Features of valence band structure of TlAlF$_4$

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Abstract. Modulation of the upper edge of valence band of ionic solids by $6s^2$ occupied
states of Tl$^+$ is a primary origin of the changes in optical and electrical properties of host
materials containing Tl$^+$. Semiquantitative estimation of mixing of $6s^2$ states on Tl$^+$ ions with
$2p^6$ on F$^-$ ions in the TlAlF$_4$ crystal was carried out by photoemission, optical absorption,
photoluminescence and photocurrent measurements. Photoemission spectra were measured with
excitation energies of 60, 130 and 1486.7 eV. The separation between the uppermost two
bands was found to be 2.5 eV for TlAlF$_4$ and TlF, which were considerably greater than
the corresponding values for TlCl and TlBr. This was interpreted as due to the fact that the
energy level of F 2p is deeper than Cl 3p and Br 4p. It was concluded from the excitation
energy dependences of the intensities of the respective peaks in the valence band region that the
contribution of Tl 6s to the top edge of the valence band of TlAlF$_4$ and TlF was several tens
of a per cent. A large Stokes shift of about 2 eV and the long lifetime (1.2 μs) of fluorescence
suggested that the $6s^2$ levels of Tl$^+$ ions have a tendency to localize and the top of the valence
band did not form such an extended state of TlBr. This conclusion was confirmed by the
observation that the photocurrent of TlAlF$_4$ was one fifth of that of TlBr.

1. Introduction

The monovalent thallium ion (Tl$^+$), i.e. the thallous ion, in inorganic solids plays a
central role in UV photoluminescence and photoconductivity of thallous halides [1–4]. The
electronic structure of thallous compounds has been extensively investigated so far because
of the unique properties [5–8]. The monovalent thallium ion has the $5d^{10}6s^2$ electronic
configuration in a free-ion state. In the existing inorganic crystals, however, the spatial
distribution of $6s^2$ electrons (historically called the 'inert pair') sensitively responds to the
type and number of available anionic ligands [9, 10]. Variation in the spatial distribution of
the pair gives rise to modulation of the valence band structure of the ionic solid, because
the energy of the pair on a Tl$^+$ ion is generally comparable with the outermost np^6 electrons
on anionic ligands.

One of the interesting properties of thallous halides is photoconductivity. Time-of-
flight experiments on TlBr showed large mobilities of photogenerated positive holes (about
2 cm^2 V^{-1} s^{-1}) and electrons (about 30 cm^2 V^{-1} s^{-1}) [3, 4]. This observation is stimulating,
because the high mobility of positve holes suggests that the upper edge of the valence band

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is an extended state. In most ionic crystals, the positive hole at the upper edge of valence band, which is in most cases composed of filled p orbitals of electronegative anions, has a tendency to be localized. The extended nature of the valence band of TlBr provides evidence of large participation of the Tl 6s filled band in the upper edge of the valence band. Therefore, thallous halides (TlX) are candidates for p-type semiconductors with a wide band gap (e.g. the band gap of TlCl is about 3.4 eV), if p- or n-type doping is successfully achieved. However, most TlXs are very hygroscopic, and the materials are not useful in practical applications.

We intend to determine the contribution of the Tl 6s orbital to the valence band edge of ionic solids. In the present study, $TlAlF_4$ was selected, because it is less hygroscopic than chlorides, and its valence band structure was examined by photoemission spectroscopy (PES). Some physical properties of thin films and sintered pellets were also investigated.
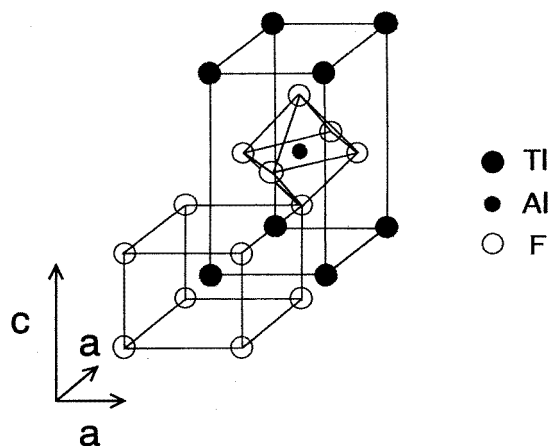

Figure 1. Crystal structure of $TlAlF_4$. This belongs to the tetragonal system.

2. Characteristics of the crystal structure of $TlAlF_4$

TlXs have ionic crystal strucures, e.g. NaCl type or CsCl type, as well as alkali halides. $TlAlF_4$ has a structure derived from the ionic crystals. The structure was studied first by Brosset [11]. Recently, by means of differential scanning calorimetry and powder neutron diffraction, Bulou and Nouet [12] reported several small structural phase transitions which were caused by only the tilts of the AlF_6 octahedra. The crystal structure seems to consist of repetition of the stacking layers of F, Tl, F and AlF_2 in this order (figure 1). In other words, the structure is based on a simple layer of vertex-sharing AlF_6 octahedra, $(AlF_4)^-$ and a layer of Tl^+. The apex F^- ions are coordinated by four Tl^+ ions and one Al^{3+} ion. In-plane F^- ions which share the corner of the octahedra are coordinated only by two Al^{3+} ions. The Tl^+ ion which has a large ionic radius is confined between two $(AlF_4)^-$ layers. The layer of Tl and two layers of apex F^- ions seem to have a caesium chloride structure similar to those of TlCl and TlBr. TlF_8 polyhedra, where the Tl^+ ion lies in a highly symmetric coordination of F^-, are connected by sharing faces each other in the two-dimensional sheet. Accordingly, the distance from a Tl^+ ion to an adjacent Tl^+ ion is very short, about 0.36 nm. In the case of TlCl and TlBr, the lengths are 0.384 nm and 0.39 nm, respectively. The short distance of Tl–Tl in $TlAlF_4$, which is probably due to the

ionic radius of F$^-$ ion which is the smallest of the halogen ions, is expected to cause the interaction between adjacent Tl 6s orbitals.

3. Experimental details

3.1. Sample preparation

Polycrystalline TlAlF$_4$ samples were prepared in the form of sintered discs and thin films. Starting TlAlF$_4$ powders were synthesized by heating a stoichiometric mixture of TlF (99.9%) and AlF$_3$ (99.9%) in an evacuated quartz tube at 773 K for 10 h. Polycrystalline discs of the flouride were obtained by pressing the powders into pellets of 10 mm diameter and heating them in an evacuated quartz tube at 773 K for 10 h. A polycrystalline thin film sample was first prepared by a conventional vacuum evaporation process. A silica glass of Cu plate was used as a substrate. The evaporation source used was the polycrystalline powders, which were heated in an alumina-coated tungsten basket. Since the as-deposited thin film was amorphous, post-annealing for crystallization was carried out at 400 K for 1 h in the preparation chamber with a pressure of 9×10^{-6} Torr.

The crystal phase and the composition of the sample were determined by means of x-ray diffraction and SEM–EDS measurements, respectively.

3.2. Measurements of optoelectronic properties

In order to investigate the valence band structure, photoemission measurements were made at 300 K. The angle-integrated ultraviolet photoemission spectroscopy measurements (UPS) were performed at the BL2B1 beam line of an electron storage ring (UVSOR) operated at 750 MeV installed in the Institute for Molecular Science. A grass-hopper monochromator was used to cover the photon energy region from 60 to 200 eV. Thin film samples were prepared *in situ* by vacuum evaporation onto a molybdenum sample holder in a preparation chamber with a base pressure of 2×10^{-9} Torr, and the holder was transferred as soon as possible to an analysing chamber with a base pressure of 1×10^{-10} Torr. The double-pass cylindrical mirror analyser (Perkin–Elmer 15-255G) was used as an electron energy analyser. X-ray photoelectron spectra were obtained with a Perkin–Elmer ESCA-5500MC, using monochromated Al Kα radiation. The total resolution of both measurement systems was about 0.5 eV. The spectra of the TlF thin film prepared by the vacuum evaporation method was also measured for comparison. The TlAlF$_4$ thin film for x-ray photoelectron spectroscopy (XPS) measurement was evaporated onto a silica glass substrate. To minimize the charging effect, the analysed area was restricted to the opening of a metal ring placed on the sample.

Optical absorption and reflectivity measurements were made for the thin film samples. Optical absorption was measured with a spectrometer (Hitachi U-4000) in the region 0.4–6.3 eV at 300 K. Reflectivity meausrements were performed in the region 3.9–12 eV at 300 and 15 K at the BL7B beam line of UVSOR.

Photoluminescence spectra from the polycrystalline disc sample were measured with a spectrofluorimeter (Shimadzu RF-5000) at 300 and 77 K. The fluorescence lifetime was measured by a TAC system with use of a spectrofluorimeter (Horiba NAES-550) at 300 K. A hydrogen spark lamp with a bandpass filter (central wavelength, 250 nm) was used as the excitation light source. The pulse width of the source was shorter than 2 ns.

The photocurrent measurement was carried out at 300 K. A xenon–Hg lamp (Ushio deep UV lamp) was used as the excitation light source for the measurements. Au electrodes

were sputtered on the same surface of the thin film sample. An electric field of 160 V cm^{-1} was applied. The excitation light was illuminated from a direction vertical to the applied electric field. The photocurrent was detected by use of an electrometer (Advantest TR8652). No correction for the spectral intensity of the light source was carried out.
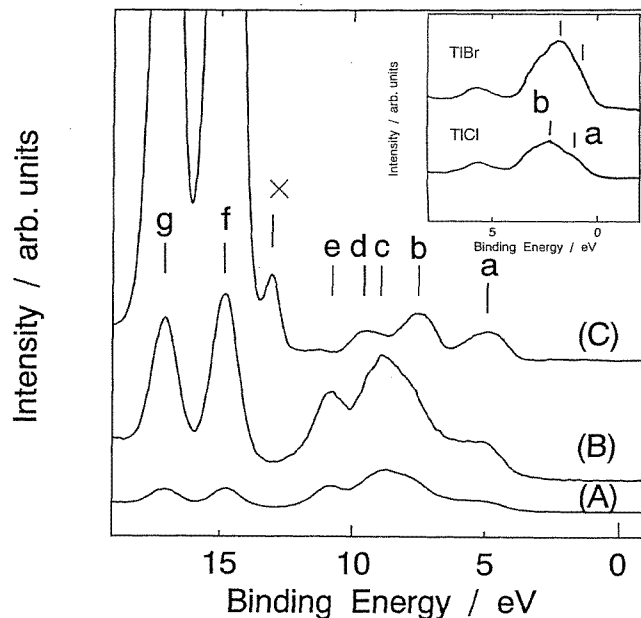

Figure 2. Photoemission spectra of an evaporated thin film of TlF in the region of valence bands. Excitation photon energies for curves (A) and (B) are 130 eV and 60 eV, respectively. Curve (C) is the x-ray photoelectron spectrum obtained by Al Kα radiation (1486.7 eV). The binding energy is measured from the Fermi level. The peak labelled by a cross seems to be a spurious band (probably due to defects induced by x-ray irradiation), because the peak intensity started to increase gradually during the x-ray irradiation. The inset shows the x-ray photoelectron spectra of TlCl and TlBr [14] obtained with Al Kα radiation. In the inset the binding energies are given relative to the edge of the valence band.

4. Results

Figures 2 and 3 show valence band photoelecron spectra of TlF and TlAlF$_4$ obtained for excitation photon energies of 130 eV (curves (A)), 60 eV (curves (B)) and 1486.7 eV (curve (C)). In the figures, curves (A) and (B) are ultraviolet electron spectra and curve (C) is the x-ray photoelectron spectrum. The position of the Fermi level in the ultraviolet photoelectron spectra was determined from a freshly evaporated Au film (about 10 nm thick) onto the molybdenum sample holder, and binding energies were taken from the Fermi level for these spectra. As mentioned above, the x-ray photoelectron spectrum of TlAlF$_4$ was obtained for a sample which was evaporated onto an insulating glass substrate. Therefore, the charging effect must be removed. The x-ray photoelectron spectra were shifted horizontally so that the positions of peak f and g agree with those in the ultraviolet photoelectron spectra.

The peaks observed in the x-ray photoelectron and ultraviolet photoelectron spectra are
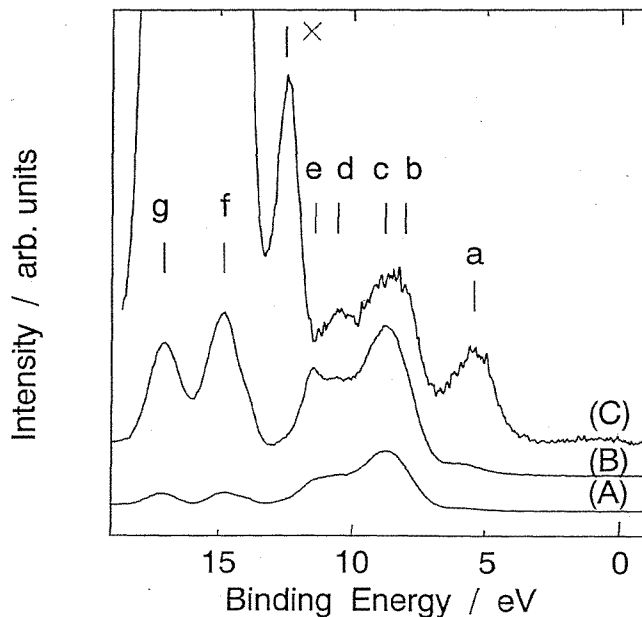
Figure 3. Photoemission spectra of an evaporated thin film of TlAlF$_4$ in the region of valence bands. The notation is the same as in figure 2.

Table 1. Peak energies obtained from the photoelectron spectra. The energies were measured from the Fermi level.

	Peak energy (eV)				
Compound	a	b	c	d	e
TlF	4.9	7.5	9.0	9.6	10.8
TlAlF$_4$	5.4	7.9	8.8	10.6	11.4

labelled from a to g. The peak positions are summarized in table 1. The peak labelled with a cross observed for TlF and TlAlF$_4$ which was detected only in the x-ray photoelectron spectra is a spurious feature. It was tentatively assigned to a peak due to a defect induced by the x-ray photons used for excitation. The reasons are as follows. The peak was not discernible immediately after the start of the measurements but increased during the measurements in which samples were continuously subjected to x-ray irradiation. After the XPS measurements, the sample became slightly darker. The band was not induced upon UV irradiation. Therefore, the photochemical reaction was initiated by excitation of core levels and the peak could not be an intrinsic band.

Figure 4 shows the optical absorption and reflection spectra of the TlAlF$_4$ thin film. In the absorption spectrum, an intense band is located at around 5.6 eV. A small shoulder at about 5.9 eV is also discernible. The reflection spectrum of the TlAlF$_4$ thin film showed the presence of two strong bands in the energy region 5–7 eV.

Violet luminescence was observed visually when TlAlF$_4$ was excited with ultraviolet light, x-rays or an electron beam. Figure 5 shows the emission spectrum of the TlAlF$_4$ polycrystalline disc obtained by irradiation with 5.4 eV light and the excitation spectrum
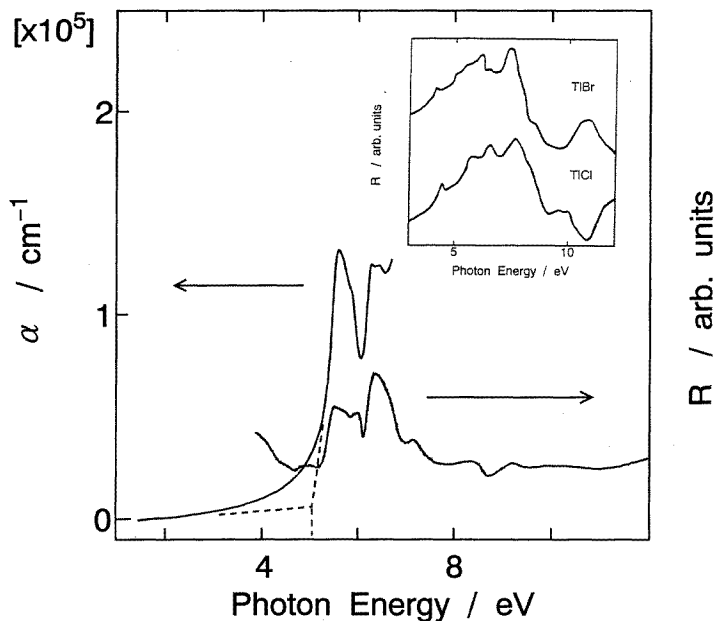
Figure 4. Absorption and reflection spectra of a TlAlF$_4$ polycrystalline thin film deposited on a silica glass substrate measured at 300 K. The sample thickness is about 500 nm. The reflection spectrum shows two strong peaks in the region 5.1–7.0 eV.

monitored at 3.2 eV. A large Stokes shift of about 2 eV was noted. Excitonic luminescence was not observed at 300 or 77 K. The excitation peak increased sharply from about 5 eV. There are two main bands peaking at 5.4 and 5.9 eV, both of which agree with the peaks in absorption spectrum shown in figure 4. The fluorescence lifetime at 300 K was 1.2 μs.

Figure 6 shows the photocurrent spectrum of the TlAlF$_4$ thin film at 300 K. The thickness of the fluoride film is about 500 nm and the total resolution of the photon energy is 0.15 eV at around 5 eV. The photocurrent started to increase steeply at 4.9 eV, which is almost the same as the increasing energy of the photoexcitation peak in figure 5. It is rational to estimate an E_g-value of 4.9 eV at 300 K from the photocurrent spectrum, because the excitonic structure has no influence. The photocurrent measured under the same conditions was approximately a fifth of that of the TlBr thin film (prepared by the vacuum evaporation method).

5. Discussion

5.1. Valence band structure

First, the valence band structure of TlF is discussed with reference to the photoelectron spectra. The two deeper peaks, f and g are ascribed to spin–orbit-split Tl 5d$_{5/2}$ and 5d$_{3/2}$ emissions as judged from their binding energies, the large splitting and the ratio of emission intensities.

The upper bands a–e consist mainly of Tl 6s and F 2p electrons. Our primary interests are in the semiquantitative estimation of the contributions of Tl 6s and F 2p to each band in the valence band region. Since the ionization cross section of each atomic orbital varies
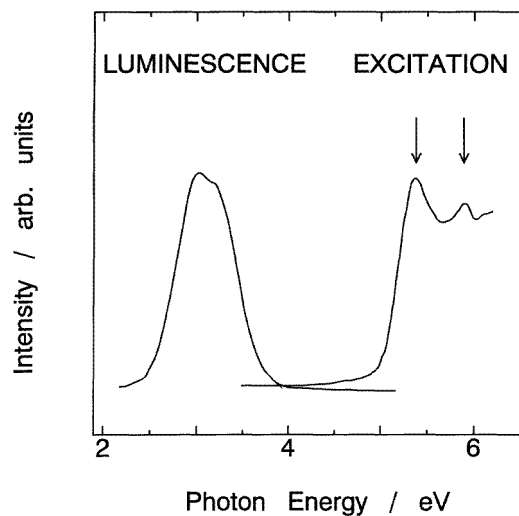
Figure 5. Photoluminescence spectrum obtained by excitation with 5.4 eV light and the excitation spectrum monitored at 3.2 eV for the TlAlF$_4$ sintered disc. A very large Stokes shift of 2 eV was observed. The excitation spectrum shows two peaks indicated by arrows, the energies of which are similar to those in the absorption spectrum.
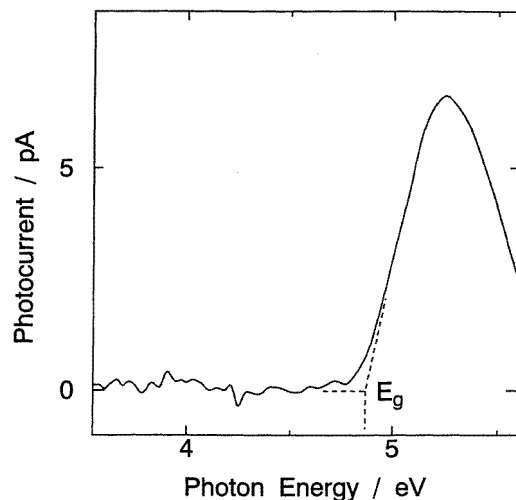

Figure 6. Photoconductivity spectrum of the TlAlF$_4$ thin film. The sample thickness is about 500 nm. A xenon–Hg lamp is used as an excitation light source. The total resolution of the photon energy is 0.15 eV at around 5 eV.

with changing excitation photon energy [13], semiquantitative determination of the fraction of each basis orbital is in principle possible from the energy dispersion curves obtained at various excitation photon energies. The ionization cross sections of the Tl 6s and F 2p orbitals on the photon energies used in the present experiment are summarized in table 2.

It is found that we can make predictions from the excitation energy dependence of the cross sections. Judging from table 2, the cross section ratios of Tl 6s to F 2p at 60 eV,

Table 2. Ionization cross section ratios of each atomic orbital at the photon energy relevant to this measurement [13].

$h\nu$ (eV)	Tl 6s-to-Tl 5d	F 2p-to-Tl 5d	Tl 6s-to-F 2p
130[a]	0.06	2	0.04
60[a]	0.004	0.2	0.02
1486.7	0.02	0.02	1.3

[a] The order of the excitation energies is the same as in figures 2 and 3.

130 eV and 1486.7 eV excitations are 0.02, 0.04 and 1.3, respectively. In the case of UPS, the contribution of Tl 6s is negligible compared with that of F 2p; thus ultraviolet photoelectron spectra would show the distribution of F 2p in the valence band region.

The cross section ratios of F 2p to Tl 5d, which is the semi-inner shell, at 60 eV, 130 eV and 1486.7 eV excitations are 0.2, 2 and 0.02, respectively. As noted in figures 2 and 3, this is really the case; the intensities of peaks f and g were far larger than those of the upper valence peaks a–e in XPS, and the intensity ratios became smaller with decreasing excitation photon energy.

The contributions of Tl 6s and F 2p to the upper peaks in the valence band are our primary concern. As previously pointed out, the Tl 6s contribution is enhanced in XPS compared with UPS. Peaks a, b and d were intensified in XPS compared with UPS and contain considerable (probably of the order of tens of a per cent) Tl 6s character. The assignment of peak a is considered to be a σ-type antibonding state between Tl 6s and F 2p. However, peaks b–d cannot be assigned definitely, since no band calculation has been reported so far, as far as we are aware.

The separation (about 2.7 eV) between peaks a and b is larger than those of TlCl and TlBr shown in the inset of figure 2 and reported by Porte and Tranquard [14]. In the latter two compounds, the separations are not clearly discernible. The reason is as follows. Since the energy level of Cl 3p or Br 4p is much shallower than that of F 2p, the mixing of Cl 3p or Br 4p with Tl 6s is larger than that of F 2p. The large separation between peaks a and b for TlF is an indication of the fact that the energy of F 2p is deeper than the valence p orbitals of Cl and Br.

Second, the photoelecron spectra of TlAlF$_4$ are discussed. The spectra are semiquantitatively similar to those of TlF except that peak e was not obviously seen because of overlapping with the peak labelled with a cross. Judging from figure 3, peaks a, b and d have a large Tl 6s character, and peaks c and e have large F 2p character.

Third, it is shown that the above-mentioned explanation of the electronic structure of TlAlF$_4$ is supported by the optical measurements. The two strong reflection bands in the energy region 5.1–7.0 eV is probably due to the allowed intra-atomic transition from Tl 6s to 6p, judging from the rough description of the electronic structure which has been mentioned previously. However, the total band width of these two bands of about 1.9 eV is much narrower than that of TlCl or TlBr shown in the inset of figure 4 and reported by Hinson and Stevenson [15]. Taking the band gap of 4.9 eV into consideration, the two strong optical transitions are related only to peak a among the seven occupied states shown in figure 3 as an initial state of the transition.

Also, because the FWHM of peak a in figure 3 is about 1.0 eV, the unoccupied states which relate to this transition are expected to have a band width of about 1 eV. As mentioned above, the widths of both the valence band and the conduction band are narrow and the band dispersions are small in TlAlF$_4$.

5.2. Valence band structure and related properties

Finally, we discuss the optical and electrical properties of $TlAlF_4$. The observed low photocurrent of $TlAlF_4$ relative to that of TlBr is attributed to the low carrier mobility or the lower carrier generation efficiency of $TlAlF_4$. Also, the very large Stokes shift in figure 5 suggests that the hole, which has a lower mobility than the electron does generally, is easily self-trapped, when electron and hole pairs are generated by photoexcitation. This seems to be consistent with both no excitonic luminescence at 77 K and the low mobility of the carriers, which is suggested from the low photocurrent.

The reflection bands located at 5.6 eV, 6.0 eV and 6.2 eV are similar to the well known bands A, B and C, respectively in the absorption spectrum of alkali halides doped with Tl^+ [1, 2]. In addition, the broad photoluminescence band is very similar to that of alkali halides doped with Tl^+. The value of the fluorescence lifetime is of the same order of magnitude. Although $TlAlF_4$ contains a much larger amount of Tl^+ ions than alkali halide doped with Tl^+, a lifetime shortening due to a concentration quenching does not appear at all. On the other hand, no intense emission has been reported so far for TlBr at room temperature, as far as we know. These facts, therefore, indicate that the top of the valence band in $TlAlF_4$ does not form extended states, differing from TlBr.

6. Summary

Thin films and sintered discs of $TlAlF_4$ were prepared and their optical and electronic properties were examined.

(1) The electronic structures of $TlAlF_4$ and TlF thin films were examined by PES. Taking into consideration the dependences of the ionization cross sections of each basis orbital on excitation photon energies, the Tl 6s character at the top of valence band of each fluoride was found to be large.

(2) Optical absorption due to electronic transitions gave two intense bands at 5–7 eV in $TlAlF_4$. Only the shallowest peak in the photoelectron spectra were related to these optical transitions. The narrow reflection band width suggested that the width of the conduction band composed primarily of Tl 6p is narrow.

(3) A large Stokes shift of about 2 eV and a long fluorescence lifetime of 1.2 μs for $TlAlF_4$ suggested that the interaction between Tl^+ ions is not strong enough to cause concentration quenching.

(4) The band gap determined by photocurrent measurment was about 4.9 eV. The magnitude of the photocurrent was about a fifth of that of TlBr measured under the same conditions.

(5) The valence band electronic structure of $TlAlF_4$ differs considerably from that of TlCl or TlBr, although the Tl^+ ions in $TlAlF_4$ have a coordination structure similar to that of Tl^+ ions in TlCl or TlBr. It is considered that this difference originates from the much deeper energy level of F 2p compared with that of Cl 3p or Br 4p.

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