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journal or publication title	Journal of Physics - Condensed Matter
volume	13
page range	11077-11085
year	2001-12
URL	http://hdl.handle.net/10098/1561

In situ optical absorption and reflection spectroscopy of doping CsCl crystal with Pb^{2+} ions

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Abstract

Behaviours of Pb^{2+} ions during thermal treatments of PbCl_2 -deposited CsCl crystals have been observed *in situ* by optical absorption and reflection spectroscopy. In the early stages of the treatments, the Pb^{2+} ions take part in the formation of Cs_4PbCl_6 crystallites near the surface of the CsCl crystals. The crystallites exhibit a novel absorption spectrum suggesting that the 6s and 6p states of the Pb^{2+} ions are strongly localized. On heavy annealing at a high temperature (673 K) followed by a rapid cooling to room temperature, the Pb^{2+} ions are uniformly dispersed throughout the CsCl crystals, exhibiting the absorption spectrum attributable to isolated Pb^{2+} -ion centres.

1. Introduction

A number of papers have been published on the optical properties of lead-doped alkali halide crystals. Many authors have, however, dealt with the crystals of fcc structure, and data [1–8] on lead-doped cesium halides (bcc structure) are insufficient in some respects. In particular, the nature of optical absorption of isolated Pb^{2+} ions in Pb^{2+} -doped CsCl crystals [1, 4] has not yet been well elucidated. In [1], which tabulates the peak positions of the A, B and C absorption bands of $\text{CsX}:\text{Pb}^{2+}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the absorption spectrum for $\text{X} = \text{Cl}$ is not shown (though the spectra for other X are presented explicitly). Furthermore, the table values for $\text{X} = \text{Cl}$ are by no means well reproduced in the absorption spectrum available in [4], which is the only paper that presents the absorption spectrum of $\text{CsCl}:\text{Pb}^{2+}$ explicitly. These situations have motivated the present study.

Previously we reported on amorphous films of PbX_2 , CsPbX_3 and TiX ($\text{X} = \text{Cl}, \text{Br}$) [9, 10]. Amorphization of these compounds, whose electronic energy bands near the gap are composed of the cation 6s (valence band) and 6p (conduction band) orbitals [11–13], gave rise to strong localization of the extended states near the gap, exhibiting a distinct absorption band (first absorption band) due to localized 6s ($j = 1/2$) to 6p ($j = 1/2$) transitions. In the present

paper, starting from amorphous films of PbCl_2 deposited onto CsCl crystals, we monitored thermally induced diffusion of Pb^{2+} ions into the crystals by optical absorption and reflection spectroscopy. In the early stages of the diffusion, the Pb^{2+} ions were densely dispersed near the surface of the crystals, exhibiting the absorption spectrum characterized by a very sharp first peak with nearly the same peak energy and nearly the same integrated absorption intensity as the first absorption band of the starting amorphous PbCl_2 film. On heavy annealing at higher temperatures followed by quenching procedures, there occurred essential changes in the spectral shape, finally resulting in the absorption structures attributable to isolated Pb^{2+} -ion centres dispersed throughout the crystal.

2. Experimental

Amorphous PbCl_2 films were prepared on the polished surfaces of CsCl single crystals (grown by the Bridgman technique) by quench deposition similar to that employed previously [9]. In brief, the deposition was carried out onto CsCl crystal substrates 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 substrates; the deposition rate was about 20 nm min^{-1} . Changes in spectroscopic morphology of thus-prepared samples ($\text{PbCl}_2/\text{CsCl}$ samples) due to heating or annealing were monitored by *in situ* optical absorption and reflection spectroscopy, using an improved double-beam method described in [9]. The method is based on simultaneous measurements of transmittance and reflectance from which it is possible to monitor the change of the samples both near the reflecting surface (reflection spectrum) and in the deeper interior (absorption spectrum corrected for reflection loss) of the samples.

3. Results and discussion

Figures 1 and 2 illustrate the changes of absorption and reflection spectra, respectively, during heating of a $\text{PbCl}_2/\text{CsCl}$ sample. The thicknesses of the PbCl_2 film and CsCl crystal were about 32 nm and 0.86 mm, respectively (the film thickness was determined by an interference method [14]). Spectra (curves 77 K) were first measured at 77 K for the as-prepared sample. Then the sample was heated at a rate of 1 K min^{-1} to measure the spectra at various temperatures indicated; the temperatures during the measurements (measurement time, 260 s for each) were kept constant. The first absorption band appearing around 4.36 eV (curves 77 K to 250 K in figure 1) in the amorphous PbCl_2 comes from localized 6s ($j = 1/2$) to localized 6p ($j = 1/2$) transitions in the Pb^{2+} ions strongly affected by an inhomogeneous local electric field in the amorphous environment [10]. The abrupt change in the spectral structure occurring for temperatures between 250 and 280 K (both in the absorption and reflection spectra) is due to crystallization of amorphous PbCl_2 (the crystallization temperature is about 280 K [15]). By crystallization, the first band was changed to the excitonic peak at around 4.56 eV (curve 280 K in figure 1), with the FWHM (full width at half maximum) reduced by about 50% (motional narrowing) and with the transition energies blue shifted by about 0.2 eV (reduction of Coulomb and exchange interactions between 6p electron and 6s hole).

In the temperature range from 340 to 460 K, a new absorption structure showed up at around 3 eV (figure 1), which grew to the sharpest peak at 430 K and then became less prominent at 460 K, while the PbCl_2 exciton peak decreased in intensity with increasing temperatures and finally disappeared at 460 K. Judging by the transition energy of 3 eV [9], the new structure is considered to be due to exciton of CsPbCl_3 , indicating that there occurred solid-state chemical reaction between PbCl_2 and CsCl producing CsPbCl_3 crystallites (the

Figure 1. The change of the absorption spectrum with temperature of a PbCl_2 -deposited CsCl crystal measured *in situ* at the various temperatures indicated.

absorption spectrum at 430 K is very similar in feature to that of CsPbCl_3 measured at 77 K [9], although fine structures are missing in the former because of thermal effects). It can be seen from the corresponding reflection spectra (curves 340 K to 460 K in figure 2), in which a marked peak was located at around 3 eV, that the CsPbCl_3 crystallites were embedded at and/or near the surface of the sample.

Further heating to 500 K gave rise to an essential change in the spectral outline. As seen from curve 500 K in figure 1, the exciton transitions of CsPbCl_3 disappeared completely and instead a prominent peak showed up at around 4.3 eV. In the reflection spectra, however, the corresponding structure (around 4.3 eV) was very weak as seen from curve 500 K in figure 2. Therefore, it is inferred that by heating to 500 K the CsPbCl_3 crystallites were destroyed and the Pb^{2+} ions migrated to a further interior in the sample, thus forming a new absorbing material in the CsCl crystal environment.

Figure 2. The change of the reflection spectrum with temperature of a PbCl_2 -deposited CsCl crystal measured *in situ* at the various temperatures indicated.

The absorption spectrum of the resulting sample is rather similar in outline to that of the starting amorphous PbCl_2 film. In particular, both spectra locate the first peak (or band) at almost the same photon energies (about 4.3 eV). Since the first band of the amorphous PbCl_2 is attributed to the localized $6s$ ($j = 1/2$) to $6p$ ($j = 1/2$) transitions [10], the first peak of the new spectrum (curve 500 K in figure 1) is considered to have a similar origin to (but not 'the same origin as', see later) the A band (spin-orbit allowed $^1S_0 \rightarrow ^3P_1$ transitions; transitions) observed for Pb^{2+} -doped fcc alkali halides. In this connection, the higher energy absorption band at around 5.5 eV in the new spectrum corresponds to the B band (which borrows intensity from the C band due to lattice vibration) and the band around 5.75 eV to the C band (dipole allowed $^1S_0 \rightarrow ^1P_1$ transitions).

Figure 3 shows the absorption spectrum at 77 K (solid curve) of the same sample together with that at 500 K (dashed curve, identical to curve 500 K in figure 1). From the figure two

Figure 3. The absorption spectra of a PbCl_2 -deposited CsCl crystal, measured at 77 K (curve 1) and 500 K (curve 2) after annealing at 500 K for 10 min.

characteristics are seen, i.e., the very sharp line shape of the first peak at 77 K (FWHM of 147 meV, peak energy of 4.35 eV) and the structure around 5.5 eV more enhanced at 500 K than at 77 K. The latter characteristic very well corresponds to the vibration-induced nature of the B band. We note that the sample subsequently annealed at 500 K for 30 min exhibited entirely the same spectral features as those in figure 3, indicating high stability of the absorption centres.

Since the spectral characteristics in figure 3 were by no means similar to those of Pb^{2+} -doped CsCl crystal reported in [1] nor to those in [4], we further investigated the effect of thermal treatment on our sample in the expectation of further change in the spectrum. The thermal treatment was made as follows. The sample was taken out of the vacuum chamber of the cryostat, annealed in dry air at 673 K for various periods, t_a ; each period was followed by a rapid cooling to room temperature (in the way of a quick thermal contact with a room temperature copper block). Thus-treated sample was again mounted on the sample holder to measure absorption spectrum. The measurement results are shown in figure 4, where curves 2, 3 and 4 represent the absorption spectra at 77 K for $t_a = 30, 60$ and 240 min, respectively (the absorption spectrum before the thermal treatments is also shown as curve 1 for comparison). The main features of the spectral changes due to the thermal treatments were (1) the conversion of the sharp peak at 4.35 eV (curve 1) into the doublet (peaking at 4.11 and 4.29 eV, curve 4) via the triplet (curves 2, 3), (2) the occurrence of a new, small peak at 5.17 eV (curves 3, 4) and (3) the red shift of the higher energy peak from 5.74 eV (curve 1) to 5.56 eV (curves 2–4). Presumably, these changes are due to diffusion of the Pb^{2+} ions throughout the bulk crystal of CsCl, since the quenching was preceded by annealing at very high temperature, as high as 673 K. It was shown that further thermal treatments employing longer annealing times (at the same annealing temperature) no longer gave rise to further change in the spectral shape of curve 4. Therefore, the Pb^{2+} ions in the thus-treated $\text{PbCl}_2/\text{CsCl}$ sample are considered to be

Figure 4. The effects of thermal treatments on the absorption spectra of a PbCl_2 -doped CsCl crystal quenched from 673 K to room temperature, see text.

uniformly dispersed in the CsCl crystal, the majority of which are embedded as single ions (isolated Pb^{2+} -ion centres) in the crystal matrix.

To compare curve 4 with the absorption spectrum of Pb^{2+} -doped CsCl crystals grown from the melt, we prepared crystals of CsCl:Pb^{2+} of a very low PbCl_2 concentration of 1×10^{-4} wt% in the melt by the Bridgman method (under such a very low concentration, the majority of the Pb^{2+} ions would be embedded as isolated centres in the quenched crystals). The absorption spectrum of the (quenched) crystals is shown in figure 5 (curve 0) together with curve 4 in figure 4 (curve 1). The two curves exhibit almost the same spectral outline. However, they do not reproduce the absorption profile of CsCl:Pb^{2+} crystals reported in [1] (where the authors tabulated the peak energies of the A, B and C bands of the isolated Pb^{2+} -ion centres without presenting the absorption spectrum, as mentioned in section 1). They rather resemble the absorption spectrum in [4] (where the spectrum of isolated Pb^{2+} ions in Pb^{2+} -doped CsCl crystals is presented only for room temperature because the main object of interest is the Pb^{2+} -ion aggregated phase).

According to [4], the isolated Pb^{2+} -ion centres embedded in the CsCl crystal have the property to aggregate to form microcrystals of CsPbCl_3 by annealing at temperatures about

Figure 5. The absorption spectrum of Pb^{2+} -doped CsCl crystals, grown from the melt (curve 0), or prepared by thermal treatments of a PbCl_2 -deposited CsCl crystal (curves 1, 2), see text.

200 to 250 °C for 12 to 14 h. This was confirmed in the present sample too. Curve 2 in figure 5 is the spectrum into which curve 1 changed after annealing the sample at 523 K for 500 min. The new spectrum, which exhibits a sharp peak at 3.020 eV characteristic of CsPbCl_3 exciton transitions, is very similar in feature to the absorption spectrum of CsPbCl_3 films [9] except the prominent peak at 5.16 eV (which is absent in [9]). The 5.16 eV peak is probably due to small clusters of the Pb^{2+} ions. A small amount of such clusters is considered to have already existed before the annealing, since the corresponding peak at 5.16 eV is, though less prominent, observed in curve 1. This, in turn, leads to the conclusion that, of the four peaks in curve 1, the peaks at 4.11, 4.29 and 5.56 eV can be addressed as being due to the isolated Pb^{2+} -ion centres. A possible assignment for these peaks would be that the doublet peaking at 4.11 and 4.29 eV are the A band and the peak at 5.56 eV the C band, although the reason for such a distinct splitting of the A band is not clear at present. Similar annealing experiments were carried out on curves 2 and 3 in figure 4. However, almost no changes occurred in their structures.

In view of the above results of the thermal treatments, the absorption centres responsible for the 'novel' spectra shown in figure 3 are considered to be composed of a high density of Pb^{2+} ions embedded in the CsCl crystal. This was, in fact, demonstrated by preliminary

Figure 6. The absorption spectra at 77 K (curve 1) and 450 K (curve 2) of a thin film of $(\text{CsCl})_{0.9}(\text{PbCl}_2)_{0.1}$ deposited onto a silica glass substrate.

measurements on film samples of the mixed system of CsCl and PbCl_2 . Figure 6 shows the absorption spectra of a film of $(\text{CsCl})_{0.9}(\text{PbCl}_2)_{0.1}$ deposited onto a silica substrate heated to 450 K (the nominal ratio, $\text{CsCl}:\text{PbCl}_2 = 9:1$, was shown to be retained within a few percent of scatters from surface to surface of the film by electron probe x-ray micro-analyzer measurements). Curve 1 was measured at 77 K and curve 2 at 450 K. The spectra are not only similar in feature to those shown in figure 3 but they more clearly show novel characters, i.e., the very sharp, prominent 4.35 eV peak at 77 K (FWHM, 105 meV) well spaced in energy from the high-lying structures by a wide, very weakly absorbing window (width, about 1 eV) and clear evidence for the vibration-induced character of the 5.5 eV band.

In particular, the presence of such a window suggests that the 6s and 6p states of the Pb^{2+} ions are localized without forming extended states (Bloch states), since otherwise the optical absorption due to the band-to-band transitions will obscure such a transparency of the window. It is nevertheless unacceptable that such a quantity of Pb^{2+} ions (10 mol%) can exist as isolated impurity ions in the CsCl crystal. It is considered that the observed spectrum is due to the intrinsic (fundamental) absorption of a certain aggregated phase (which is stable even at 500 K).

According to the study of the phase diagram of the $(\text{CsCl})_{1-x}(\text{PbCl}_2)_x$ system by Nitsch *et al* [16], there exist two stable ternary compounds in the system, namely the congruently melting compound CsPbCl_3 and incongruent Cs_4PbCl_6 . In particular, Cs_4PbCl_6 is the only stable compound in the CsCl-rich region ($x < 0.5$). Of the two compounds, the fundamental optical absorption of CsPbCl_3 is characterized by a sharp (Wannier-type) exciton peak appearing around 3 eV (depending on the measuring temperature) as indeed observed in the present heat-treated $\text{PbCl}_2/\text{CsCl}$ sample (e.g. curve 400 K in figure 1 or curve 2 in figure 5). Concerning Cs_4PbCl_6 , however, there has been no literature on the fundamental optical absorption. Presumably, the absorption spectrum shown in figure 6 (or figure 3) is attributed to the fundamental absorption due to the Cs_4PbCl_6 phase. Indeed, the onset energy of the

positive slope of the first peak in the spectrum corresponds to the onset of optical absorption for the bulk Cs_4PbCl_6 phase, about 4 eV at room temperature, reported in [17]. In our films (or heat-treated $\text{PbCl}_2/\text{CsCl}$ sample), it is considered that crystallites of Cs_4PbCl_6 coexist with CsCl crystals (or, are embedded in the CsCl crystal). Individual Pb^{2+} ions in the Cs_4PbCl_6 lattice, being surrounded by six Cl^- ions (forming a nearly ideal octahedron [16]) and further being well separated from one another by intervening Cs^+ ions, behave like isolated ions as far as optical absorption is concerned, thus exhibiting such a novel window as above despite the crystalline entity of the Cs_4PbCl_6 phase. Details will be reported soon.

4. Conclusion

Behaviours of Pb^{2+} ions during thermal treatments of PbCl_2 -deposited CsCl crystals were observed *in situ* by optical absorption and reflection spectroscopy. In the early stages of the treatments at temperatures up to 500 K, the Pb^{2+} ions were densely dispersed near the surface of the CsCl crystals via the decomposition of CsPbCl_3 formed by chemical reaction between PbCl_2 and CsCl . The resulting samples suggested the formation of Cs_4PbCl_6 crystallites in the CsCl crystals, showing a novel absorption spectrum due to the localized nature of 6s to 6p transitions of the individual Pb^{2+} ions. On subsequent annealing at a very high temperature of 673 K, followed by a rapid cooling to room temperature, the Pb^{2+} ions were uniformly dispersed throughout the CsCl crystals, exhibiting the absorption spectrum attributable to isolated Pb^{2+} -ion centres.

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