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In situ optical absorption spectroscopy of annealing behaviours of quench-deposited films in the binary system CsI–PbI_2

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Abstract

We have investigated annealing behaviours of quench-deposited films of the binary CsI–PbI_2 system by *in situ* optical absorption spectroscopy. Various films composed of multiple crystalline phases of $CsPbI_3$ and/or Cs_4PbI_6 as well as of CsI and/or PbI_2 are obtained, depending on the mixing ratio of the CsI and PbI_2. It is difficult to prepare films purely composed of a single $CsPbI_3$ or Cs_4PbI_6 phase alone. However, it is possible to obtain films where crystallites of either $CsPbI_3$ or Cs_4PbI_6 coexist with the CsI phase. Using such films, we measure the fundamental optical absorption spectrum of $CsPbI_3$ and Cs_4PbI_6 for the first time. Cs_4PbI_6 exhibits stronger oscillator-like absorption compared to $CsPbI_3$, due to the localized nature of both the Pb 6s and 6p states.

1. Introduction

Preparation of film materials by quench deposition is effective in obtaining solid solutions in the amorphous form over the full mixing range. Recently, we obtained films of amorphous solid solutions of the binary systems CdI_2–BiI_3 [1] and TlCl–CuCl [2], despite the different crystal structures of the constituent compounds (and even different valences of the constituent cations in the former system). Their crystallization yielded novel films depending on the concentration ratio of the constituents. For example, two-dimensional small BiI_3 clusters coupled to the lattice of the CdI_2 host matrix were produced by annealing the $(CdI_2)_{1-x}(BiI_3)_x$ films with x less than 0.3. In the $Tl_{1-x}Cu_xCl$ system, on the other hand, annealing of the film with $x \sim 0.4$ caused Cu^+ ions to migrate to form clusters in the amorphous environment and the clusters grew until the amorphous environment had a particular atomic composition ratio suggestive of a new compound, which exhibited a well defined crystallization temperature, 300 K.

Very recently, we reported on annealing behaviours of quench-deposited films of the binary CsCl–$PbCl_2$ system [3] studied by optical absorption spectroscopy over the full mixing range. On annealing the films, various crystalline states occurred, exhibiting characteristic absorption spectra, depending on the composition ratio between the two compounds. The fundamental absorption spectrum of Cs_4PbCl_6 was observed for the first time. It was found that the spectrum has novel features. The experiments, together with those in [1, 2] mentioned above, suggested that amorphization and subsequent thermal treatments of the films prepared by co-evaporation were effective in obtaining new possible compounds or clusters in the binary systems of metal halides. In the present work, a similar technique was applied to the system CsI–PbI_2.

2. Experimental results

We summarize the experimental procedures. To prepare the source materials for the co-evaporation, nominal amounts of CsI and PbI_2 in powder form, of 99.9% purity, were mixed together and dehydrated at 150 °C in a vacuum of about 0.1 Pa for 1 h. The mixed powder was made into an ingot in a silica-tube container filled with Ar gas; the container was heated to 670 °C (which is about 50 °C above the highest melting point of the two component compounds), held at that temperature for 30 min and then quenched in ice water to achieve homogeneity in the concentration of the mixture.

The mixture was deposited onto a fused-silica substrate cooled to 77 K in a vacuum of about 9×10^{-6} Pa using a tungsten basket heating element placed 8 cm in front of the substrate; the deposition rate was about 20 nm min^{-1}. Such high deposition rates were favourable for achieving the nominal composition ratio of CsI and PbI_2 in the films. Elemental analyses carried out for several films using an electron probe x-ray micro-analyser showed that the nominal composition ratios were indeed achieved within the deviation about 5% (in this paper, we used the nominal values to describe the compositions of the films).

An improved optical absorption spectroscopy [4] was applied to *in situ* monitoring of the annealing behaviours of the thus-prepared films. The method is based on simultaneous measurements of transmittance and reflectance of films, from which their accurate optical densities can be determined *in situ*. The measurements were made in the region of photon energies below 5.4 eV, in which CsI is transparent and PbI_2 exhibits the main low-energy spectral structures, including the band-gap exciton peak.

For particular cases of the mixing ratio between CsI and PbI_2, alternative films were prepared in a different way (as described in the next section) and their annealing behaviours were monitored in the same way.

3. Results and discussion

It was possible to obtain film samples of the binary $(CsI)_{1-x}(PbI_2)_x$ system over the full mixing range by the method of quench deposition. Their absorption spectra are shown in figures 1 and 2. For each value of x (the nominal mole fraction of PbI_2), the spectrum was first measured at 77 K for the as-deposited film (figure 1). Then the film was heated at a rate of 1 K min^{-1} up to 400 K, annealed for 10 min at that temperature and cooled again to 77 K at a rate of 10 K min^{-1} to measure the spectrum shown in figure 2. To visualize the change of structures of the spectrum with x, the individual spectra in the figures are normalized in such a way that the maximum absorption intensities (in the measured energy region) of the as-deposited films are unity, except the spectrum for $x = 0$; the latter spectrum is the spectrum of a film (for $x = 0$) with the same thickness as that of the film for $x = 0.05$.

The spectral outline of the as-deposited films (with the nonzero values of x) changed continuously with x, as seen from figure 1. In the Pb-rich region ($x > 0.5$), where the change is rather slow, the films may be in the amorphous solid solution state, considering our previous result that PbI_2 films obtained in the same way were in the amorphous state [5]. On the other

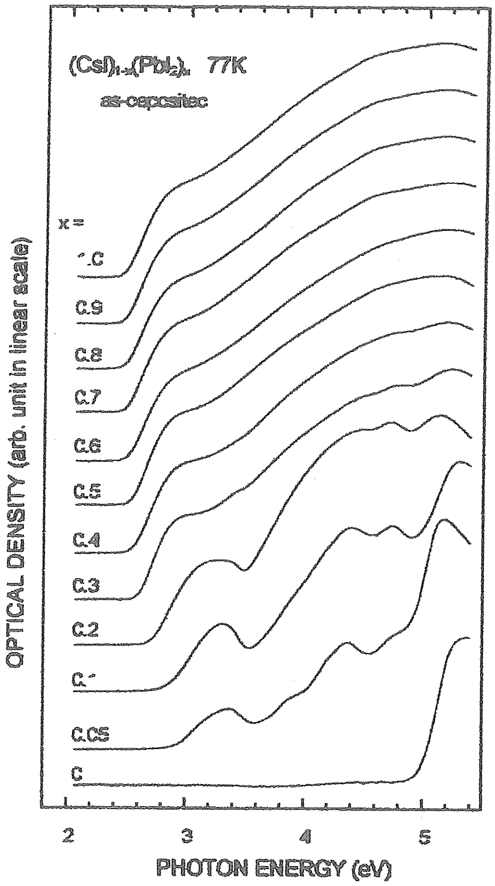

Figure 1. Absorption spectra of quench-deposited $(CsI)_{1-x}(PbI_2)_x$ films, measured at 77 K for various values of x before annealing the films.

hand, in the opposite concentration region (presumably, for $x < 0.2$), the films may be in the crystalline state, since alkali halides, including CsI, even when quench deposited onto substrates at liquid helium temperature, were in the crystalline state [6, 7]. The implication is that the Pb^{2+} ions, uniformly dispersed in the films over the full mixing range, may be situated in the amorphous or crystalline surroundings according to whether their concentration is large or small, although structural studies are necessary for further discussion (*in situ* measurements at 77 K are necessary for the structural studies).

When the films were annealed, drastic changes occurred in the spectral structure (figure 2). There arose three characteristic absorption peaks depending on the values of x, namely, the peaks at 2.51, 3.02 and 3.38 eV, which were typically observed, for example, for $x = 1, 0.3$ and 0.1, respectively. Of the three, the lowest-energy peak is due to exciton transitions in the PbI_2 crystal. The 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 in the binary CsI–PbI_2 system. The corresponding compounds may be $CsPbI_3$ and Cs_4PbI_6, because they are the only ternary compounds in the system [8, 9]. These considerations (together with the discussion below) lead to the conclusion that the 3.02 eV peak is due to exciton transitions occurring in the $CsPbI_3$ crystalline phase and the 3.38 eV peak is due to those in the Cs_4PbI_6 crystalline phase.

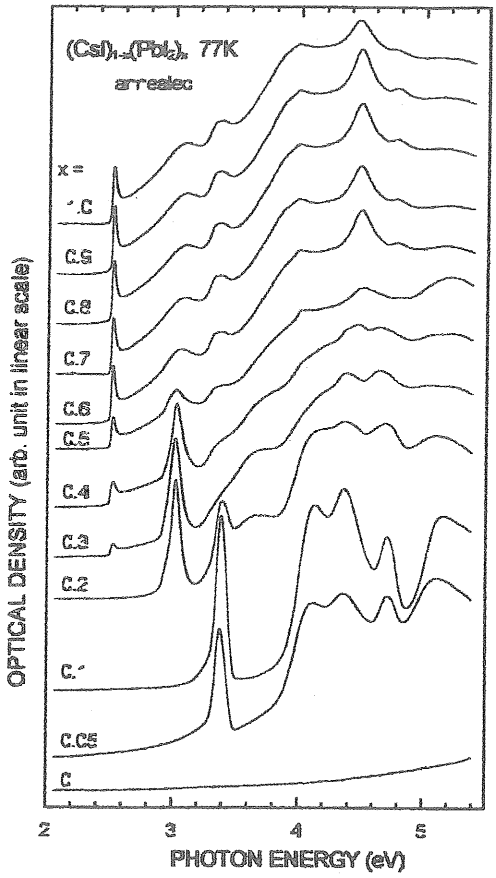

Figure 2. Absorption spectra of quench-deposited $(CsI)_{1-x}(PbI_2)_x$ films, measured at 77 K for various values of x after annealing the films at 400 K for 10 min.

The exciton spectroscopy reveals that there occurred phase separation in all the films throughout the full mixing range. The crystalline phases of PbI_2, $CsPbI_3$ and Cs_4PbI_6 occurred in the ranges $x \geqslant 0.3$, $0.2 \leqslant x \leqslant 0.5$ and $x \leqslant 0.1$, respectively. It should be noted that, in the film with $x = 0.5$, which corresponds to the stoichiometry of $CsPbI_3$, the $CsPbI_3$ exciton absorption was very weak (as compared to the PbI_2 exciton absorption). This means that the majority of the Pb^{2+} ions in the film, though uniformly dispersed by the quench deposition, aggregated to form PbI_2 crystallites due to annealing, with the crystallites dispersed in the polycrystalline CsI film. Similarly, in the annealed film with $x = 0.2$, which corresponds to the stoichiometry of Cs_4PbI_6, two competing aggregated phases of $CsPbI_3$ and Cs_4PbI_6 coexisted in the polycrystalline CsI film.

The present results are somewhat similar to those reported in [10], where two types of film sample were prepared, one by evaporation of $CsPbI_3$ powder and the other by co-evaporation from two sources (PbI_2 and CsI). The x-ray diffraction studies of the films showed the coexistence of the $CsPbI_3$ and PbI_2 phases for the former and all the phases of PbI_2, $CsPbI_3$, Cs_4PbI_6 and CsI for the latter. The exciton spectroscopy of the films indeed confirmed the coexisting phases (except the CsI phase, which was transparent in the measured region, 300–700 nm).

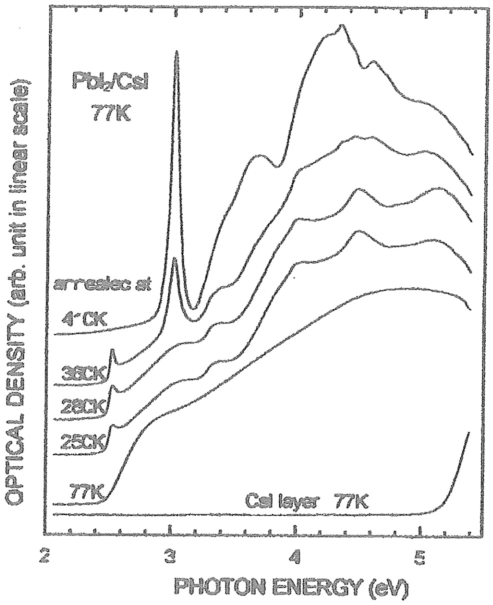

Figure 3. The change of the absorption spectrum with temperature for a two-layer PbI$_2$/CsI film prepared on a silica-glass substrate, measured *in situ* at the various temperatures indicated.

Concerning CsPbI$_3$, excitonic absorption (around 3 eV) has been observed in the reflection spectrum of CsPbI$_3$ single crystals [11] and in the absorption spectrum of CsPbI$_3$ aggregates produced in heat-treated CsI:Pb crystals [12]. However, both spectra have been presented only in a very narrow photon energy region, from about 2.9 to about 3.2 eV. In the absorption spectrum for $x = 0.3$ (or $x = 0.2$) in figure 2, although the CsPbI$_3$ exciton peak was indeed clearly observed in this narrow photon energy region, exciton absorption due to the coexisting PbI$_2$ (or Cs$_4$PbI$_6$) aggregates was also recognized to coexist. In the present experiment, as described below, it was possible to measure the absorption spectrum attributable to intrinsic absorption of CsPbI$_3$ crystals (free from the competing, or coexisting, PbI$_2$ and/or Cs$_4$PbI$_6$ phases), over the full photon energy region measured.

Figure 3 illustrates the change of absorption spectrum due to annealing of a two-layer film, PbI$_2$/CsI/silica glass. The two compounds were evaporated (in a vacuum of about 9×10^{-6} Pa) from separated sources *in situ* onto a silica-glass substrate cooled to 77 K. The thicknesses of the PbI$_2$ and CsI layers were about 60 and 140 nm, respectively, which correspond to the molar ratio PbI$_2$:CsI = 1:3. The spectrum was first measured for the CsI layer (before evaporation of PbI$_2$). After evaporating PbI$_2$, the two-layer film was annealed at various annealing temperatures and its absorption spectrum was measured at 77 K for each annealing temperature. Heating and cooling in each annealing cycle were performed at rates of 1 and 10 K min^{-1}, respectively, and the annealing time was 10 min for each. The spectrum labelled 77 K was obtained for the as-deposited (two-layer) film. Then the film was subject to the first annealing cycle with the annealing temperature 250 K. Other spectra in the figure were obtained for subsequent cycles at the annealing temperatures indicated. The first three spectra of the two-layer film represented the characteristic of the intrinsic absorption of the PbI$_2$ layer in the amorphous (labelled 77 K) and crystalline (labelled 250 and 280 K) states. In the fourth spectrum (labelled 360 K), however, a sharp peak (at 3.02 eV) due to CsPbI$_3$ exciton transitions showed up together with the 2.51 eV exciton peak of PbI$_2$, very similar to the case

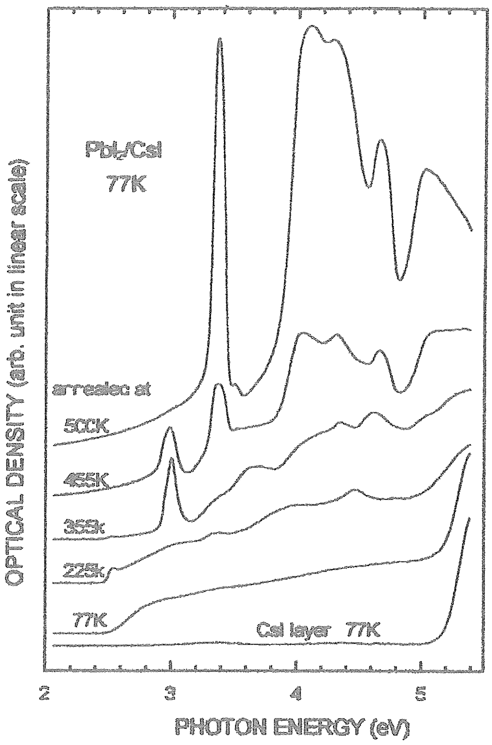

Figure 4. The change of the absorption spectrum with temperature for a two-layer PbI_2/CsI film prepared on a silica-glass substrate, measured *in situ* at the various temperatures indicated.

for the spectrum for $x = 0.4$ in figure 2. This means that parts of the PbI_2 layer near the PbI_2/CsI interface reacted chemically with CsI producing a third, $CsPbI_3$ layer. On annealing the film at the higher temperature, 410 K, the spectrum became quite $CsPbI_3$-like, indicating that the PbI_2 layer reacted completely with the CsI layer.

A method like that described above was also effective for measuring the absorption spectrum of Cs_4PbI_6 as illustrated in figure 4. The starting two-layer film, PbI_2/CsI/silica glass, had a thickness of about 23 nm for the PbI_2 layer and about 150 nm for the CsI layer, which correspond to the molar ratio PbI_2:CsI = 1:9. In this case, it was possible to observe the absorption spectra of $CsPbI_3$ and Cs_4PbI_6, separately, at the low (355 K) and the high (500 K) annealing temperatures, as shown in the figure. This indicates that the chemical reaction in the film first occurred between PbI_2 and CsI yielding $CsPbI_3$ and then between the $CsPbI_3$ product and the remnant of CsI, thus producing the final compound Cs_4PbI_6.

It is notable that the optical absorption of Cs_4PbI_6 is very strong compared to that of $CsPbI_3$, as seen from figure 4. The reason for this may be as follows. The low-energy fundamental optical absorption of $CsPbI_3$ and Cs_4PbI_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 [13]. The crystals of $CsPbI_3$ and Cs_4PbI_6 are both built up of nearly regular $Pb^{2+}(I^-)_6$ octahedra with Pb^{2+} ions located at their centres [8, 9]. In $CsPbI_3$, however, each I^- ion is shared between two adjacent octahedra, while, in Cs_4PbI_6, adjacent octahedra are separated by intervening Cs^+. Therefore, in Cs_4PbI_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 (since otherwise the energetic dispersion of extended states coming from the Pb 6s and 6p states would give rise to optical absorption over a wide energy range). This is favourable for understanding the strong absorption intensities of Cs_4PbI_6 in the measured photon energy region.

4. Conclusions

The method of amorphization and subsequent thermal treatments of the films prepared by co-evaporation, which was previously shown to be effective in obtaining new compounds or clusters in the binary systems of metal halides, was applied to the system CsI–PbI_2. Various films composed of multiple crystalline phases of $CsPbI_3$ and/or Cs_4PbI_6 as well as of the starting compounds (CsI and/or PbI_2) were obtained, depending on the mixing ratio of the CsI and PbI_2. It was difficult to prepare films purely composed of a single $CsPbI_3$ or Cs_4PbI_6 phase alone. However, it was possible to obtain films where crystallites of Cs_4PbI_6 coexist with the CsI phase and, using such films, we observed the fundamental optical absorption spectrum of Cs_4PbI_6 for the first time. In a subsidiary effort, which was motivated by the above results, we found that, by annealing the two-layer PbI_2/CsI films quench deposited on silica-glass substrates cooled to 77 K, a third, intervening $CsPbI_3$ or Cs_4PbI_6 layer is generated by the chemical reaction of the PbI_2 and CsI layers. The two-layer method was successfully applied to the measurement of the fundamental optical absorption spectra of both $CsPbI_3$ and Cs_4PbI_6, whose former spectrum was obtained in the extended photon energy region (up to 5.4 eV) for the first time. Cs_4PbI_6 exhibited strong oscillator-like absorption compared to $CsPbI_3$, due to the localized nature of both the Pb 6s and 6p states. The two-layer method is effective for investigating the differences in the absorption intensities associated with Pb 6s to 6p transitions between the Pb-containing compounds (PbI_2, $CsPbI_3$ and Cs_4PbI_6) in terms of electronic state localization or delocalization. For detailed discussions based on such a viewpoint, however, it is necessary to measure the optical constants of the individual 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. The measurement results and related discussions will be reported later.

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