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Localized optical absorption in Cs_4PbBr_6

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Abstract

The fundamental optical absorption of Cs_4PbBr_6 crystals, which are built up of nearly regular $Pb^{2+}(Br^-)_6$ octahedra mutually bound by Cs^+ ions, exhibits novel features: despite the crystalline entity of Cs_4PbBr_6, it shows oscillator-like absorption peaks and a wide window just above the first peak. The Cs^+ ions prevent the Pb^{2+} 6s and 6p states from taking part in the construction of extended states. These states form a set of localized states confined to within respective octahedra, similar to the case of isolated Pb^{2+} ions doped in face-centred cubic alkali halide crystals.

1. Introduction

There are two stable ternary compounds in the mixed system of CsX–PbX_2 ($X = Cl, Br$), namely the congruent melting compound $CsPbX_3$ and incongruent Cs_4PbX_6 [1, 2]. In the growth of Cs_4PbX_6 crystals, both in the bulk and thin-film systems, it is difficult to hold back the occurrence of the $CsPbX_3$ phase because of an unavoidable incongruent melting crystal growth process [2]. Concerning the fundamental optical absorption of these compounds, only a few, room-temperature data are available on Cs_4PbX_6 [2, 3], although several studies have been reported on $CsPbX_3$ [4–12]. Nikl *et al* [2] reported that, in the optical absorption spectrum of Cs_4PbBr_6 films, an unavoidable extra absorption occurs due to the $CsPbBr_3$ phase. In a subsidiary effort [3] they also exemplified that, by annealing alternating $CsBr/PbBr_2$ multilayer films or $PbBr_2$-deposited CsBr bulk crystals, it is possible to obtain specimens composed of Cs_4PbBr_6 and CsBr. Such specimens can be used to study the intrinsic optical absorption of Cs_4PbBr_6 because the coexisting CsBr is transparent in the region up to a considerable photon energy, about 6.3 eV. In this paper we study the optical absorption of similar specimens prepared by several different methods. The fundamental absorption spectrum of Cs_4PbBr_6 is shown to have a novel feature.

2. Results

Figure 1 illustrates the changes of the absorption spectrum during the heating of a two-layer film prepared on a silica–glass substrate, $PbBr_2$/CsBr/silica–glass. The two compounds were

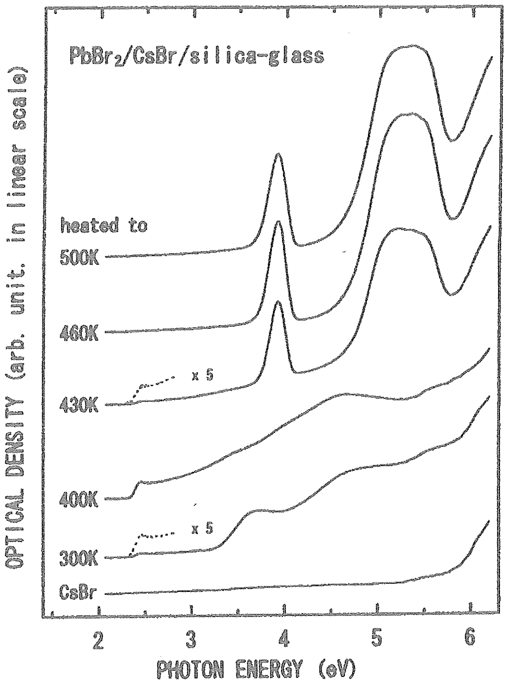

Figure 1. The change of the absorption spectrum with temperature of a two-layer $PbBr_2$/CsBr film prepared on a silica–glass substrate, measured *in situ* at the various temperatures indicated.

evaporated in a vacuum of about 9×10^{-6} Pa from separated sources *in situ* onto a room-temperature silica–glass substrate put on a sample holder of an optical cryostat. The thicknesses of the $PbBr_2$ and CsBr layers were about 46 and 340 nm, respectively, which correspond to the molar ratio, $PbBr_2$:CsBr = 0.1:0.9. *In situ* spectral measurements were carried out by an improved double-beam method described in [11]. The method is based on simultaneous measurements of transmittance and reflectance from which accurate optical densities of a film can be determined. The spectrum was first measured on the CsBr layer (before evaporation of $PbBr_2$). After evaporating $PbBr_2$, the specimen $PbBr_2$/CsBr/silica–glass was heated at a rate of 1 K min^{-1} to measure the spectrum at various temperatures; the temperatures during the measurements (with a measurement time of 390 s for each) were kept constant. In figure 1 five spectra are shown, which were measured at 300, 400, 430, 460 and 500 K, respectively. In the spectrum measured at 300 K, which exhibited the main absorption features of $PbBr_2$ (absorption edge, about 3.4 eV), there arose weak absorption due to $CsPbBr_3$ (absorption edge, about 2.4 eV). With heating to 400 K the spectrum became entirely $CsPbBr_3$-like. This indicates that the $PbBr_2$ layer reacted chemically with CsBr completely but at the expense of a small part (about 1/9) of the CsBr layer near the $PbBr_2$/CsBr interface. At 430 K a new absorption feature occurred although the weak absorption due to the $CsPbBr_3$ phase still existed. This spectrum is rather similar in outline to the absorption spectrum of Cs_4PbBr_6 films in [2], for which unavoidable extra absorption due to the coexisting $CsPbBr_3$ phase occurs as mentioned above (the coexistence of both phases in the films was demonstrated by the measurement of x-ray diffraction). In the present film, the trace of the $CsPbBr_3$ phase was completely held back at 460 K, indicating that the $CsPbBr_3$ products reacted chemically with the remnant of the CsBr layer completely. The resulting spectrum was attributed to intrinsic absorption of Cs_4PbBr_6 (see the first paragraph in the next section). Entirely the same spectral

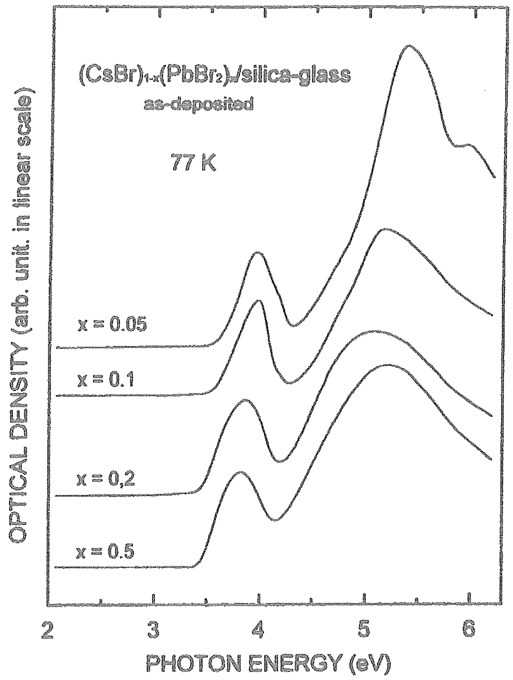

Figure 2. Absorption spectra of quench-deposited $(CsBr)_{1-x}(PbBr_2)_x$ films, measured at 77 K for several values of x before annealing the films.

shape was observed for further heating to 500 K indicating the stability of the Cs_4PbBr_6 phase. We conclude, therefore, that the favourable annealing temperature for synthesizing Cs_4PbBr_6 is 500 K.

Next we prepared single-layer films of the mixtures of $PbBr_2$ and CsBr using the method of evaporating the mixtures onto silica–glass substrates cooled to 77 K and subsequent annealing at 500 K. Many of the metal halide films produced via such a procedure (evaporation onto low-temperature substrates and subsequent annealing) have been shown to have very high transmittance compared with films prepared directly onto hot substrates; this is particularly the case for lead-based metal halide films [13]. Figures 2 and 3 show the absorption spectra at 77 K of the $(CsBr)_{1-x}(PbBr_2)_x$ films with $x = 0.05$, 0.1, 0.2 and 0.5. Here, the nominal x values of the mixtures were used to represent the composition of the films. According to elemental analyses carried out for several films by an electron probe x-ray micro-analyser, the deviation of the composition ratios from the nominal ratios was within 5% (to minimize the deviation, we deposited the films rapidly, at a rate of about 20 nm min^{-1}; such a high deposition rate was previously shown to be favourable for achieving nominal ratios in the films of mixed metal halides [14]). The value $x = 0.2$ corresponds to Cs_4PbBr_6, and $x = 0.5$ to $CsPbBr_3$ (the latter was taken up for the purpose of comparison). For each value of x, the spectrum was first measured at 77 K on the as-prepared film (figure 2). 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 figure 3. 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-prepared films are unity at the peaks of the first band around 3.9–4 eV (which originates from localized $6s_{1/2}$–$6p_{1/2}$ transitions [12]).

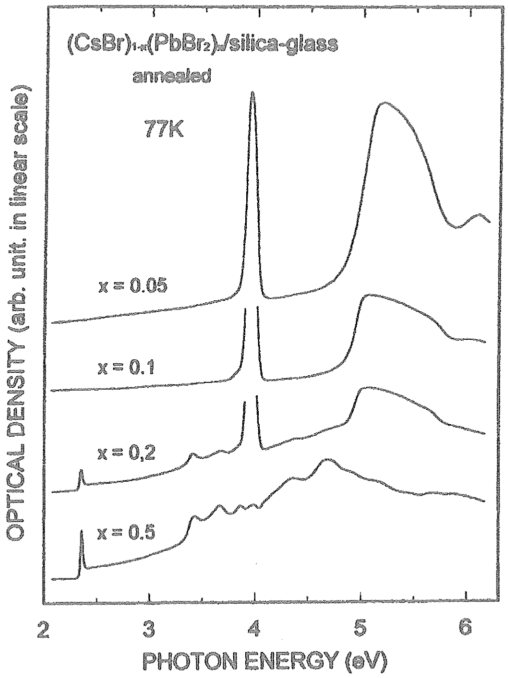

Figure 3. Absorption spectra of quench-deposited $(CsBr)_{1-x}(PbBr_2)_x$ films, measured at 77 K for several values of x after annealing the films at 500 K for 10 min.

Although there was no large difference in the spectral shape among the as-prepared films (figure 2), the annealing of the films gave rise to drastic changes in the spectral structure depending on the values of x (figure 3). In the annealed films with $x = 0.05$ and 0.1, a sharp peak showed up at 3.95 eV characteristic of the Cs_4PbBr_6 phase, and no structures were recognized in the lower photon energies. In the film with $x = 0.2$, however, a composite spectrum resulted exhibiting the absorption characteristics of the $CsPbBr_3$ phase (in particular, the low-energy structures below 3.9 eV) as well as of the Cs_4PbBr_6 phase. It was difficult to obtain films composed of the single Cs_4PbBr_6 phase, probably due to an incongruent melting crystal growth process as pointed out in [2].

The annealing of the films (with $x \leqslant 0.2$) also gave rise to nonzero optical densities in the transparent photon energy region suggesting devitrification of the films, although the resulting films were completely transparent to the eyes. The degree of devitrification was roughly proportional to photon energy as seen from the upward spectral slopes in the otherwise transparent region (figure 3). We note that films prepared by evaporation onto 500 K substrates were more highly devitrified.

Figure 4 shows a comparison of the spectra between three different phases of the same starting film, namely the amorphous (a-)$PbBr_2$ phase and the $CsPbBr_3$ and Cs_4PbBr_6 phases. For all the phases, contributions due to excess CsBr were eliminated; to do so, we used a CsBr-coated silica–glass plate as a substrate and corrected the measured spectra for their absorption. The measurements were carried out as follows. An a-$PbBr_2$ film was prepared by evaporating $PbBr_2$ onto the substrate cooled to 77 K (in a vacuum of about 9×10^{-6} Pa). Then the spectra (solid curves) were measured at three different temperatures, i.e., 77 K (a-$PbBr_2$), 400 K ($CsPbBr_3$) and 500 K (Cs_4PbBr_6), in the same way as above. For the Cs_4PbBr_6 phase, a spectrum was also measured at 77 K (dashed curve). As seen from the figure, all the spectra

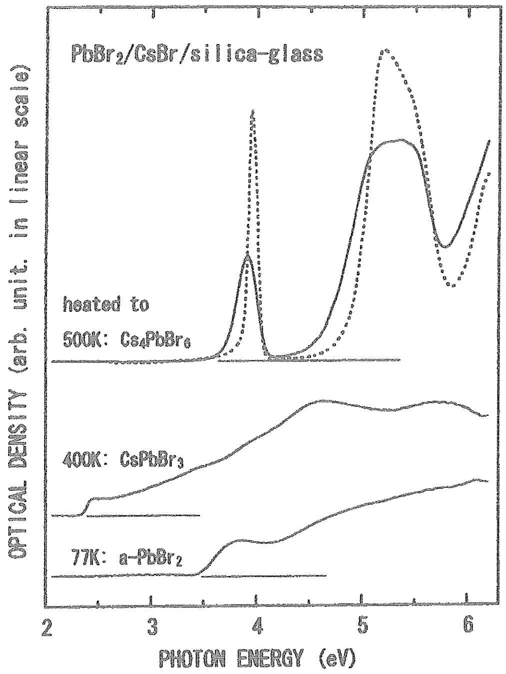

Figure 4. Fundamental absorption spectra of the three phases achieved by heating the same starting film to particular temperatures: 77 K for a-$PbBr_2$, 400 K for $CsPbBr_3$ and 500 K for Cs_4PbBr_6, measured at the respective temperatures (solid curves). For Cs_4PbBr_6, a measurement was also made at 77 K (dashed curve).

exhibit almost no slopes in the transparent photon energy regions. These spectra represent the intrinsic absorption of the respective phases. The integrated absorption intensity ratio was 1 (a-$PbBr_2$):1.78 ($CsPbBr_3$):1.80 (Cs_4PbBr_6) in the measured region (up to 6.2 eV). Notably, in the spectra of Cs_4PbBr_6, there arise strong, oscillator-like absorption peaks. Furthermore, there is a wide, very weakly absorbing window (width, about 1 eV) in the region between the first peak and high-lying structures. In the case of the Cs_4PbBr_6-film spectrum reported in [2], such a transparency of the window was by no means observed because of unavoidable extra absorption due to the coexisting $CsPbBr_3$ phase. The occurrence of the window (despite such an entity as the crystalline phase of Cs_4PbBr_6) suggests a peculiarity of the associated energy band structure; the band structure should have the property of strongly suppressing the interband transitions in the window region.

3. Discussion

To begin with, we should mention the relevance of the attribution of the above-obtained new spectrum (e.g. the uppermost curve in figure 1) to the intrinsic absorption of Cs_4PbBr_6, since it is known that Pb^{2+} ions can be doped in the CsBr crystal as impurities which exhibit several absorption bands in a similar photon energy region. For example, five bands, at energies around 3.6, 3.7, 4.1, 4.9 and 5.5 eV at liquid-nitrogen temperature, have been reported [15–17] for the isolated Pb^{2+} ions in the CsBr crystals (according to the study of dielectric relaxation [18], the isolated Pb^{2+} ions in the CsBr crystal are substituted for Cs^+ ions in the body-centred cubic (bcc) lattice of the crystal). However, these bands are only observed for crystals which are very lightly doped with Pb^{2+} ions (of the order of 0.1 wt% of $PbBr_2$ or less, as compared with, for example, 16 wt% in the film sample with $x = 0.1$ of the $(CsBr)_{1-x}(PbBr_2)_x$ system). In film samples, it is difficult to observe such absorption bands as being due to extremely diluted absorption centres. In our films (with a thickness in the range of 300–400 nm for $x = 0.1$), the corresponding absorption was indeed not discernible. On the other hand, attempts to heavily dope CsBr crystals with Pb^{2+} ions may result in the formation of aggregated phases such as $CsPbBr_3$ and/or Cs_4PbBr_6, as suggested by the phase-diagram studies [1,2] mentioned in section 1. These considerations strongly support the above attribution described in section 2.

The low-energy fundamental optical absorption of Cs_4PbBr_6 may be dominated by electronic transitions from 6s to 6p states in the Pb^{2+}-ion sublattice, as in the case of $CsPbBr_3$ [4,5]. Both the crystals of Cs_4PbBr_6 and $CsPbBr_3$ are built up of nearly regular $Pb^{2+}(Br^-)_6$ octahedra with Pb^{2+} ions located at their centres. In $CsPbBr_3$, however, each Br^- ion is shared between two adjacent octahedra (the octahedra are embedded in a simple cubic matrix of Cs^+ ions, with six Br^- ions located at the face-centred positions of the cube and the cation Pb^{2+} at the cube centre), while, in Cs_4PbBr_6, adjacent octahedra are separated by intervening Cs^+ ions (the Cs^+ ions play a role of bounding adjacent octahedra to form a hexagonal crystal structure [1]). Therefore, in Cs_4PbBr_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 $Pb^{2+}(Br^-)_6$ octahedra. The situation is rather similar to the case of isolated Pb^{2+} ions doped in alkali halide crystals with a face-centred cubic (fcc) structure, where the Pb^{2+} ions are located at the centres of octahedral quasi-complexes $Pb^{2+}(X^-)_6$ (X^- is a halogen ion). It is, therefore, instructive to compare the absorption spectra of Cs_4PbBr_6 with those of Pb^{2+}-doped fcc alkali halide crystals.

The absorption spectra of isolated Pb^{2+} ions in fcc alkali halide crystals are generally composed of A, B, C and D bands in order of increasing photon energy. (Sometimes, the A band is split into two structures, and the C and D bands into three; a review article is available in [19].) 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, and the D band is due to charge transfer from ligand halogen p to Pb^{2+} 6p states. In Pb^{2+}-doped KBr crystals [20], for example, these bands (at room temperature) are located at 4.15, 5.1 and 5.52 eV, respectively, and the D_1 band is at 5.79 eV. The dipole strength ratio of the A band to the C band is 0.16 and that of the D_1 band to the C band is about 0.3.

In the absorption spectra of Cs_4PbBr_6 (at 77 K, dashed curve in figure 4), the first peak at 3.948 eV and the prominent band with the structures at around 5.16 and 5.5 eV are fairly compared, both in their relative energy locations and in their relative absorption intensities, with the A, C and D_1 bands, respectively, of the Pb^{2+}-doped KBr crystals, except that all the structures of the former are somewhat redshifted relative to the latter ones (by about 0.2 eV or more). Furthermore, the stronger absorption intensity around 4.8 eV at 500 K than at 77 K corresponds to the vibration-induced nature of the B band (in Pb^{2+}-doped KBr mentioned above, the B band is discernible only when a spectral analysis is performed). Therefore, the spectra of Cs_4PbBr_6 can be explained based on a model of Pb^{2+}-ion excitation of the $Pb^{2+}(Br^-)_6$ quasi-complexes; the four structures under consideration correspond to creations of Frenkel excitons. In a one-electron scheme, the (Pb^{2+} 6s-like) valence and the (Pb^{2+} 6p-like) conduction bands related to these excitons should have very low energetic dispersions and thus have very high densities of states, since then it is possible to construct such exciton states.

4. Conclusion

We have measured the fundamental absorption spectra of Cs_4PbBr_6 crystals, which usually coexist with the $CsPbBr_3$ and/or CsBr phases as an incongruent melting compound in the mixed system of $PbBr_2$–CsBr. The spectrum exhibits novel features: despite the crystalline entity of Cs_4PbBr_6, it shows oscillator-like absorption peaks and a wide, very weakly-absorbing window just above the first peak. The absorption characteristics can be explained in terms of Pb^{2+}-ion excitation of the octahedral $Pb^{2+}(Br^-)_6$ quasi-complexes, similar to the case of Pb^{2+}-doped fcc alkali halide crystals. Since Cs^+ ions in Cs_4PbBr_6 prevent the Pb^{2+} 6s and 6p states from taking part in the construction of extended states, these states form a set of localized states confined within respective quasi-complexes. Electroabsorption experiments on Cs_4PbBr_6 crystals are in progress to measure coupling between the 'confined' states, in order to investigate the effect of translational regularity (periodicity) of the quasi-complexes. The results will be reported soon.

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