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メタデータ	
	言語: English
	出版者:
	公開日: 2008-02-12
	キーワード (Ja):
	キーワード (En):
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URL	http://hdl.handle.net/10098/1582

Fundamental optical absorption of $CsPbI_3$ and Cs_4PbI_6

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Abstract

The fundamental optical absorption spectra of $CsPbI_3$ and Cs_4PbI_6 have been measured for the first time. There are distinct differences in the absorption characteristic between the two compounds: Cs_4PbI_6 exhibits strong, oscillator-like absorption and a prominent, blue-shifted excitonic peak, compared to the case of $CsPbI_3$. The differences are explainable in terms of whether the $Pb^{2+}(I^-)_6$ octahedra are weakly ($CsPbI_3$) or strongly (Cs_4PbI_6) mutually isolated in the respective compounds.

Although it has been known from old times that there are two stable ternary compounds in the binary system of CsI–PbI_2, namely, $CsPbI_3$ and Cs_4PbI_6 [1,2], little is known about the optical properties of the compounds. The only knowledge is that exciton absorption of $CsPbI_3$ [3–5] and Cs_4PbI_6 [5] lies at photon energies around 3.0 and 3.4 eV, respectively. The reason for such a poor knowledge on these compounds is probably due to difficulty in obtaining their specimens. For example, as reported in Ref. [1], it is difficult to obtain Cs_4PbI_6 in a pure state by melting CsI and PbI_2 together in the stoichiometric proportion. In the present work, we prepared specimens suitable for optical studies of $CsPbI_3$ and Cs_4PbI_6 by two different ways and observed intrinsic absorption spectra of these compounds for the first time.

In measuring the fundamental optical absorption spectrum of materials, it is necessary to prepare specimens of very thin films or crystallites dispersed in transparent matrices. Previously we showed that quench deposition of a mixture of metal halides (binary system) and subsequent annealing of the deposits are effective in obtaining clusters and/or ternary compounds of metal halides [6,7]. This was indeed successfully applied to produce crystallites of Cs_4PbCl_6 in $CsCl$ matrices [8]. Such specimens were favorably used to measure the fundamental absorption spectrum of Cs_4PbCl_6 because the host $CsCl$ was transparent up to a considerable photon energy (about 6.8 eV). Therefore, in the present experiments, we first attempted to produce crystallites of $CsPbI_3$ and/or Cs_4PbI_6 in CsI matrices in a similar manner.

Fig. 1 shows the absorption spectra at 77 K of the binary $(CsI)_{1-x}(PbI_2)_x$ system with $x = 0.4$, 0.2 and 0.1. Here, the nominal x values of the mixtures of CsI and PbI_2 were used to represent the composition in the system. According to elemental analyses carried out for several films by an electron probe X-ray micro-analyzer, the deviation of the composition ratios from the nominal ones was within 5% (to minimize the deviation, we deposited the films rapidly, at a rate of about 20 nm/min; such a high deposition rate was previously shown to be favorable for achieving nominal ratios in the films of mixed metal halides [9]). The spectral measurements were carried out in situ on the films quench deposited onto 77 K substrates (silica glass) and subsequently annealed at 400 K for 10 min, by the method [10] of simultaneous measurements of transmittance and reflectance of the films, from which accurate absorption structures were determined. In these spectra,
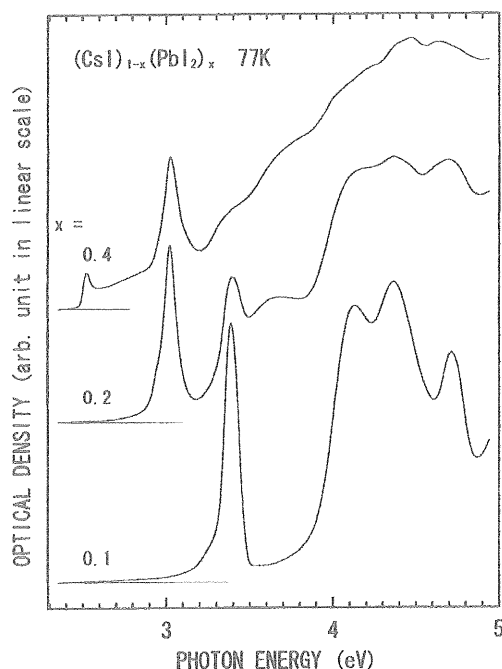
Fig. 1. Absorption spectra at 77 K of $(CsI)_{1-x}(PbI_2)_x$ films prepared by quench deposition onto 77 K substrates and subsequent annealing at 400 K for 10 min.

three characteristic absorption peaks were observed at 2.51, 3.02 and 3.38 eV, depending on the values of x. Of the three, the lowest-energy peak is due to exciton transitions in the PbI_2 crystal. Other two peaks are also considered to be of excitonic origin in view of their very sharp absorption features. Therefore, we see that there are two different crystalline phases addressable as due to ternary compounds. They are considered to be $CsPbI_3$ and Cs_4PbI_6. Indeed, the 3.02 eV peak corresponds to the reported $CsPbI_3$ exciton absorption (peaking around 3.0 eV [3–5]), and the 3.38 peak, to the Cs_4PbI_6 exciton absorption (around 3.4 eV [5]). The film with $x = 0.1$ is considered to represent intrinsic absorption of Cs_4PbI_6, as compared with the reported absorption spectra in Ref. [5], where weak absorption due to $CsPbI_3$ exciton transitions arose together with the Cs_4PbI_6 exciton absorption.

It was difficult to measure intrinsic absorption spectrum of $CsPbI_3$ using the films prepared from the mixture of CsI and PbI_2, because the $CsPbI_3$ phase always coexisted either with the PbI_2 phase (for $0.2 < x < 0.5$) or with the Cs_4PbI_6 phase (for $0.1 < x < 0.3$) as well as with the CsI phase. We note that the reported spectra [3,4] of the $CsPbI_3$ exciton absorption have only been presented in a very narrow photon energy region, from about 2.9 to about 3.2 eV, probably because of the same reason. Therefore, we employed an alternative preparation method of specimens, i.e. solid-state chemical reaction between the starting compounds. Such a method was shown, in the previous study of the $CsCl–PbCl_2$ system [8], to be effective in
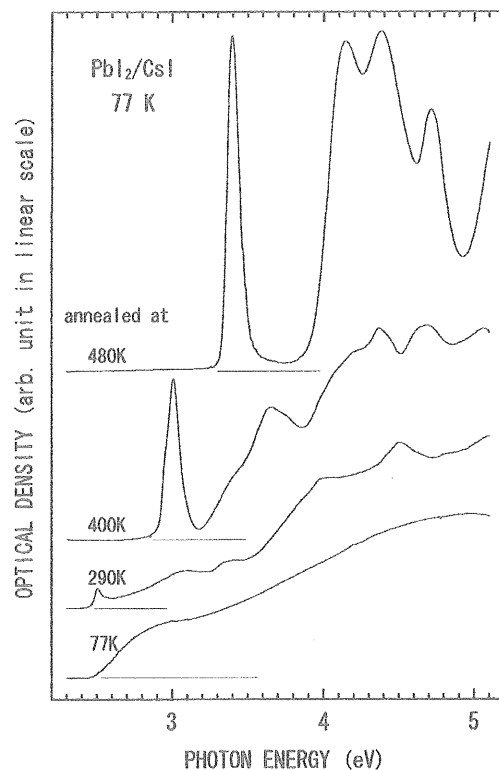

Fig. 2. The change in the absorption spectrum due to annealing of a PbI_2-deposited CsI crystal, measured in situ at 77 K for increasing annealing temperatures indicated.

dispersing crystallites of Cs_4PbCl_6 in the bulk crystal of CsCl. To apply the method to the present system of $CsI–PbI_2$, we prepared amorphous PbI_2 films (by quench deposition) on the polished surfaces of CsI bulk crystals cooled to 77 K and investigated the annealing behaviors of the prepared samples (PbI_2/CsI samples) by in situ optical absorption and reflection spectroscopy [10].

Figs. 2 and 3 show the changes of absorption and reflection spectra, respectively, due to annealing at various temperatures of a PbI_2/CsI sample. For each annealing temperature, an in situ spectral measurement was carried out at 77 K. Heating and cooling in each annealing cycle were performed at rates of 1 and 10 K/min, respectively, and the annealing time was 10 min for each. The spectrum labeled 77 K was obtained for the as-deposited PbI_2 film. Then the PbI_2/CsI sample was subject to the first annealing cycle of annealing temperature 290 K. Other spectra in the figure were obtained for subsequent cycles at the annealing temperatures indicated.

The spectra labeled 77 K very well reproduces earlier results [11] on amorphous PbI_2 films (which was characterized by missing exciton absorption). Exciton absorption (at 2.51 eV) of PbI_2 was observed in the sample annealed at 290 K for both the absorption and reflection spectra, indicating that the amorphous PbI_2 was transformed to the crystalline state.
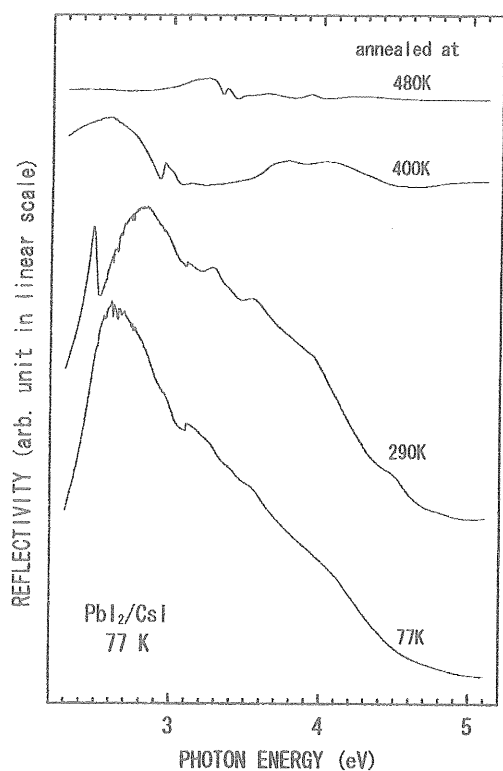
Fig. 3. The change in the reflection spectrum due to annealing of a PbI$_2$-deposited CsI crystal, measured in situ at 77 K for increasing annealing temperatures indicated.

When the sample was annealed at 400 K, the absorption spectrum exhibited a prominent peak at 3.02 eV. The peak can be assigned as due to CsPbI$_3$ exciton, considering the energetic position. Unlike the absorption spectra of the $(CsI)_{1-x}(PbI)_x$ films with $x = 0.2$ and/or 0.4 (Fig. 1), this spectrum showed no trace of excitonic absorption of PbI$_2$ nor of Cs$_4$PbI$_6$. The crystalline PbI$_2$ that had existed on the surface of the CsI crystal was considered to have reacted chemically with CsI completely by the annealing (at 400 K), yielding CsPbI$_3$. Therefore, the spectrum is attributed to intrinsic absorption of CsPbI$_3$. It should be noted here that the corresponding reflection spectrum (curve 400 K in Fig. 3) exhibited only a weak structure at energies around 3 eV, despite the strong CsPbI$_3$ exciton absorption around the same energies (Fig. 2, curve 400 K). This suggests that the CsPbI$_3$ products are embedded in the bulk, but near the surface, of the CsI crystal, forming crystallites. It seems impossible to produce a layer purely composed of CsPbI$_3$ only, but instead, a mixed phase of CsPbI$_3$ and CsI was achieved, from which we were able to obtain the fundamental absorption spectrum of CsPbI$_3$ for the first time.

On annealing the sample at a higher temperature, 480 K, a further, drastic change occurred in the spectral structure, as seen from curve 480 K in Fig. 2. The resulting absorption spectrum was quite the same in outline as that (curve 0.1 in

Fig. 1) of Cs$_4$PbI$_6$. This means that a further chemical reaction occurred between the above-produced CsPbI$_3$ crystallites and the CsI environment in the CsI crystal, yielding the crystallites of Cs$_4$PbI$_6$. The new crystallites were also embedded in (and not 'on' the surface of) the bulk CsI crystal, as seen from the very weak structures in the corresponding reflection spectrum (curve 480 K in Fig. 3) throughout the measured energy region (compared with the marked absorption structures in curve 480 K in Fig. 2).

As seen from Fig. 2, Cs$_4$PbI$_6$ exhibited strong, oscillator-like absorption and a prominent, blue-shifted exciton peak, compared with the case of CsPbI$_3$. These characteristics may be explained as follows. Low-energy fundamental optical absorption of CsPbI$_3$ and Cs$_4$PbI$_6$ crystals may be dominated by electronic transitions from 6s to 6p states in the Pb^{2+}-ion sublattice, as in the case of PbI$_2$ crystals [12]. Both the crystals of CsPbI$_3$ and Cs$_4$PbI$_6$ are built up of nearly regular Pb^{2+}(I$^-$)$_6$ octahedra with Pb^{2+} ions located at their centers [1,2]. In CsPbI$_3$, however, each I$^-$ ion is shared between two adjacent octahedra, while, in Cs$_4$PbI$_6$, adjacent octahedra are separated by intervening Cs$^+$. Therefore, in Cs$_4$PbI$_6$ the dilution of the sublattice by the intervening Cs$^+$ ions may have the effect of preventing the Pb^{2+} electronic states from forming extended states. To a first approximation, these states may form a set of localized states confined to within the individual Pb^{2+}(I$^-$)$_6$ octahedra. Due to the localized nature of both the Pb 6s and 6p states, the 6s to 6p electronic transitions may result in a large oscillator strength in a narrow energy range. This is favorable for understanding the strong absorption intensities, as well as the enhanced (first) exciton absorption, of Cs$_4$PbI$_6$. The localization of both the Pb 6s and 6p states has the effect of confining the exciton created in the Pb^{2+}-ion sublattice, thus giving the reason for the blue shift of the exciton energy of Cs$_4$PbI$_6$ with respect to that of CsPbI$_3$.

The localized nature of, and thus the absorption structures related to, the Pb 6s and 6p states in Cs$_4$PbI$_6$ is rather similar to the case of isolated Pb^{2+} ions doped in fcc alkali halide crystal, where the Pb^{2+} ions are located at the centers of octahedral quasi-complexes Pb^{2+}(I$^-$)$_6$. For example, in Pb^{2+}-doped KI crystals, the lowest-energy absorption band (named A band, coming from spin–orbit allowed $^1A_{1g}$ to $^3T_{1u}$ transitions) is observed at 3.6 eV, and the second band (C band, dipole-allowed $^1A_{1g}$ to $^1T_{1u}$ transitions) at 4.5 eV, together with a weak shoulder (B band, vibration-induced $^1A_{1g}$ to $^3T_{2u}$ or ^3E_u transitions) at energy between the two bands, around 4.2 eV [13]. However, the spectral structures of Cs$_4$PbI$_6$ does not so well resemble any of the reported spectra of Pb^{2+}-doped fcc alkali iodides [14–17]. The main reason for this is probably due to the associated charge-compensating Cs$^+$-ion vacancies in the latter case.

Fig. 4 compares the absorption spectrum of Cs$_4$PbI$_6$ with that [18] of $(CH_3NH_3)_4PbI_6\cdot2H_2O$. There is a striking resemblance in the spectral structures and their energetic positions between the two compounds, i.e. between

a: Cs_4PbI_6 290K
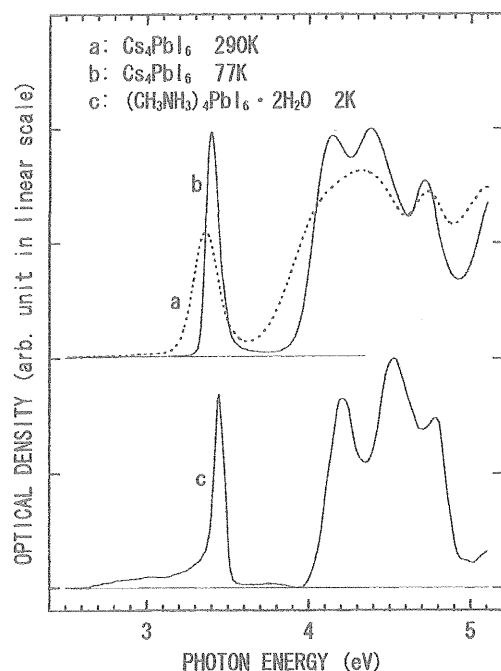b: Cs_4PbI_6 77K
c: $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ 2K

Fig. 4. The absorption spectra of Cs_4PbCl_6 measured at 77 K (a) and 290 K (b) are compared with that of $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ measured at 2 K (c). The latter spectrum is cited from Ref. [18], where the absorption spectrum was deduced from a reflection spectrum.

spectrum b, measured at 77 K for Cs_4PbI_6 and spectrum c, measured at 2 K for $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ (in Ref. [18], spectrum c was deduced from a reflection spectrum through the Kramers–Kronig analysis); in the latter compounds, octahedral $Pb^{2+}(I^-)_6$ clusters are nearly isolated (by the countercations $(CH_3NH_3)^+$), similar to the case of Cs_4PbI_6. Therefore, a similar spectral-structures assignment described for $(CH_3NH_3)_4PbI_6 \cdot 2H_2O$ in Ref. [18], where the fine absorption structures in the region 4–5 eV are attributed to crystal-field splitting of the C band due to deviation from O_h symmetry of the $Pb^{2+}(I^-)_6$ clusters, may be applicable to Cs_4PbI_6. In the spectrum a, measured at 290 K for Cs_4PbI_6, the vibration-induced nature of the B band is indeed evidenced by the enhanced absorption intensities at around 3.9 eV.

In conclusion, it was difficult to prepare the films of the ternary compounds of $CsPbI_3$ and Cs_4PbI_6 purely composed of a single phase of the compounds. However, it was possible to disperse crystallites of these compounds separately in a CsI environment by making use of solid-state chemical reaction between CsI and PbI_2 of PbI_2-deposited CsI bulk crystals. Using such specimens, we measured the fundamental optical absorption spectra of

$CsPbI_3$ and Cs_4PbI_6 for the first time. The spectra showed distinct differences in the structure between the two compounds. The differences are explainable in terms of whether the $Pb^{2+}(I^-)_6$ octahedra are weakly $(CsPbI_3)$ or strongly (Cs_4PbI_6) mutually isolated in the respective compounds.

We are now developing a novel method for determining optical constants of crystallites dispersed in, or near the surface of, a transparent crystal. The method is applicable to the present system. Detailed discussions of the absorption characteristics of the $CsPbI_3$ and Cs_4PbI_6 crystallites will be reported later, including the determination of oscillator strengths and/or effective numbers of electrons contributing to their optical absorption, and also including the comparison with the chlorides, i.e. $CsPbCl_3$ and Cs_4PbCl_6 obtained for the previous, $CsCl-PbCl_2$ system.

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