C and 700 °C have same features. Their spectra were different from those of typical Ag compounds while the absorption edge of the samples agrees that of Ag foil. These results indicated that Ag in the samples were metallic, but it has different local environment from bulk Ag metal. They

were still maintained in the partially collapsed zeolites. It has been reported that some Ag-doped zeolite phosphors are affected by humidity. [5] Our results lead to new phosphors stable in air since partially collapsed zeolite lost continuous pores.



Fig. 1. Ag- L_3 XANES of Ag-doped PHI samples and references.

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Local Structure Investigations of Mg_{1-x}Ni_xAl₂O₄ by NEXAFS

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Spinel oxides with the general formula AB₂O₄ can be formed with various kinds of divalent A and trivalent B cations. Owing to their unique mechanical, electronic, and magnetic properties, the spinel oxides have gained considerable attention not only from the fundamental research fields but also from the industrial application point of view. Some spinel compounds accommodate a large degree of cationic disorder. The cationic disordering naturally affects the structural properties of the spinels. For example, magnesium aluminate (MgAl₂O₄) and nickel aluminate (NiAl₂O₄) spinels are generally known as normal and inverse spinel structures, respectively. However, their inversion degrees for synthetic specimens were also reported to be fluctuating between 0 and 1, respectively, due to the cationic disordering. Recently, the structure of Mg1-xNixAl2O4 was reported using neutron total scattering to understand the cationic disordering process [1]. X-ray absorption spectroscopy (XAS) is a powerful structure characterization method that uses an X-ray probe to reveal local atomic coordination and electronic structures. In this study, we focus on the local structures in MgAl₂O₄-NiAl₂O₄ solid solutions, particularly cationic-disordered structures.

The polycrystalline samples of Mg_{1-x}Ni_xAl₂O₄ (x = 0.0, 0.05, 0.2, 0.5, 0.8, 1.0) were synthesized by a solidstate reaction. They were sintered in air at 1300 °C for 10 h followed by furnace. Mg and Al *K*-edge XANES measurements were performed on BL2A beamline at UVSOR Synchrotron Facility, Okazaki, Japan, using the partial fluorescence yield method. A KTiOPO₄ doublecrystal monochromator gives Mg and Al *K*-absorption edges in the energy regions 1290 – 1340 eV and 1540 – 1610 eV, respectively. The measurements of Mg and Al *K*-edge XANES spectra were carried out in vacuum at a pressure and temperature of 1×10^{-4} Pa and 20 °C, respectively. Fluorescence X-rays of Mg K_{α} and Al K_{α} were collected utilizing an energy-dispersible silicon drift detector.

The Al *K*-edge XANES spectra for Mg_{1-x}Ni_xAl₂O₄ are shown in Fig. 1 with the composition values x = 0, 0.05, 0.2, 0.5, 0.8, and 1.0. The intensity of each spectrum was normalized to a value of 1 at the photon energy of 1588 eV after the removal of the background intensity. The spectral shapes of the Al *K*-edge XANES clearly changed depending on the Ni content *x* in Mg_{1-x}Ni_xAl₂O₄. It is seen that the identical peak appeared at the absorption edge as indicated by an arrow in Fig. 1, and its intensity increased with the increasing *x*. Alternatively, in the higher energy region, the large peak at 1579 eV broadened with the increasing *x* or Ni content. Such spectral changes suggest that the Al at tetrahedral sites increased with increasing Ni concentrations instead of Al at octahedral sites.



Fig. 1. Al K-edge XANES spectra of Mg_{1-x}Ni_xAl₂O₄.

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X-ray Absorption Fine Structure Measurements of Sulphur Chain Encapsuled in Carbon Nanotubes

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Chalcogen atoms are bonded with two-fold covalent bonds, and form rings or chains. They bind each other with inter-ring or inter-chain interactions. The chalcogen atoms form isolated chains within narrow space, such as, carbon nanotube, morodenite, and so on [1-3]. In this study, we are studying structure of sulfur chain in the CNT (S@CNT) with X-ray absorption fine structure (XAFS) measurements.

The XAFS measurements of crystalline S (c-S) and S@CNT were done at BL2A in UVSOR with total electron yield and SDD detectors. Intensity of incident X-ray were observed with Au or Cu meshes. Figure 1 shows spectrum of S@CNT with Au mesh. A sharp white line of S K-edge and XAFS oscillations were observed. Unfortunately, steps were observed around 2.5 and 2.9 keV. The steps may be brought about by monitoring of the intensity of the incident X-ray with Au mesh.

Figure 2 shows extended X-ray absorption fine structure (EXAFS) oscillations reduced from the spectrum of Fig. 1 with miXAFS code [4]. EXAFS oscillation is obtained. It contains steps around 8.5 and 11.5 A^{-1} , which correspond with the steps of Fig. 1.

Figure 3 shows Fourier transform of EXAFS oscillation to account for backscattering form factor, phase shift calculated with FEFF code. There is a main peak around 2.0 A, which is close to the covalent bond length of c-S. The position of the peak coincident with the covalent bond length of c-S. However, it is necessary to verify whether the peak position is coincidental because the correct EXAFS function is obtained, or whether they coincide by chance.

The EXAFS spectra were obtained, but the qualities were not sufficient for the EXAFS analysis to obtain the structural parameters, such as, interatomic distances, coordination numbers, and so on. To obtain the structure parameters of S@CNT much improvements may be required, such as, monitoring of the intensity of the incident X-ray, increment of the intensity above 3.0 keV.



Fig. 1. Spectrum of S K-edge for S@CNT.



Fig. 2. EXAFS oscillation of S@CNT.



Fig. 3. Fourier transform of EXAFS oscillation of S@CNT.

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BL3U

First Trial of Precise Analysis of Super-structures of Chiral Smectic Liquid Crystals by Resonant Soft X-ray Scattering (RSoXS) at UVSOR

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Smectic liquid crystals have one-dimensional positional order, so-called layer structures. In particular, chiral tilted chiral smectic phases have attracted much attention because molecular clinicity in neighboring layers influence the macroscopic polarity; ferroelectric and antiferroelectric order appears in synclinic and anticlinic structures, respectively. Furthermore, the successive phase transition between synclinic SmC* and anticlinic SmCA* is one of the most interesting subjects, in which the appearance of some subphases due to the competition between SmC* and SmCA* has been experimentally determined and the existence of further subphases has been theoretically predicted based on the long-range interlayer interaction and the frustration of clinicity (synclinic or anticlinic). Conventional X-ray diffraction is a powerful tool for studying the layer structure, but difficult to distinguish the difference of the clinicity because the electron density along the layer normal of left and right tilting molecules are the same.

This subject was resolved by resonant X-ray scattering. In this technique, by using X-ray whose energy is coincident with a certain atom absorption edge, the structure factor becomes a tensor instead of the scalar in conventional X-ray diffraction. As a result, scattering intensity is sensitive for the system symmetry, and also molecular orientation. In this technique, the structure analysis of tilted chiral phase has dramatically evolved. So far, however, sample compounds have to possess an atom with the same absorption energy as the used X-ray, and such atoms as sulphur, selenium, chlorine and bromine. Recently, carbon K edge resonant scattering has been applied to study, and successful in obtaining the precise structures of polymer blends, block copolymer, and liquid crystals. Hence this time we tried to perform this technique, and to investigate the precise structures of chiral liqud crystals.

The experiment was performed at BL3U of UVSOR (Okazaki). For the measurement, a new vacuum chamber was created, as shown in Fig. 1. Liquid crystals was filled in the isotropic phase between two pieces of 100 nm-thick Si_3N_4 membranes (NTT-AT). The scattering was detected by CCD (ANDOR DO940P-BN). Incident X-ray beam was tuned between 270~300 eV. Typical absorption spectrum was shown in inset of Fig.1; in this compound, carbon K-edge energy is 286 eV.

Figure 2 shows the first obtained results of RSoXS. When the incident energy E_0 is 285 eV(a), clear scattering

peaks are observed at wider angle, while these peaks disappear at $E_0=270$ eV. Center position of two peaks just corresponds to twice of the fundamental layer spacing of this chiral smectic SmCA* phase, which proves the anticlinic bilayer structure. Furthermore, two resonant peaks comes from the macroscopic helical structure of SmCA*, and splitting width corresponds to ca. 250 nm, which is coincident with the obtained helical pitch from the optical measurement.



Fig. 1. Photo of experimental setup & absorption spectrum of chiral liquid crystals.



Fig. 2. Schematic image of experimental geometry(a), and obtained 2D scattering image at E0=285 eV(on resonance) (b) and E0=270 eV(off resonance)(c).

BL3B

Intrinsic Luminescence from Self-trapped Excitons in BaMBe₂(BO₃)₂F₂ (M=Mg,Ca) Crystals with Two-dimensional Single Layers upon VUV Excitation

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Mixed anion compounds have gained increasing attention recently from the point of view of their increased degree of freedom regarding parameters such as electric charge, electronegativity, polarizability, and orbital energy, arising from the coordinated anions. The formation energy and luminescence properties of excitons are considered to depend on the degree of twodimensionality or two-dimensional modulation. To date, very little research has focused on the formation of selftrapped excitons (STEs) in terms of the dimensionality and modulation of the structure. Fluorine-beryllium borates $BaMBe_2(BO_3)_2F_2$ (M = Mg, Ca) have a layered structure which consists of flexible two-dimensional $[Be_3B_3O_6F_3] \propto$ single layers. [1] We examined the correlation between the intrinsic luminescence intensity and the degree of two-dimensionality in BaCaBe₂(BO₃)₂F₂ (BCBF) and BaMgBe₂(BO₃)₂F₂ (BMBF) crystals. We discuss the structural correlation of the intrinsic luminescence intensity from STEs.

Under VUV excitation at 50 and 160 nm, intrinsic luminescence from STEs was observed in these crystals. The excitation spectral intensity for BCBF and BMBF increased rapidly below about 180-200 nm. These observations support the conclusion that the luminescence band originates from STE formed by band-gap excitations, or to molecular transitions in the BO_3^{3-} group.

Figures 1(a) and 1(b) show the luminescence spectra for BCBF and BMBF excited at 160 nm in the range of 13-293 K. One luminescence band with a peak at 305-340 nm associated with STE appears for BCBF, and the corresponding peak appears at 310-320 nm for BMBF. In BCBF, the STE intensity decreases gradually from 13 K to 193 K. The BMBF crystal exhibited an STE intensity that increased gradually as the temperature increased to 125 K, above which the intensity decreased. These decreases in the intensity of STE luminescence likely resulted from a thermal quenching process. The peaks of the STE emission band in the two samples shifted to slightly shorter wavelengths with increasing temperature from 13 to 293 K.

Figure 2 shows the luminescence spectra for BCBF and BMBF excited at 160 nm at 13 K. The dependence of the intensity and bandwidth of the intrinsic luminescence on the substitutional effects of Ca^{2+} for Mg^{2+} was examined for these crystals. As an example, Fig. 2 shows the luminescence spectra for BCBF and BMBF excited at 160 nm in the range of 13 K. We found the intensity of the STE for BCBF to be greater than that for BMBF under excitation at 160 nm as seen in Fig. 2. The same is true for luminescence under excitation at 50 nm. There are two plausible explanations for the dependence of luminescence intensity on the Ca2+-substitution for Mg²⁺, involving (i) a two-dimensional effect or (ii) an incommensurate structural modulation effect. The magnitude of two-dimensionality is defined as the ratio of the interlayer distance to the intralayer distance. Here, the magnitude of two-dimensionality can be expressed by the c/a axis ratio. The magnitude of two-dimensionality for BCBF with c/a ratio of 3.42 is higher than that for BMBF with the c/a ratio of 3.34, with the increase being due to the larger ionic radius of Ca²⁺ than of Mg²⁺. Taking into account the above result, the dependence of the STE intensity on Ca2+substitution can be explained in terms of a two-dimensional effect. The other possible explanation is that the structural modulation effect increases the number of local sites with larger distortion potentials. These structural changes would result in broadening of the luminescence. This possibility is unlikely because there is no significant difference in the STE bandwidth between the BCBF and BMBF crystals.



Fig. 1. Temperature dependence of luminescence spectra of (a) $BaCaBe_2(BO_3)_2F_2$ and (b) $BaMgBe_2(BO_3)_2F_2$ excited at 50 nm in the range of 13-293 K.



Fig. 2. The luminescence spectra for $BaCaBe_2(BO_3)_2F_2$ and $BaMgBe_2(BO_3)_2F_2$ excited at 160 nm at 13 K.

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Intrinsic Nature of Luminescence Bands for undoped and Sn doped β-Ga₂O₃ Crystals

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β-Ga₂O₃ is a wide-gap semiconductor with the bandgap of 4.8 eV. Tetravalent cations doping causes the ntype conductivity in β -Ga₂O₃. The electric properties are changed by high-temperature annealing under various atmospheres. The high-temperature annealing under nitrogen atmosphere (nitrogen annealing) remarkably lowers the electrical resistance of β -Ga₂O₃, resulting in high electrical conductivity. The oxygen annealing keeps the electric insulation with high electrical resistance. Because high-temperature annealing varies lattice defects, it is likely that the change in electrical resistance of β -Ga₂O₃ is caused by the interaction of tetravalent cations with lattice defects. Such lattice defects influence luminescence properties of β -Ga₂O₃. So far, there are many studies on luminescence properties of β -Ga₂O₃. Luminescence spectra exhibited a prominent band at around 400 nm. Bient et al. were assigned the 400 nm band to an intrinsic nature due to radiative annihilation of relaxed excitons or radiative recombination between donor-acceptor pairs [1]. Usui et al. assigned the 400 nm band to an extrinsic origin associated with Sn 5s-5p transitions [2]. Thus, the nature of the 400 nm band still remains unclear.

In the present study, luminescence properties of undoped and Sn-doped β-Ga₂O₃ crystals were investigated at the BL3B beamline [3]. Here, an undoped crystal, and Sn-doped crystals annealed under oxygen and nitrogen atmosphere were named as #1, #2,and #3 samples, respectively. Figure 1 shows absorption spectra of #1-#3 samples, measured at 15 K. The absorption spectra exhibit a stepwise structure at around 260 nm, which corresponds to the indirect absorption edge of β-Ga₂O₃ crystals. Luminescence spectra of #1-#3 samples were measured at 15 K under excitation above the indirect absorption edge. The results are shown in Fig. 2. The photon energy was 200 nm. A prominent band appears at around 400 nm. A weak band is also observed at around 340 nm. These bands were effectively excited in the region above the indirect absorption edge. This feature indicates that the 340 and 400 nm bands are of intrinsic feature in β -Ga₂O₃ crystals. Other bands are seen in the long wavelength side of the 400 nm band. Because they were excited at the longer wavelength side than the indirect edge, they are attributed to extrinsic origins.

Luminescence spectra of #1-#3 samples were measured under two-photon excitation (TPE) with THG pulses from a Nd:YAG laser system. The TPE luminescence spectra of #1 and #2 samples exhibited the 340 and 400 nm bands. The intensities of the 340 and 400 nm bands increased in proportion to the square of the laser power. It is therefore concluded that the 340 and 400 nm bands are intrinsic origins in β -Ga₂O₃. Further experiments are needed to identify the origins of the 340 and 400 nm bands.



Fig. 1. Absorption spectra of #1-#3 samples, measured at 15 K.



Fig. 2. Luminescence spectra of #1-#3 samples, measured at 15 K under excitation with 200 nm photons. The intensities for #2 and #3 samples were multiplied by 10.

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Temperature Dependence of Ce-doped CaHfO₃ Crystals Synthesized by the Core Heating Method

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High-melting-point oxides are frontier and attractive materials for scintillators with higher gamma-ray stopping power. Although the Skull-melting process is commercial use to grow such materials, growth time was too long to feedback the growth conditions or parameters in the research and development phase. Thus, we developed a novel crystal growth method, Core Heating (CH) method. In previous research, we reported the CH method is available for the material quick search [1, 2].

In this report, we focused on Ce-doped CaHfO₃ (Ce:CHO) as a first step of crystal growth of high melting point materials by the CH method. Ce:CHO has a melting point of 2440 °C, and higher gamma-ray stopping power than conventional scintillators such as Ce:(Lu,Y)₂SiO₅ because of the highly effective atomic number (65).

We succeeded in growing transparent (>50%) Ce:CHO samples by the CH method for the first time. The use of transparent samples is expected to determine the scintillation light output with more accuracy when compared to non-transparent samples such as ceramics.

Optical and radio photoluminescence spectra of Ce:CHO crystals were similar to the low transparency Ce:CHO samples or powders. However, the light outputs of our crystals were smaller than previous studies with that of 4,000-5,000 photons/MeV [3,4] at room temperature (RT).

One of the possible reasons for the low light output is the thermal quenching of Ce^{3+} 5d-4f emission in Ce:CHO at RT, so that we measured the temperature dependence (TD) of photoluminescence (PL) spectra of Ce:CHO at the UVSOR-III facility. TD of PL emission for the main emission band located at ~ 400 nm was measured with a CCD SPEC-10 (Roper Scientific) at the beamline BL3B operating in a multi-bunch mode. Additionally, the TD of PL decay times were also measured under the single-bunch mode.

Figure 1 shows the TD of emission intensity for Ce:CHO excited with 193 and 330-nm photons. Each emission intensity was calculated by integrating the emission spectra. The TD results showed different behavior clearly between two excitation energy; The emission intensity for Ce:CHO excited at 193 nm continuously increased from 150 to 300K, and decreased above 300K.

Figure 2 shows TD of PL decay times of Ce:CHO excited with 193 and 330-nm photons; The decay times of Ce:CHO excited 193 nm rapidly increased at 200 and 250K, while at over 300K, the times were

almost the same value as that at low temperature. Meanwhile, decay times excited at 330 nm were stable from 10 to 250K, and gently decreased above 250K.

These results of TDs suggested (i) thermal quenching of Ce^{3+} 5d-4f emission is not the main reason for the low scintillation light yield at RT, (ii) the sample had additional trap level(s) related to defect(s) corresponding to 200-300K at TD of emission intensity and decay time. Moreover, One of the possible causes for the low output of Ce:CHO is due to such trap(s).



Fig. 1. TD of emission intensity of Ce-doped CaHfO₃ excited at 193 and 330 nm.



Fig. 2. TD of PL decay times of Ce-doped CaHfO₃ excited at 193 and 330 nm.

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Temperature Dependence of Photoluminescence Properties of Cs₂HfCl₃Br₃

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Intrinsic-luminescence halide scintillators with the chemical formula of A_2BX_6 (*A*: alkali metal, *B*: tetravalent ion, *X*: halogen ion) have been reported to exhibit the excellent scintillation performances such as Cs₂HfCl₆ with the blue emission around ~400 nm [1] and Cs₂HfBr₆ with the emission peak at ~450 nm [2]. We developed Cs₂HfI₆ as the novel red-emitting scintillator with the emission peak around ~700 nm [3]. Above studies imply the emission peak shifts towards the longer wavelength depending on the host *X* ion (Cl < Br < I).

The emission mechanism of A_2BX_6 halides is still unclear. To reveal the luminescence phenomena in A_2BX_6 halides, the relationship of the host ions, structures and luminescence properties should be understood. As a first step, the halogen-mixture compound Cs₂HfCl₃Br₃ was studied in this study.

 $Cs_2HfCl_3Br_3$ crystal was grown by the vertical Bridgman method. The crystal structure was analyzed by the single-crystal X-ray diffraction to be cubic (space group: $Fm\overline{3}m$) which is the same as that of Cs_2HfCl_6 and Cs_2HfBr_6 [4]. The photoluminescence properties were evaluated in BL3B. The temperature dependences were measured at 10, 50, 100, 150, 200, 250, 300 and 350 K.

Figure 1 shows the photoluminescence excitation and emission spectra of $Cs_2HfCl_3Br_3$. The excitation and emission spectra were illustrated as the dashed and solid lines, respectively. At 300K, $Cs_2HfCl_3Br_3$ had two photoluminescence bands. One band with the blue emission peak at ~435 nm was excited by ~270 nm. The other band had the broad green emission at ~515 nm excited by 315 nm. These two photoluminescence bands stably existed at the whole temperature range. The emission intensities of such blue- and greenemission bands gradually increased as cooled down from 350K to 10K. The emission peak wavelengths of both bands shifted towards the longer wavelengths from 350K to 10K.

The photoluminescence emission wavelength of Cs_2HfCl_6 , $Cs_2HfCl_3Br_3$, Cs_2HfBr_6 were summarized in Table 1. $Cs_2HfCl_3Br_3$ rather had the quite similar emission wavelength to Cs_2HfBr_6 than the medium wavelength between Cs_2HfCl_6 and Cs_2HfBr_6 . Therefore, the emission wavelength of A_2BX_6 halides might be determined by the host halogen ion X. For further study, more crystals with the different Cr/Br ratios, Br-I mixture and Cl-I mixture compounds are synthesized, and the photoluminescence properties should be evaluated.



Fig. 1. Temperature dependence of photo-luminescence excitation and emission spectra of $Cs_2HfCl_3Br_3$.

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lable	1.	Photoluminescence	emission peak	S

Compounds	Emission wavelength at 300K
Cs ₂ HfCl ₆	375nm, 440 nm [5]
Cs ₂ HfCl ₃ Br ₃	435 nm, 515 nm
Cs ₂ HfBr ₆	435nm, 525 nm [2]

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Emission Spectra of Pr-doped Y₃Ga_{5-x}Zn_xO_{12-δ}

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In this study, the excitation spectra and emission spectra of Pr^{3+} in $Y_3Ga_5O_{12}$ crystal have been measured and changes in the spectra with doping of Zinc and hydration are examined. The samples are synthesized by solid state reactions followed by annealing in N₂-H₂ atmosphere in order to reduce Pr^{4+} to Pr^{3+} . The oxygen vacancies are created in Zn-doped $Y_3Ga_5O_{12}$ and protons are incorporated by hydration of the vacancies. The concentration of Pr is 0.5 mol% and that of Zn are 3, 10 and 15 mol%. The Zn-doped samples are hydrated at 523 K in humidified N₂. The emission spectra and excitation spectra are measured at 30 K.

The emission spectra of $Y_3Ga_{5-r}Zn_rO_{12-\delta}$: Pr at 275 nm excitation are shown in Fig. 1. The sharp peaks around 500-700 nm originate from 4f-4f transitions of Pr^{3+} . The emissions of 5*d*-4*f* transitions are not observed in Zn-doped samples as in the case of Y₃Ga₅O₁₂:Pr. The emission intensities of Pr³⁺ increase with 3 mol% Zn doping, but they do not increase monotonically and decrease above 10 mol%. Figure 2 shows the excitation spectra of Pr^{3+} in Y₃Ga_{5-x}Zn_xO_{12- δ} at 485 nm. The host absorption band (-220 nm) and 4f-5d absorption band (230-300 nm) are observed in each sample. The absorption spectrum of $Y_3Ga_{5-x}Zn_xO_{12-\delta}$ shows that the band gap becomes smaller with the addition of Zn. The decrease in the emission intensity of Pr³⁺ with Zn addition shown in Fig. 1 may relate to the change in the energy difference between band gap and the 4f-5d transition. Since the addition of Zn promotes the formation of oxygen vacancies, there should also be a contribution of the defect level in the band gap in the emission decrease. The excitation spectrum of $Y_3Ga_{5-x}Zn_xO_{12-\delta}$: Pr (x = 0.75) at 485 nm and 617 nm are shown in Fig. 3 and Fig. 4. The emission changes before and after hydration are found to be different for host and 4f-5d excitation. These characteristic changes can be attributed to the defect levels of oxygen vacancy and hydrogen, respectively.



Fig. 1. Emission spectra of $Y_3Ga_{5-x}Zn_xO_{12-\delta}$: Pr at 30 K ($\lambda_{ex} = 275$ nm).



Fig. 2. Excitation spectra of $Y_3Ga_{5-x}Zn_xO_{12-\delta}$:Pr. at 30 K ($\lambda_{em} = 485$ nm).



Fig. 3. Change in the excitation spectra with hydration in $Y_3Ga_{4.25}Zn_{0.75}O_{12-\delta}$: Pr ($\lambda_{em} = 485$ nm).



Fig. 4. Change in the excitation spectra with hydration in $Y_3Ga_{4.25}Zn_{0.75}O_{12-\delta}$: Pr ($\lambda_{em} = 617$ nm).

Optical Conductivity Spectra of a Locally Noncentrosymmetric Material LaRh₂As₂

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Recently, noncentrosymmetric crystal structure and inversion symmetry breaking at crystal surfaces have attracted attention for physical properties combined with spin-orbit interaction (SOI). By using the SOI and the electric field gradient generated by the spatial symmetry breaking, spin-polarized current originating from spin-polarized bands is generated and is regarded to be useful for spintronics applications.

The breaking of the spatial inversion symmetry also generates a Cooper pair with a helical spin structure, which produces a superconducting state with a high critical field. Actually, the heavy-fermion superconductor CePt₃Si ($T_c \sim 0.75$ K) has an extremely high upper critical field H_{c2} as high as 5 T has been observed [1].

Recently, CeRh₂As₂ was discovered as a new heavy fermion superconductor ($T_c = 0.26$ K) with the local inversion symmetry breaking while overall crystal structure remains centrosymmetric [2]. RM_2X_2 (R = rareearth, M = transition metals, X = Si, Ge) compounds usually have a tetragonal ThCr₂Si₂-type crystal structure with inversion symmetry (14/mmm), CeRh₂As₂, however, crystalizes in the CaBe₂Ge₂-type structure, which lacks local inversion symmetry as the Ce and one of Rh and As sites (P4/nmm) as shown in Fig. 1. This results in a local electric field at the Ce site. Therefore, the Ce band undergoes Rashba splitting. It is necessary to investigate how this Rashba splitting affects the electronic structure. In this study, we measured the optical conductivity $[\sigma(\omega)]$ spectra of LaRh₂As₂, a reference material without 4f electrons, and compared them with the LDA band calculations to investigate the electronic structure without spatial inversion symmetry.

In the experiment, the vacuum-ultraviolet reflectivity spectrum measured at BL3B was connected to the infrared THz spectrum measured in the laboratory, and the $\sigma(\omega)$ spectrum was obtained by using the Kramers-Kronig analysis.

Figure 2 shows the experimental $\sigma(\omega)$ spectrum below 1.2 eV and the calculated spectrum for interband transitions with and without SOI. In comparing the calculated spectrum with SOI with that without SOI, almost no change is observed. Since the Rashba parameter is as large as 0.1eV Å (not shown here), the Rashba splitting is not effective so much to the band structure. While, the comparison of the calculated $\sigma(\omega)$ spectra of *P4/nmm* structure to that of *I4/mmm* structure, the increase of the $\sigma(\omega)$ intensity below 0.8 eV suggests that the bands of the *P4/nmm* structure are clustered near the *E*_F. It can be seen that the calculated $\sigma(\omega)$ spectrum of P4/nmm explains the experimental results well. In particular, the experimental 0.4-eV peak can be explained by the calculation. This peak is hardly observed in I4/mmm structure, which suggests a unique electronic structure in the P4/nmm structure.



Fig. 1. Crystal structure of RRh_2As_2 (R = La, Ce).



Fig. 2. Optical conductivity $[\sigma(\omega)]$ spectrum of LaRh₂As₂ (Experiment, dotted line). The interband transition part of the $\sigma(\omega)$ spectra subtracted by the Drude fitting curve is the thick line. Calculated $\sigma(\omega)$ spectra with and without spin-orbit interaction are shown by red and blue lines, respectively. The calculated spectrum with the *I4/mmm* crystal structure is also plotted as a dashed line.

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Optical Investigation on Fluoro-olefins in Vacuum-Ultraviolet for New Refrigerant Gas Development

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Chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC), and hydrofluorocarbon (HFC) have been used as a refrigerant. These gases have high global warming potential (GWP) over 100. Recently, the hydrofluoroolefin (HFO) gases are expected as new low environmental load refrigerant due to its low GWPs since olefin gas is unstable and easily decompose by ultraviolet light in nature. In order to put HFO into practical use as a refrigerant, it is necessary to clarify the physical characteristics of HFO such as UV absorption and decomposition process. In this study, we measured the vacuum ultraviolet (VUV) light induced decomposition of HFO.

The decomposition spectra measurements were carried out in BL3B in UVSOR facility. C2H2F2 gas was flowed into vacuum chamber through the capillary tube. The pressure in vacuum chamber was kept less than $3x10^{-4}$ Pa. The VUV light from 12 to 30 eV was irradiated on sample gas and the ionized molecular fragments were detected TOF-mass spectrometer shown in Fig. 1.

Figure 2 shows the decomposition spectra of $C_2H_2F_2$. We could clearly observe the ionization energies of each fragments. The ionization threshold of C₂HF₂, C₂H₂F, C₂HF, CH₂F, and C₂F₂ were 12.8 eV, 14.2 eV, 14.4 eV, 14.8 eV, and 17 eV, respectively. From our previous results, the $C_2H_2F_2$ has the absorption from 135 nm (9.2 eV) to190 nm (6.5 eV) as shown in Fig. 3. The absorption at 145 nm is attributed to the stretching and twisting of carbon double band and the 190 nm is the transition from π to π^* in C=C bonds, respectively [1]. However the ionization threshold is quite higher than these absorption.

In conclusion, we could observe the optical properties and ionization energy of decomposition process of $C_2H_2F_2$ in VUV region. The results let us know the UVor VUV-induced decomposition dynamics of fluoroolefins as refrigerant in next-generation.



Fig. 1. Schematic image of the experimental setup in BL3B.



Fig. 2. Decomposition spectra of $C_2H_2F_2$



Fig. 3. Absorption spectrum of $C_2H_2F_2$.

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Absorption Bands of Tl⁺ Centers in KCaCl₃ and CsCaCl₃ Crystals

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 Tl^+ centers in alkali halide crystals exhibit the optical bands called A, B, and C, which are attributed to intra-ionic transitions from the ${}^1A_{1g}$ ground state to the ${}^1T_{1u}$, ${}^3T_{2u}$ + 3E_u , and ${}^3T_{1u}$ excited states, receptively [1-3]. Though the optical properties of the Tl^+ centers in alkali halide crystals have been studied for a long time, there have been few reports on the Tl^+ centers in ternary halide compounds, which recently have an attracted attention as host crystals of new scintillator materials [4,5]. In this study, we focused on Tl^+ centers in ternary halide crystals of KCaCl₃ and CsCaCl₃.

KCaCl₃:Tl⁺ and CsCaCl₃:Tl⁺ crystals were grown by the Bridgman method from the starting material powders. The optical measurements were performed at low temperatures at the BL3B line of UVSOR.

Figure 1 shows the absorption spectra of (a) $KCaCl_3:Tl^+$ and (b) $CsCaCl_3:Tl^+$ crystals at 10K. The several absorption bands are observed in the transparent energy region below the respective fundamental absorption edge. These absorption bands exhibit no simple Gaussian shape.

Owing to the dynamical Jahn-Teller effect, the A and C bands of the Tl⁺ centers in alkali halide crystals often exhibit the double or triple structures, respectively [1-3]. We resolved the absorption bands observed in KCaCl₃:Tl⁺ and CsCaCl₃:Tl⁺ into two or three Gaussian shapes. As shown by thin curves in Fig.1, the absorption bands located around 5.4 eV for KCaCl₃:Tl⁺, and 5.6 eV for CsCaCl₃:Tl⁺ can be resolved into two Gaussian shapes. The intense absorption bands around 6.8 eV for KCaCl₃:Tl⁺, and 7.1 eV for CsCaCl₃:Tl⁺ can be resolved into three Gaussian shapes. Thus, the absorption bands at 5.4 eV for KCaCl₃:Tl⁺, and 5.6 eV for CsCaCl₃:Tl⁺ are assigned to the A band of the Tl⁺ centers, and the absorption bands at 6.8 eV for for KCaCl₃:Tl⁺, and 7.1 eV for CsCaCl₃:Tl⁺ are assigned to the C band of the Tl⁺ centers. Furthermore, a small absorption band is observed at 6.4 eV in KCaCl₃:Tl⁺ and the shoulder structure is observed at 6.6 eV in CsCaCl₃:Tl⁺. The absorption band and the shoulder structure are assigned to the B band of the Tl⁺ centers.

On the basis of a theoretical treatment for the Tl⁺ centers [1-3], the relative positions of the absorption bands and their relative intensity ratios are determined by the Coulomb energy F, the exchange energy G between the s- and p-electron, the spin-orbit interaction energy ξ of the p-electron and the King-Van Vleck factor λ , which account for the differences between the radial wave functions of the p-electron in the triplet and singlet states. These parameters F, G, ξ and λ can be evaluated from the energy positions of the center of the A, B and C absorption bands and the dipole strength ratio R of the C to A bands. These parameters characterizing the Tl⁺ centers were estimated by analyzing our experimental

data, as shown in Table I. In the same Table, similar data for the Tl⁺ centers doped in alkali chloride crystals are also presented. From a comparison of these values, it is found that our assignment of the absorption bands observed in the KCaCl₃:Tl⁺ and CsCaCl₃:Tl⁺ crystals is reasonable.



Fig. 1. Absorption spectra of (a) $KCaCl_3:Tl^+$ and (b) $CsCaCl_3:Tl^+$ crystals at 10K. The thin curves represent Gaussian components decomposing the absorption bands.

Table 1. Parameters characterizing the TI^+ centers. Except for λ , all parameters are in eV.

Crystals	F	G	ζ	λ	Ref.
KCaCl ₃ :Tl ⁺	5.9	0.25	0.72	1.2	
CsCaCl ₃ :Tl ⁺	6.1	0.31	0.83	0.89	
NaCl:Tl ⁺	5.7	0.26	0.66	1.1	[1]
KCl:Tl ⁺	5.7	0.28	0.7	0.99	[1]

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Influence of Crystal Structures of CsCaI₃:Tl⁺ and Cs₄CaI₆:Tl⁺ on Absorption Bands

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Thallium impurity centers in alkali halides, which are binary compounds, have been extensively investigated [1]. However, thallium impurity centers in ternary compounds, which have attracted attention as scintillator materials, have been less reported. In this study, we investigated absorption bands of $CsCaI_3:TI^+$ and $Cs_4CaI_6:TI^+$.

The single crystals of $CsCaI_3:TI^+$ and $Cs_4CaI_6:TI^+$ were prepared by a cell method [2]. The quartz-cells with the narrow gap are made of a pair of two quartz plates. The melt of the staring materials was percolated into the gap of the quartz-cells through capillary action and thin crystals were grown in the gap by natural cooling.

Figure 1 shows the absorption spectra of $CsCaI_3$: Tl^+ and non-doped $CsCaI_3$ crystals. In the non-doped $CsCaI_3$ crystal, no absorption bands are observed in the energy region below the fundamental absorption edge of 5.7 eV. On the other hand, the three absorption bands are observed in $CsCaI_3$: Tl^+ .

Figure 2 shows the absorption spectrum of $Cs_4CaI_6:Tl^+$ crystals. The five absorption bands are observed in $Cs_4CaI_6:Tl^+$. That is to say, the appearance of the absorption bands of $Cs_4CaI_6:Tl^+$ is complicated than those of $CsCaI_3:Tl^+$.

In both crystals, the Tl⁺ ions replaced the Cs⁺ ions because of the equal valance of both ions. Thus, the nearest neighbor ion of the Tl⁺ ion is iodide ions. In CsCaI₃:Tl⁺, the Tl⁺ ion is surrounded with a distorted square antiprism geometry by eight iodide ions [3]. In Cs₄CaI₆:Tl⁺, on the other hand, there are two types of Tl⁺-occupied sites: one with a distorted square antiprism geometry and another with a trigonal prism geometry. In the site with the trigonal prism geometry, the Tl⁺ ion is surrounded by six iodide ions [4]. The Tl⁺ ions occupied two types of sites exhibit the diverse absorption bands. Thus, the appearance of the absorption bands of Cs₄CaI₆:Tl⁺ becomes complex as against those of CsCaI₃:Tl⁺.

In the case of the Tl⁺ centers in alkali halides, the absorption bands often exhibit the double or triple structures due to the Jahn-Teller effect. The double or triple structures due to the Jahn-Teller effect become conspicuous with increasing temperature. The bandshape of the absorption bands in Cs₄CaI₆:Tl⁺ may be seen as the double structures. However, the bandshape of the absorption bands in Cs₄CaI₆:Tl⁺ did not become conspicuous with increasing temperature. Thus, the complicated absorption bands in Cs₄CaI₆:Tl⁺ do not come from the Jahn-Teller effect.



Fig. 1. Absorption Spectrum of $CsCaI_3$: TI^+ at 10K. Insert shows an absorption spectrum of non-doped $CsCaI_3$ at 25K.



Fig. 2. Absorption Spectrum of Cs₄CaI₆:Tl⁺ at 10K

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Photoluminescence and Scintillation of CsCl-based Ternary Crystals

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Auger-free luminescence (AFL) is caused by the radiative transition of an valence electron to a core hole state. The transition is competitive with the Auger process, which is a much faster process, efficient AFL cannot be observed in many compounds. In other words, efficient AFL has been observed in limited compounds such as alkaline- or alkaline-earth fluorides or CsCl-based compounds.

AFL has been applied to fast scintillators owing to its fast decay. A representative one is BaF₂; however, CsCl-based compounds have an advantage of long emission wavelength appropriate for detection with a photomultiplier tube. Thus far, we have developed fast scintillators based on ternary CsCl-based compounds [1-2]. In this report, we present some results on the photoluminescence properties with VUV excitation and scintillation properties of several CsCl-based ternary compounds.

Crystal samples of the ternary CsCl-based compounds were fabricated using a self-seeding solidification method and the Bridgman method. Raw materials were mixed in a stoichiometric ratio. The mixed powders were poured into quartz ampoules and heated at 350 °C in vacuum for 1 day to remove adsorbed water. For the self-seeding solidification method, the quartz ampoule was set in a tubular furnace, and the furnace was heated to 950 °C for 12 h and subsequently cooled to room temperature over 72 h. For the Bridgman method, the ampoule was set in a Bridgman furnace. The temperatures of the upper and lower heaters in the furnace were set at 950 °C and 750 °C, respectively, during crystal growth, and the ampoules were lowered at a rate of 1.5 mm/h.

The luminescence properties were characterized with vacuum ultraviolet (VUV) light as an excitation source. Measurements were performed at BL3B for temporal profiles at the UVSOR facility at the Institute for Molecular Science, Japan, using a time-correlated single photon counting.

Photoluminescence temporal profiles of the CsClbased ternary compounds are presented in Fig. 1. The excitation wavelength was 84 nm, whose photon energy corresponds to the excitation from the outermost core level to the bottom of the conduction band. The emission wavelengths correspond to the emission peak whose excitation spectra have a step at around 84 nm, which strongly suggests that the emission is owing to the AFL. The decay behavior shown in Fig. 1 was fitted with an exponential decay function. The decay time constants were 0.8 - 1.2 ns, which are typical for the AFL. Scintillation temporal profiles of the CsCl-based ternary compounds are presented in Fig. 2. The decay behavior is similar to those of the photoluminescence, which indicates that the scintillation of these compounds is mainly of AFL.



Fig. 1. Photoluminescence temporal profiles of CsClbased ternary compounds.



Fig. 2 Scintillation temporal profiles of CsCl-based ternary compounds.

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BL4U

Microscopic Evidence of Complex Cobalt Oxides Electrodeposited on Graphene Window

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The X-ray-in (electron-in) and electron-out techniques [1,2] using the surface-sensitive analysis are quite important for the electrochemical interface. Graphene as an early example of two-dimensional materials has been received a lot of attentions i.e. a promising use of window membrane, because of the remarkable points (such as separation, vacuum-liquid environment thinnest thickness, and X-ray/electron transparency). Studies for an essential role of graphene-based working electrode are still missing in the wide-range applications due to the difficulties in solid-liquid phase and nanoscale-resolved approaching. The electrocatalytic project is one of interests of energy materials; thus, the critical factor and diverse function are devoted for the heterogeneous system owing to the interface correlation.

In the work, we have investigated various oxidation states of electrodeposited Co and underlying graphene window by using scanning transmission X-ray microscopy (STXM) at BL4U. The electronic structure and bonding configuration of electrodeposited Co layer were studied to solve the answer of the catalytic synergy of oxygen evolution reaction. The electrochemical reduction and deposition of the aqueous Co²⁺ ions were formed on the graphene electrode through the cathodic electron reduction in the CoSO₄ solution. Diverse lattice structures of cobalt nanoparticles (Co-NPs) grown on the graphene electrode were characterized through transmission electron microscopy (TEM) measurement, shown in Fig. 1(a)~(c). High-magnified TEM images highlights the local region (green squares) of Co-NPs for the ordered particle size ranging from 5 to 10 nm for the initial stage and the amorphous structure for the later and thick stage. The inset images of Fig. $1(d) \sim (f)$ were taken at the pre-edge energy to observe the background images, which consistent with the same area of TEM image. The X-ray absorption (XA) spectra at C K-edge in Fig. 1(d) show absorption peaks at photon energies (PEs) of 284.9, 286.6, 288.4, 290.2, and 292.5 eV, which are known for $\pi^*(C=C)$, $\pi^*(C=OH)$, $\pi^*(C=O in HO-C=O)$ or defect, $\pi^*(O-C(O)-O \text{ or } C=O \text{ at the edge})$, and $\sigma^*(C=C)$ bonds [3,4]. The spectral evidences between region 1, 2, and 3 reflect the oxidation evolution of graphene with a function of Co NPs thickness. The XA spectra at O Kedge in Fig. 1(e) indicate three π^* resonances (530.8, 532.4, and 534.0 eV) and two σ^* resonances (536.8 and 538.9 eV), corresponding to the oxidation states of the graphene electrode and the electrodeposited Co-NPs [4,5]. The hybridized O 2p-Co 3d states [6] are located at two peaks at PEs of 532.4 and 534.0 eV, and the hybridized O

2p-Co 4s state are located at the broad peak at PE of 538.9 eV [6].

In Fig. 1(e), the multiple features of the Co XA spectra at the L_{3^-} and L_{2^-} edges were divided into two regions (774–781 eV and 789–795 eV), which are involved by the oxidation state, crystal field splitting, and low/high spin states of Co 3*d* [6]. Our theoretical simulation indicated three components (Metal Co⁰, Oct. symmetrical Co²⁺, and Oct. symmetrical Co³⁺ species) existed in region 1, 2, and 3, depending on the linear combination of three reference spectra through the lowest deviation between the experimental and fit data. The curve-fitting statistics reflects the increasing metal Co⁰ and Oct. Co²⁺ state by the elimination of Oct. Co³⁺ state for the mixing state of Co NPs in region of 1, 2, and 3.

Through STXM, the multiple carbonyl-like states (C– OH, HO–C=O, and O–C(O)–O/C=O) and multiple Co states (Co⁰, Co²⁺, and Co³⁺) were found on the surface. Our chemical mapping evidence signified the bonding tendency of graphene and de-oxidation stages of Co-NPs, which accounts for the synergistic reason of Co-based energy materials.



Fig. 1 (a)–(c) High-resolution TEM images of electrodeposited Co–graphene membranes. (d)–(f) Selected areas of the XA spectra of the C K-edge, O K-edge, and Co L-edge and the corresponding averaged areas (insets) of the element maps.

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BL5U

High-resolution ARPES Study of Topological Dirac-semimetal Candidates

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The search for novel fermions, which has long been an important research target in elementary-particle physics, is recently becoming an exciting challenge in condensed-matter physics, as highlighted by the discovery of two-dimensional (2D) Dirac fermions in graphene and helical Dirac fermions at the surface of three-dimensional (3D) topological insulators. The recent discovery of 3D topological Dirac semimetals (TDSs) that host massless Dirac fermions further enriches the category of exotic fermions. TDSs show exotic quantum phenomena such as high carrier mobility and giant linear magnetoresistance governed by the linearly dispersive Dirac-cone energy band. Also, TDS can be switched to other novel topological phases, e.g., by breaking the time-reversal/crystalline symmetry or by chemical substitution. Therefore, TDS provides a fertile playground for realizing a variety of topological phases. However, despite many theoretical predictions for TDS candidates, TDSs that have been experimentally verified are still rare. In addition, wellknown TDSs, Na₃Bi and Cd₃As₂ [1-3], are not well suited for the physical-property measurements and device applications because Na₃Bi is extremely active in the air and there exists a critical controversy between experiments and theories in Cd₃As₂ on the Dirac-cone states. Thus, it is highly desirable to explore new TDS materials that overcome such difficulties.

It was recently predicted that BaMg₂Bi₂ is a TDS [4]. In BaMg₂Bi₂, Ba atoms can be easily replaced with other elements, so this system seems suitable for manipulating topological and physical properties. In this study, we performed high-resolution angle-resolved photoemission spectroscopy (ARPES) of BaMg₂Bi₂. By utilizing energy tunable photons, we mapped out the band structure over the entire 3D Brillouin zone [Fig. 1(a)] to search for the Dirac-cone band dispersions.

High-quality single crystals of BaMg₂Bi₂ were synthesized by the self-flux method. ARPES measurements were performed with micro-focused VUV synchrotron light at BL5U. Samples were cleaved *in situ* along the (0001) plane of the hexagonal crystal in an ultrahigh vacuum.

Figure 1(b) shows the 2D ARPES intensity plot at $E_{\rm F}$ measured at $k_z \sim 0$, where the presence of Diraccone bands is predicted by the band calculations. One

can find a circular Fermi surface centered at the Γ point. This Fermi surface originates from the $E_{\rm F}$ crossing of a holelike band that shows linear dispersions, as seen from Fig. 1(c). We doped electrons to the crystal surface by alkaline-metal deposition and searched for a predicted point touching between the valence and conduction bands due to the Dirac-cone band formation. The present study lays the foundation for understanding the topological property of BaMg₂Bi₂.



Fig. 1. (a) 3D bulk Brilloiun zone of BaMg₂Bi₂. (b) ARPES intensity at $E_{\rm F}$ plotted as a function of 2D wave vector. (c) ARPES-intensity plot measured along a momentum cut crossing the Γ point.

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BL5U, BL7U

Determination of Contribution of Atomic Orbital to the Valence Band in SnS

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SnS is a compound semiconductor with a band gap of ~1.2 eV, which is expected as an novel absorber material for the thin-film solar cells due to being composed of abundant and safe elements. Therefore, SnS solar cells have been actively studied for decades, whereas there has been limited experimental studies on the electronic structures of SnS. Since the electronic structure at the band edge is largely responsible for the optical and electrical properties of the material, it is important to understand them by experimental approach as well as by the theoretical analysis considering its application to the optoelectronic devices. In this study, we have experimentally determined the contribution of atomic orbital to the valence band using difference of each atomic orbital in the photoionization cross section (Fig. 1).

The electronic structure of the valence band of SnS was observed by high-resolution angle-resolved photoemission spectroscopy (ARPES) at BL5U and BL7U. Single crystalline Br-doped SnS grown by flux method [1] were subjected to the measurement after being cleaved in the measurement chamber prior to the measurement. First-principles calculations of the electronic structure of SnS were performed using the Quantum Espresso package.

Figure 2 shows the band dispersion in the Γ -Z direction measured with excitation energies of 60 eV (BL7U) and 21 eV (BL5U). It is indicated that the valence band maximum (VBM) is located at a k-point slight offset from the Z-point to Γ -point as reported in the previous first-principles calculations [2]. The relative intensity of each band differs depending on the excitation energies. For a simple comparison, Fig. 3(a) shows the energy distribution curve, which integrated over the whole wavenumber space, where the intensity was normalized at -4 eV. The valence band is composed of three major bands (Band I, II and III), which is well reproduced in the partial density of states (PDOS) obtained by first-principles calculation (Fig. 3(b)). In the measurement with excitation energy of 21 eV, the intensities of band I and III were obviously lower than those of 60 eV. Since the photoionization cross section is small only for Sn 5s at 21 eV compared to other atomic orbitals (Fig. 1), it is suggested that Sn 5s orbital strongly contributes to the band I and II. This is well consistent with the calculated PDOS. In conclusion, it is experimentally clearly shown that the VBM is mainly composed of Sn 5s orbitals.



Fig. 1. Photoionization cross-section of each atomic orbital in SnS [3].



Fig. 2. E-*k* plot of SnS measured with an excitation energy of (a) 21 eV and (b) 60 eV. The while arrows in the figures indicate the location of the VBM.



Fig. 3. (a) EDC and (b) PDOS plots of the SnS.

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BL5U

Band Dispersion Unique to the Cobalt Intercalation in the Noncentrosymmetric Antiferromagnet CoNb₃S₆

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 $CoNb_3S_6$ is a transition metal dichalcogenide NbS_2 with cobalt intercalation. Neutron scattering experiments have revealed that intercalated Co atoms emerge collinear antiferromagnetic structure along in-plane direction [1]. Furthermore, weak ferromagnetism along out-of-plane direction and anomalous Hall effect have been observed recently [2]. However, the anomalous Hall response is giant even though the ferromagnetic moments are weak, and the mechanism of this giant anomalous Hall effect has been undiscovered.

We studied the electronic structure of CoNb₃S₆ by comparing with that of NbS₂ without the intercalation. Single crystals of CoNb₃S₆ and NbS₂ were synthesized by chemical vapor transport method. Angle-resolved photoemission spectroscopy (ARPES) measurements using the vacuum ultraviolet (VUV) light were performed at BL5U of UVSOR. We used the 120 eV photons, and the energy resolution was 45 meV. The measurement temperature was kept at 20 K, lower than $T_N \sim 28$ K. All samples were cleaved *in situ* along the (001) direction at an ultrahigh vacuum of 4.0 x 10⁻⁹ Pa.

Figure 1(a) shows Fermi surfaces of NbS₂ and CoNb₃S₆. NbS₂ has pockets around the Γ and K points. These pockets are hole pockets, as revealed in Fig. 1(b) left panel. These dispersions were also observed in the band dispersion of CoNb₃S₆, as highlighted by pink dashed rectangles in Fig. 1(b). In CoNb₃S₆, these dispersions were shifted down, because of the electron doping from Co cations. This band shift is also observed as a smaller hole pocket around the Γ point in CoNb₃S₆ [Fig. 2]. Furthermore, an additional band dispersion appeared near the Fermi level [blue dashed rectangles in Fig. 1(b) right panel]. This dispersion seems to come from Co atoms, because such a band dispersion does not exist in NbS2, even if the band shift is considered. The additional band dispersion of intercalated atoms crossing the Fermi level is not reported in the ARPES study of CrNb₃S₆ [3], which has the same crystal structure as CoNb₃S₆. Therefore, we conclude that this electronic structure is unique to the cobalt intercalation, and possibly responsible for the particularly large anomalous Hall effect of CoNb₃S₆.



Fig. 1. VUV-ARPES measurements of NbS₂ and CoNb₃S₆. (a) Fermi surfaces of NbS₂ and CoNb₃S₆. Solid and dashed hexagons represent the Brillouin zones of NbS₂ and CoNb₃S₆, respectively. (b) Band dispersion along the k_{γ} direction [black arrows in (a)].



Fig. 2 Momentum distribution curves (MDCs) of NbS₂ (pink) and CoNb₃S₆ (light blue) along the k_y direction at the Fermi level. Spectrum peaks corresponding to the hole pocket around the Γ point are label by A and A'.

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BL5U

Orbital-resolved 3d Band Structure of Fe Layers

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Iron-based materials have been widely investigated for the practical uses and fundamental science. For the spintronics device applications, Fe-based alloys facing on other materials have a high potential for producing functional properties such as perpendicular magnetic anisotropy derived from the symmetry broken spinorbit effects at the film interfaces. On the other hand, clean Fe surface is required for the development of the spin- and angle-solved photoemission spectroscopy (ARPES) system as a target material of spin detector using very-low energy electron diffraction. In order to develop the researches and applications, a fundamental knowledge about the fundamental Fe 3*d* orbital-resolved band structures is necessary.

Density-functional-theory (DFT) calculation in the bcc Fe bulk exhibits the band dispersions along the Γ - Δ -H symmetric line in Fe [001] direction [1,2]. The dispersion in the Δ_1 band is well known as a fully spin polarized band which corresponds to the coherent tunneling phenomena in tunneling magnetoresistance devices. However, there are few reports detecting the band dispersions directly with orbital resolutions in ARPES. In these motivations, we aim to access the linear polarization dependence in ARPES to detect the orbital-resolved 3*d* states in Fe which is comparable with the band-structure calculation in the momentum space.

Sample was prepared on MgO (001) substrate using Fe electron-beam evaporation. The MgO substrate was cleaned by annealing at 800 °C. Then, after cooling to room temperature, Fe was deposited in the growth rate of 0.015 nm/min to 100-nm thickness. Post-annealing at 800 °C was performed to obtain clear LEED pattern. After the sample was introduced from the air condition, the sample surface was cleaned by Ar-ion sputtering to remove the oxide contamination and by annealing at 800 °C.

ARPES was performed at BL5U, UVSOR, where photoemission chamber is connected to the sample preparation chamber. The measurement conditions were set at 15 meV energy resolution and 10 K. Linear polarized beams of *s*- and *p*-polarization were used to detect the orbital symmetry. We employ the photon energy of 60 eV to enhance the Fe 3*d* photo-ionization cross section, where the Γ -H line is scanned by the angular mode of $\pm 15^{\circ}$.

For the Fe 3*d* states, *s*- and *p*-polarized beams (vertical and horizontal) probe the wave functions in odd (*xy*, *yz*) and even symmetry (*zx*, x^2-y^2 , z^2) along the mirror plane, respectively [3]. Considering the effect of matrix element in photoemission process, *s*- and *p*-

polarization enhances the yz and zx orbitals, respectively.

Figures 1(a) and 1(b) show the energy-momentum Ek curves in ARPES using p- and s-polarized beams, respectively, with different momentum points along Γ - Δ -H symmetric line. At the Γ point, specific feature is obtained such as parabolic band from the energy of 0.2 eV. The states near the Fermi level (E_F) appear in the Δ line, which is enhanced in *p*-polarization and $3z^2 r^2$ orbital contributes to the crossing of the $E_{\rm F}$. In Fig. 1(b), the dispersion feature is different. Specific features of the changes of dispersion curvatures are explained by the DFT calculation results as the spin majority- and minority-band mixing. These will be resolved by spinresolved ARPES. Therefore, the $E-k_x-k_y$ threedimensional detection of band dispersions for Fe bulk is achieved, which brings the future developments for high-quality crystal growth and spin detector for spinresolved ARPES system.

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Fig. 1. Polarization dependent APRES images of 100nm thick Fe film taken at 60 eV for (a) *p*-polarization and (b) *s*-polarization. Each image consists of energy and in-plane momentum. Another in-plane axis is shown in other panel along Γ -H line in the bcc Brillouin zone.

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Angle-resolved Photoemission Study of *i*-MAX Phase Compound (Mo_{2/3}Ho_{1/3})₂AlC₂

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MAX phase compounds, i.e., $M_{n+1}AX_n$ where M is a transition metal, A belongs to groups 13-16 and X is the C or N element, have recently been attracted much attention due to their possible application for new class of two-dimensional systems called MXenes by removing A atoms [1]. Among MAX phases, RE-*i*-MAX phase (RE = rare earth), with the general formula ($M_{2/3}RE_{1/3}$)₂AC, was recently synthesized system where the emergence of magnetic phase transition has been reported [2]. In this study, we have performed angle-resolved photoemission spectroscopy (ARPES) on RE-*i*-MAX phase compound ($M_{0/3}Ho_{1/3}$)₂AlC ($T_N = 7.8$ K) to directly investigate the electronic structure of this system, especially the role of 4*f* electrons on its physical properties.

ARPES measurements were performed at the UVSOR-III BL5U. Data were acquired at T = 20 K with hv = 96 eV and 83 eV. It should be noted that the measured axis is defined on the (001)-projected surface hexagonal Brillouin zone (BZ) (Fig. 1(c)).

Figure 1(a) show the ARPES image along the Γ KM line of $(Mo_{2/3}Ho_{1/3})_2$ AlC at the wide valence band region. PES spectrum obtained by integrating the ARPES intensity over the whole k_x region is shown in Fig. 1(b). It has been found that the electronic structure of $(Mo_{2/3}Ho_{1/3})_2$ AlC is characterized by the non-dispersive bands at the high binding energy of 4-13 eV and the highly-dispersive bands near the Fermi level (E_F), respectively. Since the relative energy positions and intensities of the former are similar with the calculated Ho³⁺ final state multiplets when taking account of the bulk and surface components, the former can be attributed to the localized Ho 4*f* states.

Figures 2(a) and (b) show the band structure near E_F along the $\overline{\Gamma M}$ and $\overline{\Gamma K M}$ lines, respectively. Clear dispersive features matching with the BZ symmetry have been observed clearly. From the comparison with DFT+U calculation (U = 3 eV) along the ΓFZ and ΓXY lines, we have found that the observed dispersive features were mostly well reproduced by the calculation. To pursue into the characteristic properties of this system, further studies across the magnetic phase transition are intended.



Fig. 1. (a,b) while valence band ART ES image along ΓKM line (a) and AIPES spectrum (b) of $(Mo_{2/3} Ho_{1/3})_2AIC$ acquired with hv = 96 eV. Blue and green vertical bars indicate Ho³⁺ final state multiplets of bulk and surface states, respectively [3]. (c) The monoclinic C2/c BZ of $(Mo_{2/3}Ho_{1/3})_2AIC$ in the extended zone scheme. Red lines are ΓF and ΓXY lines. Orange shaded area is projected surface hexagonal BZ.



Fig. 2. (a,b) ARPES image of the dispersive features along Γ M (a) and Γ KM line (b) of $(Mo_{2/3}Ho_{1/3})_2$ AlC acquired with hv = 83 eV. The white lines in Fig. 2(a) and (b) are DFT+U calculations (U = 3 eV) along the Γ FZ and Γ XY lines on the bulk BZ, respectively.

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BL5U

Change of Fermi Surface Topology in NdFeAs_{1-x}P_xO_{0.9}F_{0.1} Observed by Angle-Resolved Photoemission Spectroscopy

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Since the discovery of iron-based superconductors (IBSs), many experimental and theoretical studies have been performed, but the superconducting mechanism of this system has not yet been clarified. The IBSs are multiband systems with several two-dimensional Fermi surfaces (FSs). In this work, we have studied the change of FS topology by P-doping in NdFeAs_{1-x}P_xO_{0.9}F_{0.1} by angle-resolved photoemission spectroscopy (ARPES). The present system NdFeAs_{1-x}P_xO_{0.9}F_{0.1} is one of famous IBSs, where P doping induces the change of local crystal structure around Fe site concomitantly with the gradual decrease of critical temperature T_c from 55 K (x=0) to 4 K (x=1.0) [1,2].

In the present work, we synthesized the single crystals of NdFeAs_{1-x}P_xO_{0.9}F_{0.1} with various P concentration xs using high pressure technique. The ARPES measurements have been performed in BL5U at Institute of Molecular Science. We have measured ARPES spectra using P- and S-polarization geometries of incident beam to clarify the orbital characters of FSs and electronic bands.

Figure 1 shows the in-plane FS mapping for x=0, 0.2, 0.4, and 0.6. We observed several FSs around Brillouin zone (BZ) center ($k_x=k_y=0$) and zone corner ($k_x=k_y=\pi$). In this work, we focused the FSs around BZ center. All samples have a large hole FS around BZ center, which is observed in P-polarization and has $3z^2-r^2$ character. In addition, the middle hole FS with xz/yz character is observed in S-polarization in all P concentrations. Only in x=0.4 and 0.6, the additional FS with small size appears.

We have carefully measured polarization dependence of hole bands at BZ center. Figure 2 shows the schematic band dispersions and their orbital characters around BZ center for each P concentration samples. Below Fermi level, we have observed the *xy* band, and this band has shifted down with increasing P content. On the other hand, the most inner *xz/yz* band shifts up with increasing x, and this band makes FS above x=0.4. This band shows anomalous feature that the orbital character is *xy* at band top and *xz/yz* in other parts. In addition, the present results of polarization dependence show the P-doping-induced change of orbital character in the inner and middle hole bands from *xz/yz* to (xz+yz)/(xz-yz), as shown in Fig. 2.



Fig. 1. In plane ARPES intensity mapping for (a, b) x=0, (c, d) x=0.2, (e, f) x=0.4, and (g, h) x=0.6 in NdFeAs_{1-x}P_xO_{0.9}F_{0.1}.



Fig. 2. Schematic band dispersions for x=0-0.6 in NdFeAs_{1-x}P_xO_{0.9}F_{0.1}.

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BL5U

Doping and Temperature Dependence of the Nodal Spectral Weight in Bi2212

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Which momentum space on Fermi surfaces (FSs) contributes to superconductivity is one of the important issues to elucidate the mechanism of high- T_c superconductivity. According to the Fermi arc picture [1], carrier concentration is proportional to the Fermi arc length and the effective SC gap scales with T_c [1,2]. These results suggest that the superconductivity near the nodal direction plays an important role of superconductivity in cuprates. On the other hand, there is a report that spectral weights (SWs) which are distributed over the FSs, observed by angle-resolved photoemission spectroscopy (ARPES) would contribute to high- T_c superconductivity in cuprates [3]. Therefore, it has been unclear which parameters contribute to superconductivity dominantly so far.

In the present report, we studied that to what extent the nodal region on FSs contributes to superconductivity in the cuprate superconductors. We have performed an ARPES experiment to investigate doping and temperature dependence of SW in the nodal direction.

High-quality single crystals of underdoped (UD), optimally doped (OPT), and overdoped (OD) $Bi_2Sr_2CaCu_2O_{8+\delta}$, Bi2212 ($T_c = 70, 92$, and 75 K) were grown by the TSFZ method. ARPES experiments were caried out at BL5U of UVSOR-III Synchrotron. Clean sample surfaces were obtained for the ARPES measurements by cleaving single crystals *in-situ* in an ultrahigh vacuum better than 5×10^{-9} Pa, and total energy resolution was set at 15 meV. The measurements were performed at 20 K – 110 K.

Figures 1(a)-1(c) show AREPS spectra of symmetrized energy-distribution curves (EDCs) in the nodal direction taken at T = 20 K, 90 K, and 110 K for OD75, OPT92, and UD70 samples. EDCs are subtracted as shown in Figs. 1(d)-1(f) to see the change of SW in the SC and normal states. The difference is shown by blue shaded area in Figs. 1(d)-1(f) and the area is plotted in Fig. 1(g). In contrast with the speculation that the nodal momentum region is related with T_c , the nodal SW is almost independent of hole concentration and T_c . The present result suggests that we need to study the momentum dependence of SW on entire FSs in future work.

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Fig. 1. Doping and temperature dependence of double-layer cuprate Bi2212. (a)-(c) Temperature dependence of symmetrized EDCs in the SC and normal states. The data is fitted by phenomenological function [4] including Shirley-type background [5]. (d), (e), and (f) are symmetrized EDCs obtained from subtraction of EDC in the SC and normal states shown in (a), (b), and (c), respectively. Shaded area shown in panels (d)-(f) is plotted in panel (g) with the T_c dome of Bi2212 as a function of hole concentration.

Infrared Reflectivity Spectra for Undoped and *n*-type Mg₂Si Crystals

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Mg₂Si belongs to the cubic system with the space group Fm-3m, and it has anti-fluorite structure [1]. This material is called environmentally-friendly semiconductor, because it is composed of nontoxic and earth-abundant elements. Mg2Si attracts much attentions as optoelectronic and thermoelectric substance. The band-gap energy is reported 0.61 eV [2], and thus Mg₂Si can respond to the illumination of mid-infrared (MIR) light [3]. This feature opens the way to apply to a MIR detector. Actually, pn-junction Mg₂Si diodes were fabricated, and they showed a clear response for photons with the energies above 0.6 eV [3]. Despite an industrially important material, free carrier behaviors in Mg₂Si have been little studied so far. Plasma oscillation is regarded as a fingerprint for the creation of free carriers in semiconductors. The information on such plasma oscillation can be obtained from the measurement of reflectivity in the infrared region. In the present study, we have measured reflectivity spectra of undoped and *n*-type Mg₂Si crystals at various temperatures. Because low grade reagents were used as starting materials, carriers were naturally introduced, resulting in *n*-type Mg₂Si crystals. The carrier concentrations of undoped and *n*-type Mg₂Si crystals were 1.8×10^{15} and 2.2×10^{18} cm⁻³. The surfaces of crystals were mechanically polished.

Figure 1 shows reflectivity spectra of an undoped n-Mg₂Si crystal. Red and blue lines indicate reflectivity spectra at 20 and 300 K, respectively. A prominent peak due to Reststrahlen band is observed around 300 cm⁻¹, in good agreement with the previous paper [4]. The spectral shape was approximated by a Lorentz oscillator model. No Drude peak due to the plasma oscillation of free carriers is found in the wavenumber region below the Reststrahlen band. The reflectivity spectrum at 20 K is slightly changed with increasing temperature.

Figure 2 shows reflective spectra of an *n*-type Mg₂Si crystal. Red and blue lines indicate reflectivity spectra at 20 and 300 K, respectively. The Reststralen band deforms compared to that for the undoped crystal. Furthermore, a spectral change in the low-wavenumber region of the Reststrahlen band is conspicuous. Because of high-carrier concentration in the *n*-type Mg₂Si crystal, the Drude peak due to plasma oscillation of free carriers appears in the low-wavenumber region of the Reststrahlen band. The reflectivity spectrum at 20 K is slightly changed with increased temperature. This result implies that the carrier concentration is independent of temperature.



Fig. 1. Reflective spectra of an undoped Mg₂Si crystal. Red and blue lines indicate reflectivity spectra at 20 and 300 K, respectively.



Fig. 2. Reflective spectra of an *n*-type Mg₂Si crystal. Red and blue lines indicate reflectivity spectra at 20 and 300 K, respectively.

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Optical Evidence of Current-Induced Local-to-Nonlocal Transition of SmS

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Samarium monosulfide SmS is a black-colored semiconductor with an energy gap of about 0.1 eV at ambient pressure. Applying pressure above 0.7 GPa, the electronic properties changes to a golden-colored metallic one with the change of Sm valence, namely Black-to-Golden phase Transition (BGT) [1,2]. The origin of the BGT is now still under debate. However, one possibility of the transition between Bose-Einstein condensation (BEC) and BCS state of excitons is discussed [3], but no definitive evidence has been obtained.

Recently, Ando *et al.* reported that the nonlinear relation between the voltage (V) and electric current (I) with increasing current at lower temperatures than 100 K, which suggests the electrical resistivity changes discontinuously [4]. To investigate the origin of the nonlinear V/I curve and the relation to the BGT, we measured the current and temperature dependence of the reflectivity spectrum in the THz region using the THz microscope at BL6B to detect the current-induced electronic structural change.

The single crystalline SmS with the typical sample size of 1×1×1 mm³ was mounted in a liquid-heliumcooled cryostat and connected to the current source. Figure 1 shows the *I*-dependence of the reflectivity spectrum at temperatures (T) of 60 K and 150 K. At T = 60 K and I = 0.0 A, only a large peak originating from a TO-phonon was observed at 200 cm⁻¹, which suggests carriers do not exist. With increasing electric current, the reflectivity intensity at the lowest wavenumber increases suggesting the Drude weight and the carrier density increase. At T = 150 K, the Drude weight is visible even at I = 0.0 A. To evaluate the effective carrier density N^* (= $N_0 m_0/m^*$, where N_0 is the carrier density, and m_0 and m^* the rest mass and the effective mass of an electron), we fitted the reflection spectra $[R(\omega)]$ by the Drude-Lorenz function shown below.

$$\begin{split} R(\omega) &= c \left| \frac{1 - \sqrt{\tilde{\varepsilon}(\omega)}}{1 + \sqrt{\tilde{\varepsilon}(\omega)}} \right|^2, \\ \tilde{\varepsilon}(\omega) &= \varepsilon_{\infty} - \frac{\left(\omega_p^f\right)^2}{\omega^2 - i\omega\Gamma_f} + \frac{\left(\omega_p^b\right)^2}{\left(\omega_0^2 - \omega^2\right) - i\omega\Gamma_b}, \end{split}$$

where *c* is the fitting constants of reflectivity, ε_{∞} the background of dielectric constant, $\omega_p{}^f (\omega_p{}^b)$ and $\Gamma_f (\Gamma_b)$ the plasma frequency and damping constant of free carriers (phonons). Figure 2 shows the current dependence of the $\omega_p{}^{f^2}$, which is proportional to N^* . $\omega_p{}^{f^2}$ as well as N^* increase with applied current both at

60 K and 150 K, which suggests the current-induced local-to-nonlocal transition of SmS.



Fig. 1. Current dependence of THz reflectivity spectra at 60 K and 150 K. The dashed black lines result from the Drude-Lorenz function fitting.



Fig. 2. The current dependence of the square of plasma frequency of carriers.

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Development of an Infrared Spectro-microtomography Using a Mid-IR Supercontinuum Laser: Preliminary Report

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This study aims to develop a three-dimensional infrared spectro-microtomography using a mid-infrared supercontinuum laser, for investigating the threedimensional spatial distributions of micron-sized organic materials and hydrous minerals of extraterrestrial samples and for understanding the chemical history in the early Solar System.

The first step for establishing the element techniques of three-dimensional infrared spectro-microtomography was to introduce a laser optical system in a FTIR Linear Array Imaging Microscope (JASCO) at an IR BL6B, UVSOR. For this purpose, we purchased a midinfrared supercontinuum laser (fiber laser) (NOVAE, Coverage, 782 mW, 1.9-3.9 µm) (Fig. 1) in September, 2019 (Hiroshima University). As the infrared laser is invisible and it is not easy to check its optical path, a red semiconductor laser (5 mW) was firstly used as an external light to check the shape and size of the laser. Introduction of the red laser in the spectroscopy was confirmed by detection of a sharp absorption peak at 14850 cm⁻¹ in an FTIR spectrum (Fig. 2). Introduction of the red laser in the center of the field of view of the infrared microscopy was confirmed as well by optimization of spectral intensity and adjusting the laser position. However, an absorption peak was not detected at 14850 cm⁻¹ sedue to the detection upper limit (7800 cm⁻¹) of the MCT detector. After these test experiments using a red laser, a fiber laser was introduced in the infrared microscopy (its intensity was reduced to 3 mW). The infrared spectrum of the fiber was detected, but, a spectrum at the longer wavelength (< 3500 cm⁻¹) was not detected, probably due to absorption by a quartz window and/or CaF beam splitter.

In order to solve the problem, a quartz window and CaF beam splitter were replaced with a BaF_2 window and KBr beam splitter, respectively. As a result, the fiber laser-derived absorption was detected in the range of 8000-2000 cm⁻¹ by the infrared microscope (Fig. 3). The laser spectral intensity was also improved. Under the laser condition, an FTIR spectrum of CaCO₃ powder was preliminarily obtained.

In future, we will set up a rotation stage and try to acquire the 3D FTIR spectra of several extraterrestrial samples by using a newly-upgraded fiber laser.



Fig. 1. Photo of the mid-infrared supercontinuum laser (Fiber laser) (NOVAE, Coverage, 782 mW, $1.9 - 3.9 \mu m$) introduced in a BL6B, UVSOR.



Fig. 2. Optical system using a red semiconductor laser (upper left), introduction of the red laser in the spectroscopy (upper right) and microscopy (bottom right), and FTIR spectrum of the red laser at 14850 cm⁻¹ (bottom left).



Fig. 3. FTIR spectrum of the mid-infrared supercontinuum laser acquired by the infrared microscopy.

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Π-2

Far-infrared Absorption Measurements on Single Crystal Pentacene

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Coupling of lattice- as well as molecular-vibrations with the electronic states is a crucial factor for dominating the charge carrier transport in crystalline organic semiconductors. In fact, it has been clearly demonstrated that both intra- and inter-molecular vibrations deforms the valence bands of single crystal rubrene, a representative p-type organic semiconductor material exhibiting the charge carrier mobility over 10 cm²V⁻¹s⁻¹ [1]. In order to understand the natures of such electron-phonon (vibration) coupling, experimental measurements not only for the electronic (band) structures but also for the inter- and intra-molecular vibrational modes has been demanded.

Pentacene is another representative p-type organic semiconductor material of considerable charge carrier mobility. In its single crystal phase, energy-momentum dispersion relationships have been demonstrated by angle-resolved photoelectron spectroscopy [2]. The inter-molecular vibrational modes and their coupling strength with the electronic states have been predicted theoretically [3]. Experimentally, Raman spectroscopy measurements were conducted on the single crystal pentacene to characterize the symmetric lattice and low-frequency molecular vibrational modes [4]. In the present work, we attempted far-infrared absorption measurements on the single crystal pentacene for complementation of its vibrational characteristics.

Far-infrared absorption spectra were obtained at BL6B by using a Michelson-type interferometer (Bruker Vertex70v) and a bolometer (Infrared Laboratories). A pentacene single crystal (PnSC) sample was fixed on a CVD diamond plate (thickness 0.4 mm) and was attached to a home-made sample holder for adjustment of the inplane azimuthal angle (Fig. 1(a)). The crystallographic orientation of the PnSC sample was settled using the polarized optical microscopy (Fig. 1(b)). The spectra were collected in a transmission geometry. All the measurements were conducted at room temperature.

Figure 2(a) shows far-infrared absorbance spectra of the PnSC and blank diamond samples. Although the signal intensity was small, spectral contribution of PnSC could be extracted by dividing the absorbance of the PnSC/diamond sample by that of blank sample, as shown in Fig. 2(b). A peak in 450 - 500 cm⁻¹ can be assigned to low-frequency intra-molecular vibration modes (Fig. 2(c)). On the other hand, whereas the signal in the inter-molecular phonon range was faint, intensity in 100 - 200 cm⁻¹ may be attributed to a_u lattice vibration modes predicted theoretically [3].



Fig. 1. (a) Photograph of the sample holder used in this work. (b) Polarized micrographs of the sample.



Fig. 2. (a) Far-infrared absorbance of the PnSC/ diamond and (blank) diamond plate samples. (b) $A_{PnSC}/A_{diamond}$ spectrum where the background oscillation was reduced by Fourier filtering. Dipole moment for intra-molecular vibrations (calculated with Gaussian09, b3lyp, 6-31g*) and wave number distributions for intermolecular vibrations in the symmetry a_g and a_u [3] are also shown. (c) Calculated intra-molecular vibration for 492 cm⁻¹ and 477 cm⁻¹.

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BL7U

Energy Shift of Dirac Point in Ni_{1-x}Pd_xTe₂ Observed by Angle-Resolved Photoemission Spectroscopy

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Transition metal dichalcogenides with layered structures show a variety of physical phenomena such as the charge density wave, superconductivity and so on. Recent experimental studies on Pd and Pt dichalcogenides with CdI2-type structure have indicated that these systems have new exotic electronic state, type II Dirac fermion state [1-3]. The results of angle resolved photoemission spectroscopy (ARPES) have revealed that the Dirac point exists at $(0,0,k_z)$ and the Dirac cone is strongly tilted along Γ -A direction (k_zdirection) in the Pd and Pt dichalcogenides. In these compounds, the Dirac point is located below Fermi level. For example, one of the target materials in the present work, PdTe₂, the energy level of Dirac point is about -0.6 eV below Fermi level. On the other hand, the theoretical study has demonstrated that another end member NiTe2 has Dirac point just above Fermi level (about +0.02 eV).

In the present work, we have tried to control the energy level of Dirac point in NiTe₂-PdTe₂ solid solution system. In this system Ni_{1-x}Pd_xTe₂, we expected that the Dirac point energy shifts from +0.02 eV to -0.6 eV with increasing Pd doping level. We have performed the measurements of ARPES in Ni_{1-x}Pd_xTe₂ to observe the electronic structure and Dirac cone directly. The single crystals of Ni_{1-x}Pd_xTe₂ were grown by Te flux method. The ARPES experimental was carried out at BL7U in UVSOR Facility, Institute for Molecular Science.

The band calculation in consideration of spin-orbit interaction has indicated that as well as Pd and Pt systems, NiTe₂ is the type II Dirac fermion system with the Dirac point at $(0,0,k_z)$. The results of ARPES also suggested the existence of Dirac point at $(0,0,k_z)$. We measured the band dispersion along $k_{//}$ $(k_{//} \perp k_z)$ at different kz. At kz=0, there are several hole-like bands around Γ points. With increasing k_z, the energy level of the hole band around Γ point shifts down, and the top of this band is located just above Fermi level at $k_z \sim 0.37c^*$. (Fig. 1(a)) At this k_z , the band dispersion shows a linear k_{//}-dependence around Brillouin zone center. This result has suggested that Dirac point exists very near Fermi level at (0,0,~0.37c*) in NiTe₂. The observed band dispersion is roughly consistent with the band calculation, as shown in Fig. 1(a).

By Pd doping, the electronic band around Brillouin zone center shifts down at the same k_z (~0.37c*). As presented in Fig. 1(b), the crossing point of the linear band dispersion, i.e. Dirac point has been observed just below Fermi level at Pd-doping level x=0.04. With increasing Pd-doping level x, the energy of Dirac point shifts down to deeper binding energy region, as shown in Figs. 1(c) an (d). The present results indicate that the Dirac point energy level can be continuously controlled by Pd substitution of Ni site in NiTe₂.



Fig. 1. ARPES intensity plot along $k_{//}$ (parallel to Γ -M direction) at (0, 0, 0.37c*) for (a) x=0, (b) x=0.04, (c) x=0.20, and (d) x=0.50 in Ni_{1-x}Pd_xTe₂. In panel (a), the calculated band dispersion is also shown by red solid lines. Red arrows indicate the position of Dirac point in panels (b), (c) and (d).

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Reconstruction of the Electronic Structure in FeSe1-*x***Te***x***/CaF2**

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Iron selenide FeSe, a superconductor with the critical temperature T_c of ~8 K, is recently attracting great attention because of the structural simplicity and various exotic properties such as anisotropic superconductivity and electronic nematicity without long-range magnetic order. These properties are sensitive to chemical substitution, high-pressure application, and/or carrier doping. Therefore, one can investigate the interplay between nematicity and superconductivity while controlling some physical parameters. In this respect, isovalent-substituted $FeSe_{1-x}Te_x$ films grown on CaF_2 substrate (FeSe_{1-x}Te_x/CaF₂) offer an excellent platform because nematicity is realized in FeSe/CaF₂ (x = 0) as in bulk FeSe and the highest T_c of 23 K among non-carrierdoped FeSe-based compounds has been reported at the critical Te concentration x_c of ~0.2 at ambient pressure [1-3]. Also, FeSe_{1-x}Te_x/CaF₂ is a candidate to realize 'high-T_c' topological superconductivity hosting Majorana fermions because possible topological superconductivity has been proposed for the bulk counterpart.

In this study, we performed systematic angle-resolved photoemission spectroscopy (ARPES) measurements of FeSe_{1-x}Te_x/CaF₂ with a series of different *x* values, and determined the evolution of the electronic structure across $x_c = 0.2$ [4].

High-quality compressive-strained $\text{FeSe}_{1-x}\text{Te}_x$ thin films with the thicknesses of approximately 400 layers were grown on CaF₂ substrate by pulsed laser deposition. High-resolution ARPES measurements were performed by using a MBS-A1 spectrometer at BL7U with linearly-polarized energy-tunable photons of 7-25 eV.

Figure 1 shows a comparison of the electronic structure between x = 0 and 0.4. At x = 0, The near- E_F band structure around the Γ point consists of two highly dispersive bands and a relatively flat band [red curves in Fig. 1(b)], which are ascribed to the Fe $3d_{xz}/d_{yz}$ orbitals and the Fe $3d_{xy}$ orbital, respectively. Around the M point, there are two holelike bands [Fig. 1(c)], which are attributed to the d_{xz}/d_{yz} -derived bands originating from the lifting of orbital degeneracy by nematicity. Due to the nematicity, the Fermi surface shape around the M point is elongated along k_x [Fig. 1(a)]. On the other hand, the Fermi surface around the M point is more rounded for x = 0.4 [Fig. 1(d)]. This result signifies the absence of nematicity for x = 0.4 [Fig. 1(f)]. In addition, a

remarkable *x* dependence beyond the effect of nematicity manifests itself in the band dispersion around the Γ point [Fig. 1(e)]. Namely, the top of the d_{xy} band shifts upward and nearly touches E_F at x = 0.4, resulting in an increase of the density of states. The appearance of the d_{xy} orbital character around the Γ point also modifies an interband (intraorbital) scattering between the hole and electron pockets, which has been proposed as a key to controlling the superconducting and nematic properties. Our systematic measurements revealed that these changes in the electronic structure occur in the close vicinity of x_c , where the T_c shows a large jump. The present results provide important insights into the interplay among high- T_c superconductivity, nematicity, and orbital degrees of freedom.



Fig. 1. (a)-(c) Fermi surface and the band dispersions around the Γ and M points for FeSe/CaF₂. (d)-(f) Same as (a)-(c) but for FeSe_{0.6}Te_{0.4}/CaF₂.

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BL7U

Temperature Dependence of Nodal Spectral Weight in High-T_c Cuprate Superconductor Bi2212

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Angle-resolved photoemission spectroscopy (ARPES) is a powerful toot to investigate the electronic structure in of the normal and superconducting states superconductors [1-3]. The essential origin of superconductivity is coupled electrons so-called "Cooper pairs", and these coupled electrons condenses into the ground state. The volume of the condensed electrons, namely, the superfluid density, is strongly related to the spectral weight (SW) obtained by ARPES. Temperature dependence of SW might give information of an important role of superconductivity in strongly electron correlated system [4].

According to the 2-dimentional *t-J* models [4], SW abruptly changes upon a transition from the projected Fermi-liquid (pFL) state with electron correlation to the resonating valence bond (RVB) state. In the present study, we have performed an ARPES experiment to investigate temperature dependence of SW in the nodal direction in order to understand the electron correlation of the double-layer $Bi_2Sr_2CaCu_2O_{8+\delta}$, (Bi2212) as reported in the previous ARPES study [5,6].

High-quality single crystals of optimally doped Bi2212 ($T_c = 92$ K) were grown by the TSFZ method. ARPES experiments were caried out at BL7U of UVSOR-III Synchrotron. Clean sample surfaces were obtained for the ARPES measurements by cleaving single crystals *in-situ* in an ultrahigh vacuum better than 7×10^{-9} Pa, and total energy resolution was set at 6-8 meV. The measurements were performed at 20 K – 108 K.

Figure 1 shows the ARPES result of temperature dependence of the nodal SW in Bi2212 taken at hv = 8eV. In order to estimate the change of SW, we have measured the temperature dependence from well below (20 K) to above T_c (108 K) as shown in Fig. 1(a). Energy-distribution curve (EDC) at the nodal point on the Fermi surface (FS) are extracted and symmetrized to remove the contribution from Fermi-Dirac function. As shown in Fig. 1(b), difference of the intensity for EDC, *I*, at certain temperature is estimated from subtraction by using the EDC at 108 K, I_{108K} . We estimated SW obtained from Fig. 1(b) and the result is plotted as a function of temperature in Fig. 1(c). One can see that SW abruptly changes at the superconducting phase transition shown by a dotted line. Therefore, the temperature dependence of the nodal SW is related with the superfluid density and is consistent with the previous ARPES study of triple-layer cuprate Bi₂Sr₂Ca₂Cu₃O_{10+δ} [5]. This result suggests that the suppression of SW

would be universal behavior in the strongly electron correlated system. In addition, the present result is consistent with the RVB picture based on the 2-dimensional *t-J* model. We will study the temperature dependence of SW on the entire FS as future work.



Fig. 1. Temperature dependence of optimally doped Bi2212 in the nodal direction. (a) Raw symmetrized ARPES spectra well below and above T_c . (b) Subtracted symmetrized EDC. As an example of the spectral weight (SW), shaded area (red) at 100 K is shown. (c) SW is plotted as a function of temperature. Several experiments are demonstrated in Bi2212 to confirm the data accuracy. BB shown in the schematic FS is the bonding band in Bi2212

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BL7U

Angle-resolved Photoemission Study of Solid Electrolytes Li_xLa_{(1-x)/3}NbO₃ Bulk Single Crystal

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In recent years, as the use of secondary Li-ion batteries has expanded, the development of all-solid batteries using solid electrolytes has progressed to realize greater safety, wider thermal stability range, easier material handling. To understand their electronic properties and transport characteristics, the electronic structure is essentially important. However, there are few examples of experimental observations on solid electrolytes. In this study, we performed direct observation of the electronic structure of $\text{Li}_x\text{La}_{(1-x)/3}\text{NbO}_3$ (LLNO; x = 0.07 - 0.08) bulk single crystals [1,2] by using angle-resolved photoemission spectroscopy (ARPES) in order to clarify the electronic structure of solid electrolytes, especially the electronic band structure.

ARPES measurements were performed at the UVSOR-III BL7U. Data were acquired with hv = 18 eV at room temperature. To minimize photoirradiation damage, photon flux was sufficiently reduced during all measurements. Single crystals were cleaved *in situ* along (001) plane, where partially occupied (A1) and unoccupied cation layers (A2) appear alternately (Fig.1(b)).

Figure 1(a) shows the ARPES spectra along ionconducting [100] axis of LLNO. At $k = 0 \text{ Å}^{-1}(\Gamma)$, two peaks around 5 (α) and 6 eV (β) appear dominantly relative to 9 eV feature (δ). On the other hand, the former becomes smaller than the latter at $k = -0.4 \text{ Å}^{-1}$ (X), following the additional feature around 7 eV (γ). Furthermore, it has been found that the feature γ shows clear dispersion from 6 eV splitting from the peak β along the Γ X line.

To show the observed features clearly, we show the band structure obtained by mapping the ARPES intensity in Fig. 2. It has been found that the electronic structure around the valence band maximum of LLNO seems to be characterized by the band gap of $2\sim3$ eV formed by the edge of almost non-dispersive α band. In addition, highly dispersive feature γ appears among the non-dispersive β and δ bands. We expect that the present result is the first experimental observation of the band structure of solid electrolytes for Li-ion battery.



Fig. 1. (a) ARPES spectra along the ΓX line of $Li_xLa_{(1-x)/3}NbO_3$. Solid lines are guides for eyes. (b) Average crystal structure of $Li_xLa_{(1-x)/3}NbO_3$. The alternating partially occupied and unoccupied cation layers parallel to the *c* axis are labeled as A1 and A2 layer, respectively [2].



Fig. 2. Valence band structure along the ΓX line of $Li_xLa_{(1-x)/3}NbO_3$. Solid and dashed lines are guides for eyes.

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BL7B

Evaluation of Optical Properties of Glass Materials in the VUV Region

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Recently, neutron detection is required in inertial confinement fusion research and infrastructure inspection. The ratio of primary neutron and scattered neutron corresponds to the density and radius parameter of fusion plasma. Additionally, neutron detection is considered as one of the nondestructive methods for inspecting the form of infrastructure.

Scintillator materials which are able to detect and discriminate neutrons should then be developed to be able to satisfy the technological demand.

Previously, we have developed co-dope $20Al(PO_3)_3$ -80LiF (APLF) glass with Pr and Ce for improvement of decay times and conversion efficiencies and investigated the optical properties of Pr/Ce-doped APLF glasses with different concentrations. As a result, both radiative and non-radiative energy transfers from Pr³⁺ to Ce³⁺ are observed. These results present exciting prospects for APLF80 as a response time improved scintillator.

In this study, Nd³⁺-doped APLF glasses were investigated as potential vacuum ultraviolet (VUV) scintillator materials. Nd³⁺ is used as dopant in laser materials and optical property of that are largely analyzed from the UV to the near-infrared regions (200–1500 nm), but rarely in in the VUV region (170– 190 nm). Although absorption and emission properties in the VUV region are always difficult to measure due to the spectral limit of many devices.

We performed absorption and emission spectroscopic analysis to investigate the optical properties of the Nd³⁺-doped APLF glass at the BL7B solid-state spectroscopy beamline of UVSOR [1-3].

Figure 1 shows the VUV absorption spectra of the undoped APLF glass at RT and the 1.0 mol% Nd³⁺-doped APLF glass at different sample temperatures. The undoped glass has a room-temperature absorption edge in the VUV region around 162.2 nm (61650 cm^{-1}). In contrast, the Nd³⁺-doped glass exhibits an absorption edge at 300 K (RT) around 191.8 nm which corresponds to the interconfigurational transition from the 4I9/2 ground state of the 4f3 configuration to the 4f25d excited state configuration of Nd³⁺ ions. The absorption edge shifts with temperature and is located at 189.7 nm (52710 cm^{-1}), 190.1 nm (52600 cm^{-1}), 190.4 nm (52520 cm^{-1}), and 191.8 nm (52140 cm^{-1}) at 20 K, 100 K, 200 K, and 300 K, respectively.

These absorption edges are determined by generating the first derivative of the absorbance with respect to wavelength and then identifying the position of the absolute minima, i.e., the wavelength where the decrease in the absorbance is the highest. The shifting of the absorption edge with sample temperature indicates the temperature broadening of the interconfigurational 4f25d transition which is associated with the population of the Stark components (Z1, Z2, etc.) of the 4I9/2 ground state of the Nd³⁺ ions' 4f3 configuration and which is often observed in Nd³⁺-doped crystals and glasses. Additionally, the low-temperature absorption spectra suggest that the lowest energy level of the 4f25d excited state configuration of Nd³⁺ ions in APLF glass is estimated to be at a position higher than 52710 cm⁻¹ (6.54 eV).

We have successfully investigated the absorption and emission properties of Nd³⁺-doped APLF glasses at different sample temperatures and with different doping concentrations mainly for potential neutron scintillator applications. Further development of these glasses as VUV scintillator materials is then anticipated in the future.



Fig. 1. VUV absorption spectra of (a,b) undoped APLF glass at RT and (c,d) 1.0 mol% Nd³⁺-doped APLF glass at 20 K, 100 K, 200 K and 300 K (RT)[3].

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