Annealing behaviors of quench-deposited (CsCl)1-x(PbCl2)x films studied by optical absorption spectroscopy

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Annealing behaviors of quench-deposited $(CsCl)_{1-x}(PbCl_2)_x$ films studied by optical absorption spectroscopy

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Abstract

All the films of the $(CsCl)_{1-x}(PbCl_2)_x$ system prepared by quench deposition exhibit a similar fundamental absorption spectrum over the full mixing range. On annealing the films, drastic changes occur in the spectra showing three characteristic types of spectral features depending on the mixing ratio. Type 1 ($x \geq 0.7$) suggests the formation of mixed crystals of a $PbCl_2$ base. Type 2 ($0.5 \geq x \geq 0.3$) exhibits the spectrum of $CsPbCl_3$ crystal. Type 3 ($x = 0.1$, 0.05), the most characteristic, is the spectrum of Cs_4PbCl_6 crystal, which was observed for the first time. The spectrum of the Cs_4PbCl_6 crystal exhibits novel structures. Despite the crystalline entity of the compound, it shows oscillator-like fundamental absorption and a wide (≈ 1 eV) window just above the first absorption peak, suggesting the peculiarity of the associated energy band structure. To a first approximation, the spectrum is explainable in terms of Pb^{2+}-ion excitation of the $Pb^{2+}(Cl^-)_6$ quasi-complexes.

Keywords: Film; Optical absorption; Quench deposition; Cs_4PbCl_6; $CsPbCl_3$

1. Introduction

One of the interests for producing film materials, rather than growing single crystals, is the possibility of introducing high concentration impurities. For example, Cu^+-doped KCl films, with Cu^+ concentration ranging from 10^{20} to 10^{21} cm^{-3}, have been attained by resistive co-evaporation of KCl–CuCl mixed powders with nominally 1–15 mol.% CuCl concentration [1]. In particular, preparation of films by quench deposition is effective in obtaining solid solution in the amorphous form over the full mixing range. Recently, we obtained films of amorphous solid solutions of the binary systems of TlCl–CuCl [2] and CdI_2–BiI_3 [3], despite the different crystal structures of the constituent compounds (and even the different valencies of the constituent cations in the latter system). Their crystallization yielded novel films depending on the concentration ratio of the constituents. For example, on annealing the $Tl_{1-x}Cu_xCl$ film with $x \approx 0.4$, Cu^+ ions migrated 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. In the $(CdI_2)_{1-x}(BiI_3)_x$ system, on the other hand, two-dimensional small clusters of BiI_3 were produced by annealing the films of $x < 0.3$, with the clusters being coupled to the lattice of CdI_2 host matrix.

Nitsch et al. investigated the phase diagram of the system of $CsCl$–$PbCl_2$ [4] and showed that there can exist two stable compounds in the system, namely the congruently melting compound $CsPbCl_3$ and incongruent Cs_4PbCl_6. They predicted that the absorption edge of Cs_4PbCl_6 lies in the region 300–315 nm (4.13–3.94 eV) at room temperature [4,5]. However, its fundamental optical absorption has not been studied yet. Generally, measurements of fundamental absorption spectrum of materials require film samples.

Previously, we reported on amorphous $CsPbCl_3$ films and their crystallization, studied by in situ optical absorption spectroscopy [6]. The amorphous films were prepared by co-evaporation of CsCl and $PbCl_2$. The films, when crystallized, showed a very sharp exciton line (at 3.013 eV), with the full width at half maximum (14 meV at 77 K), much smaller than that (≈ 30 meV at 77 K) of the 'improved' $CsPbCl_3$ film reported in Ref. [7]. The experiments, together with those in Refs. [2,3] mentioned above, suggested that amorphization and subsequent thermal treatments of the films prepared by co-evaporation were effective in obtaining high quality crystalline films and/or new possible compounds or clusters in the binary systems of metal halides. In the present work, we have investigated the annealing behaviors of quench-deposited $(CsCl)_{1-x}(PbCl_2)_x$ films by optical absorption spectroscopy over the full mixing range, including $x = 0.5$ ($CsPbCl_3$). On annealing the films, various crystalline states occurred exhibiting characteristic absorption spectra, depending on the values of x. The fundamental absorption spectrum of Cs_4PbCl_6 was observed for the first time. It was found that the spectrum has novel features.

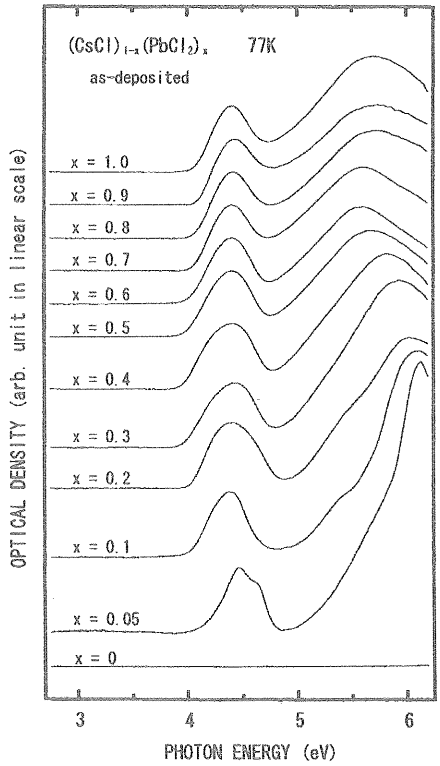

Fig. 1. Absorption spectra of quench-deposited $(CsCl)_{1-x}(PbCl_2)_x$ films, measured at 77 K for various values of x before annealing the films.

2. Experimental

It was possible to obtain film samples of the binary $(CsCl)_{1-x}(PbCl_2)_x$ system over the full mixing range by the method of quench deposition using co-evaporation of CsCl and $PbCl_2$. To prepare the source materials for the co-evaporation, nominal amounts of CsCl and $PbCl_2$ in a powder form of 99.9% purity were mixed together and dehydrated at 150 °C in a vacuum of ≈ 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 700 °C (which is ≈ 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.

Quench-deposition of the mixture was carried out in the same way as described in Ref. [6]. In brief, the mixture was deposited onto a fused-silica substrate, cooled to 77 K in a vacuum of $\approx 9 \times 10^{-6}$ Pa using a tungsten basket heating element placed 8 cm in front of the substrate; the deposition rate was ≈ 20 nm min^{-1}. Such a high deposition rate was favorable for achieving the nominal composition ratio of CsCl and $PbCl_2$ in the films. Elemental analyses carried out for several films by an electron probe X-ray micro-analyzer showed that the nominal compositions ratio were indeed achieved within the deviation $\approx 5\%$. Therefore, we used the nominal values to describe the compositions of the films in this paper.

Effects of thermal treatments on thus-prepared films were investigated in situ by an improved optical absorption spectroscopy, described in Ref. [6]. The method is based on simultaneous measurements of transmittance and reflectance of films, from which their accurate optical densities can be determined. The measurements were made in the region of photon energies below 6.2 eV, in which CsCl is transparent and $PbCl_2$ exhibits main low-energy spectral structures, including the band-gap exciton peak.

3. Results

Figs. 1 and 2 show the absorption spectra at 77 K of the binary $(CsCl)_{1-x}(PbCl_2)_x$ system. For each value of x (nominal mole fraction of $PbCl_2$), the spectrum was first measured at 77 K on the as-deposited film (Fig. 1). Then, the film was heated at a rate of 1 K min^{-1} up to 500 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 Fig. 2. To visualize the change of structures with x of the spectrum, the individual spectra in the figures are normalized in such a way that the absorption intensities of the as-deposited films are unity at the peaks of the first band (≈ 4.4 eV).

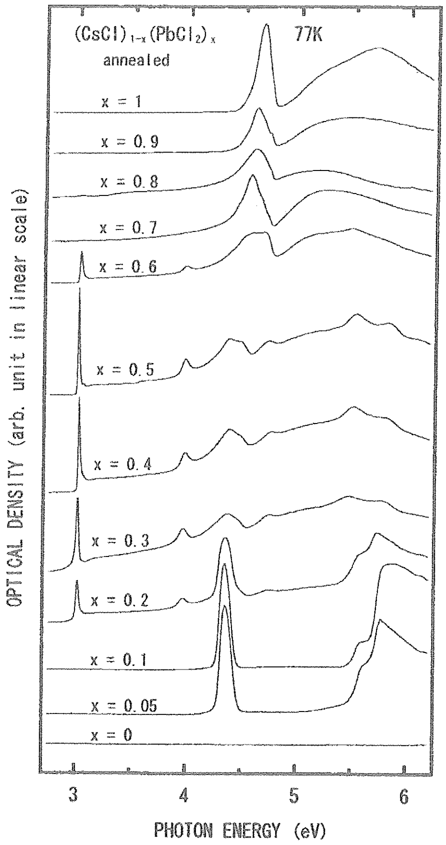

Fig. 2. Absorption spectra of quench-deposited $(CsCl)_{1-x}(PbCl_2)_x$ films, measured at 77 K for various values of x after annealing the films at 500 K for 10 min.

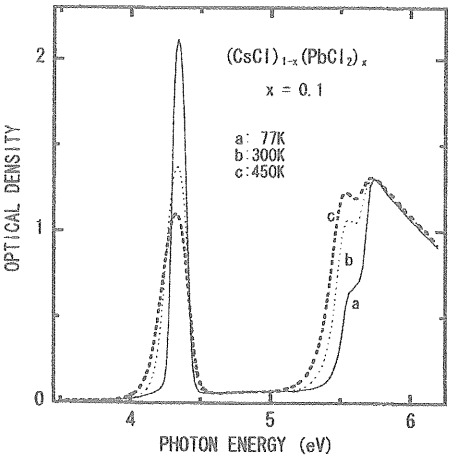

Fig. 3. Absorption spectra of a quench-deposited $(CsCl)_{1-x}(PbCl_2)_x$ film with $x = 0.1$, measured at 77 K (curve a), 300 K (curve b) and 450 K (curve c) after annealing the film at 500 K for 10 min.

As seen in Fig. 1, all the as-deposited films (with the non-zero values of x) have nearly the same optical energy gap of ≈ 4 eV. Furthermore, the spectra for $x \geq 0.1$ are all characterized by the first broad band with a full width at half maximum (FWHM) in the range 0.4–0.5 eV and with a peak energy in the range 4.35–4.40 eV, although the first band for $x = 0.05$ is somewhat shifted to the higher energy side (by ≈ 0.1 eV) exhibiting a doublet structure.

When the films were annealed, drastic changes occurred in the spectral structure depending on the values of x (Fig. 2). It can be seen that there arose three characteristic types of absorption spectrum in the annealed films, two of which were the familiar spectra, i.e. those for $x = 0.5$ (crystalline (c-)$CsPbCl_3$) and $x = 1$ (c-$PbCl_2$). The spectra for $x = 0.3$ and 0.4 are very similar in feature to that of c-$CsPbCl_3$ and the spectra for $x \geq 0.7$ resemble that of c-$PbCl_2$, more closely with increasing values of x. For $x = 0.6$, two types of spectral features characteristic of c-$CsPbCl_3$ and c-$PbCl_2$ seem to coexist. The third, and the most interesting of the characteristic types of the absorption spectra in Fig. 2 is exhibited by the spectra for $x = 0.05$ and 0.1. These spectra have a novel feature, that is, a sharp peak shows up at 4.350 eV followed by a wide 'window' extending to 5.5 eV. By increasing the value of x to 0.2, however, such a novel feature is obscured by the coexistence with the c-$CsPbCl_3$-phase spectrum.

Fig. 3 displays the novel spectra in a magnified scale measured at different temperatures, i.e. 77 K (curve a), 300 K (curve b) and 450 K (curve c). It is seen that the 'window' region has a very weak absorbing nature for all the temperatures. More interesting is that the absorption intensities in the region just above the 'window' increase with increasing temperature. In fact, the ratio of the integrated absorption intensities in the measured range of photon energy (up to 6.2 eV) was calculated to be 1 (curve a), 1.13 (curve b) and 1.21 (curve c), although the first peak was shown to have a constant integrated absorption intensity for all the temperatures (also it seems that the band with the peak ≈ 5.74 eV has a constant integrated absorption intensity for all the temperatures). We note that the first peak was Gaussian in shape at all the temperatures, with FWHM 0.103 eV at 77 K, 0.169 eV at 300 K and 0.214 eV at 450 K.

4. Discussion

As shown in the previous section, three characteristic types of absorption spectra show up in the annealed films, depending on the mixing ratio (Fig. 2). The spectra of c-$PbCl_2$ ($x = 1$) and c-$CsPbCl_3$ ($x = 0.5$) (which well reproduce previous results in Refs. [8] and [6], respectively) are characterized by the exciton peak at 4.66 eV (of a Frenkel type [9]) and the very sharp (Wannear-type [10]) exciton peak at 3.013 eV, respectively. These excitons are known to be cationic in nature. They are formed on the Pb^{2+}-ion sublattices of the respective crystals due to transitions from 6s to 6p states.

The c-PbCl$_2$ type of the spectra observed for the values of x down to 0.7, which is characterized by the gradual, continuous change in the spectral shape with decreasing x values (most importantly, with regard to the line broadening and the peak shift of the exciton absorption), means that crystalline films of a c-PbCl$_2$ base can be formed in this mixing range. Probably, the Pb^{2+}-ion sublattice is doped with Cs$^+$ ions in a particular manner despite the different valencies between the two ions. On the other hand, the spectral type characteristic of c-CsPbCl$_3$ ($x = 0.5$) is stable in shape in the CsCl-rich range: the films with $x = 0.4$ and 0.3 exhibit almost the same spectral structures as those of CsPbCl$_3$. This indicates that the films are composed of crystallites of CsPbCl$_3$ and CsCl. For $x = 0.6$, however, both spectral types coexist suggesting the occurrence of a phase separation in the film; presumably, a considerable amount of Pb^{2+} ions are expended in producing PbCl$_2$–CsCl mixed crystal of a PbCl$_2$ base and therein are embedded CsPbCl$_3$ crystallites.

A hint to explain the third of the spectral types exhibited by the films of $x = 0.1$ and 0.05 may be obtained from Refs. [4,5]. In Ref. [5], crystals of Cs$_4$PbCl$_6$ were grown (to study their photoluminescence and decay kinetics). According to the measurement of their transmission spectrum at room temperature, the absorption edge was shown to be in the region 300–315 nm (4.13–3.94 eV), although the spectrum was significantly obscured by strong absorption due to CsPbCl$_3$ crystallites embedded in the Cs$_4$PbCl$_6$ crystal. About the same absorption edge was observed in our film sample with $x = 0.1$, as seen from Fig. 3. Therefore, the novel spectra for $x = 0.1$ and 0.05 in Fig. 2 are attributable to the intrinsic absorption of c-Cs$_4$PbCl$_6$, although the smaller x values than 0.2, which corresponds to the fraction of lead in Cs$_4$PbCl$_6$, necessarily mean that the films contain a considerable amount of the CsCl phase. In the case of $x = 0.2$, however, the film sample exhibits a different spectrum. Its spectral structures suggest that the film is composed of c-CsPbCl$_3$ and c-Cs$_4$PbCl$_6$. It was difficult to yield film samples purely composed of c-Cs$_4$PbCl$_6$ for $x = 0.2$.

It is interesting to note that, despite such an entity as the crystalline phase of Cs$_4$PbCl$_6$, its first absorption peak is well spaced in energy from the high-lying absorption structures by a wide, very weakly-absorbing window (width: ≈ 1 eV) and furthermore, the second structure (≈ 5.5 eV) is enhanced by increasing the temperature (Fig. 3).

Crystal structure of Cs$_4$PbCl$_6$ was reported in Ref. [4]. Cs$_4$PbCl$_6$ has a hexagonal structure, with the lattice constants $a = 1.3155$ nm, $c = 1.6604$ nm and space group R-3c. The crystal is built up of nearly regular Pb^{2+}(Cl$^-$)$_6$ octahedra with Pb^{2+} ions located at their centers. The octahedra are mutually bounded by Cs$^+$ ions.

Low-energy fundamental optical absorption of c-Cs$_4$PbCl$_6$ may be dominated by electronic transitions from 6s to 6p states in the Pb^{2+}-ion sublattice, as in the case of c-PbCl$_2$ and c-CsPbCl$_3$. However, the dilution of the sublattice by the intervening Cs$^+$ ions may have the effect of preventing these states from forming extended states. To a first approximation, these states are considered to form a set of localized states confined to within the individual Pb^{2+}(Cl$^-$)$_6$ octahedra. The situation is rather similar to the case of isolated Pb^{2+} ions doped in alkali halide crystals with fcc structure, where the Pb^{2+} ions are located at the centers of octahedral quasi-complexes Pb^{2+}(Cl$^-$)$_6$. It is, therefore, instructive to compare the absorption spectra of c-Cs$_4$PbCl$_6$ with those of Pb^{2+}-doped fcc alkali halide crystals.

It is well known that the absorption spectra of isolated Pb^{2+} ions in fcc alkali halide crystals are composed of A–D bands in order of increasing photon energy (a review article is available in Ref. [11]). The first three bands are, respectively, spin-orbit allowed, vibration-induced and dipole allowed transitions associated with 6s → 6p excitation of the Pb^{2+} ions (they are the transitions assigned as $^1A_{1g} \to {}^3T_{1u}$, $^1A_{1g} \to {}^3T_{2u}$ or ^3E_u and $^1A_{1g} \to {}^1T_{1u}$, respectively, with the first being allowed by spin–orbit interaction and the second by lattice vibration; more strictly, see Ref. [11]). In Pb^{2+}-doped NaCl crystals (at liquid nitrogen temperature), for example, A and B bands are located at 4.55 and 5.91 eV, respectively and C band is split into three bands located at 6.14, 6.25 and 6.65 eV; the dipole strength ratio of C band to A band is 3.2 [12]. Similar magnitudes of experimental values have also been reported for Pb^{2+}-dopec KCl crystals [12].

In the absorption spectra of c-Cs$_4$PbCl$_6$ (Fig. 3), the first peak at 4.350 eV, the weak (at 77 K) structure at 5.6 eV and the prominent band with the peak at ≈ 5.74 eV are, both in their relative energy locations and in their relative absorption intensities, fairly compared with A, B and C bands, respectively, of the Pb^{2+}-doped fcc alkali chlorides, except that all the structures of the former are somewhat red-shifted relative to the three bands of the latter (by ≈ 0.2 eV or more). In particular, the vibration-induced nature of B band is clearly exhibited by c-Cs$_4$PbCl$_6$, as seen from the enhanced absorption intensities around 5.5 eV at 300 and 450 K. Therefore, the spectra of c-Cs$_4$PbCl$_6$ are explained based on a model of Pb^{2+}-ion excitation of the Pb^{2+}(Cl$^-$)$_6$ quasi-complexes. The three structures under consideration correspond to creations of Frenkel excitons, which we refer to as A, B and C excitons, respectively. The A exciton peak was shown to have a Gaussian line shape (FWHM, 0.104 eV at 77 K), similar to A band of Pb^{2+}-doped fcc alkali halides (FWHM, 0.10 eV at 77 K for Pb^{2+}-doped NaCl [17], for example) and not similar to the first exciton peaks (Lorentzian line shape) of $CsPbCl_3$ [10].

It is interesting to note that the integrated absorption intensities of A and C excitons are constant, independently of temperature, despite the drastic increase of the B exciton intensity with increasing temperature. This is different from the case of Pb^{2+}-doped fcc alkali halides, where B band borrows intensity from C band (more accurately, the total intensity of A–C bands is constant independently of temperature). In Cs_4PbCl_6, B exciton borrows intensity from other sources located in energy above C exciton. We are in the process of extending the measurement to higher photon energies to estimate the f-sum for the exciton transitions associated with the Pb^{2+} 6s to 6p excitation.

Finally, we will briefly discuss the absorption spectra of the as-deposited films. The spectra exhibit a similar outline for all the values of x ($\neq 0$) as seen from Fig. 1, in great contrast to the case of the annealed films discussed above. As reported in previous papers on amorphous (a-) films of $PbCl_2$ [8] and $CsPbCl_3$ [6], whose absorption spectra are well reproduced by the present films with $x = 1$ and 0.5, respectively, the Pb^{2+} 6s and 6p states of these compounds are strongly localized by amorphization and the electronic transitions from the localized $6s_{1/2}$ to $6p_{1/2}$ states are responsible for the first absorption bands ≈ 4.35–4.40 eV of the a-$PbCl_2$ and a-$CsPbCl_3$ films. As seen from the figure, similar bands are also observed for other films with $x \geq 0.1$. Therefore, it can be stated for all the films with $x \geq 0.1$ that the Pb^{2+} ions are situated in the amorphous surroundings. Unlike the cases of the systems of TlCl–CuCl [2] and CdI_2–BiI_3 [3] mentioned in Section 1, however, the statement does not necessarily mean that the films are in the state of amorphous solid solution for all the values of x (≥ 0.1), since it is known that alkali halides, including CsCl, even when quench-deposited onto substrates at liquid helium temperature, are in the crystalline state [13,14]. As to this respect, structural studies are necessary for solving the problem.

Concerning the film with $x = 0.05$, the situation is somewhat different in view of the (blue-shifted) doublet structure of the first absorption band. Such a resolved structure may be due to Pb^{2+} ions that are under a high-symmetry, but anisotropic, crystal field. Presumably, the individual Pb^{2+} ions are embedded as single ions in the CsCl crystalline matrix and the associated charge-compensating Cs^+-ion vacancies provide uniaxial electric fields to the Pb^{2+} ions, thus splitting the $^3P_1$ excited states of the Pb^{2+} ions into two states. On annealing the film (at 500 K for 10 min), however, the Pb^{2+} ions aggregated to form crystallites of Cs_4PbCl_6, as already discussed.

5. Conclusion

Films of the binary $(CsCl)_{1-x}(PbCl_2)_x$ system were prepared over the full mixing range by the method of quench-deposition using co-evaporation of CsCl and $PbCl_2$. All the as-deposited films (with $x \neq 0$) have nearly the same optical energy gap (≈ 4 eV) exhibiting a similar first absorption band due to localized Pb^{2+} 6s–6p transitions. It was suggested that, in the films with $x \geq 0.1$, the Pb^{2+} ions are situated in the amorphous surroundings, and, in the film with $x = 0.05$, the ions are doped in the CsCl crystalline matrix as isolated impurities.

On annealing the films, there occurred drastic changes in their spectra depending on the mixing ratios and three representative types of spectral outlines were observed, i.e. type 1 observed for $x \geq 0.7$, type 2 for $0.5 \geq x \geq 0.3$ and type 3 for $x = 0.1$ and 0.05. Type 1 is characterized by the c-$PbCl_2$-like exciton absorption, whose spectral shape and transition energies vary continuously with x, suggesting the formation of certain mixed crystals. Type 2 represents the absorption spectrum of c-$CsPbCl_3$. Type 3, which was observed for the first time, is the spectrum peculiar to c-Cs_4PbCl_6.

c-Cs_4PbCl_6 exhibits novel absorption properties. Despite the crystalline entity of the compound, it shows oscillator-like fundamental absorption and a wide window just above the first absorption peak, suggesting a peculiarity of the associated energy band structure. The Cs^+ ions in the cation sublattice have the effect of preventing the Pb^{2+} 6s and 6p states from taking part in the construction of extended states. To a first approximation, these states form a set of localized states, similar to the case of Pb^{2+} ions doped in fcc alkali halide crystals. We are measuring electroabsorption spectrum of c-Cs_4PbCl_6 to further investigate the nature of these states. Soon, the result will be reported.

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