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Effect of amorphization on the Wannier and Frenkel excitons in metal halides

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Abstract

We have investigated the effect of amorphization on the Wannier and Frenkel excitons originating from $6s \rightarrow 6p$ transitions of the $6s^2$ cations in TlX , $CsPbX_3$ and PbX_2 (X is halogen). By amorphization the Wannier-exciton peak disappears, whereas for the Frenkel exciton its amorphous counterpart appears due to localized $6s^2$ -ion excitation.

Keywords: D. Electronic states (localized); D. Optical properties; D. Order-disorder effects; E. Light absorption and reflection

1. Introduction

Optical absorption spectra of crystals with a direct band gap often exhibit sharp exciton resonance in the photon energy region near the fundamental edge. In non-crystalline solids, such an excitonic effect tends to be smeared out due to localization of the associated one-electron states near the band edges, as is particularly the case for amorphous semiconductors [1]. However, there have been a few reports on the existence of excitonic structures in the amorphous state, e.g. for SiO_2 [2], where the electron-hole binding energy is quite large (about 2 eV), and for core excitons [3], which have a very small radius. In ionic compounds such as metal halides, excitons are generally characterized by a large electron-hole binding energy and a small radius compared to the semiconductors case. Therefore, it is tempting to investigate amorphous versus crystalline states of metal halides in terms of optical absorption related to excitons.

In metal halides containing $6s^2$ -configuration cations (such as Tl^+ and Pb^{2+}) as a constituent, the $6s^2$ ions make a dominant contribution to low-energy optical absorption, exhibiting a sharp direct-band-gap exciton peak due to cationic transitions occurring on the $6s^2$ -ion sublattice. The excitonic transitions are known to be of a Wannier type for TlX ($X = I$ [4], Br [5], Cl [5]), $CsPbX_3$ ($X = Br$ [6], Cl [6]) and PbI_2 [7], and of a Frenkel type for PbX_2

($X = F$ [8], Cl [9], Br [9]). Therefore, these compounds may provide a suitable set of materials for studying the effect of amorphization on both types of exciton transitions in ionic compounds.

Concerning these compounds, we have already reported several works on their amorphous films and disclosed that the amorphous films exhibit well-defined, characteristic crystallization temperatures (121, 95 and 99 K for TlI [10], $TlBr$ [11] and $TlCl$ [12]; 296 and 302 K for $CsPbBr_3$ [13] and $CsPbCl_3$ [13]; 198, 335, 282 and 230 K for PbI_2 [14], $PbBr_2$ [15], $PbCl_2$ [16] and PbF_2 [17], respectively). However, these works have mainly been aimed at optical characterization of the amorphous films, except the works on $CsPbX_3$ (for which electronic states in the amorphous state have been discussed), and the absorption behavior associated with exciton transitions in the films has not been seen. In this paper we provide a full set of absorption spectra near the fundamental edge for both the amorphous and crystalline (crystallized) states of the films of these compounds for the sake of comparative investigation of the spectra in the two states, and give a brief, but systematic, discussion on the effect of amorphization on the Wannier- and Frenkel-exciton transitions.

2. Absorption spectra near the fundamental edge

Figs. 1–3 summarize the comparison of the absorption

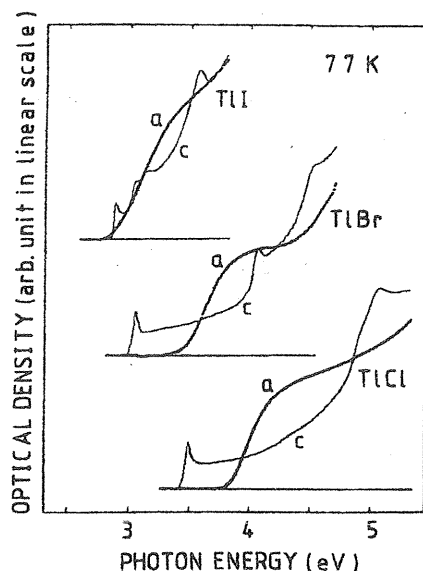


Fig. 1. Absorption spectra at 77 K near the fundamental edge of amorphous (curves a) and crystalline (curves c) films of TlX (X = I, Br, Cl).

spectra near the fundamental edge at 77 K between amorphous (curves a) and crystalline (curves c) films for TlX (Fig. 1; X = I, Br, Cl), CsPbX₃ (Fig. 2; X = Br, Cl) and PbX₂ (Fig. 3; X = I, Br, Cl, F). The amorphous films were all achieved by quench deposition onto 77 K substrates and the crystalline ones were produced via crystallization of the same (amorphous) films. The detailed procedures for

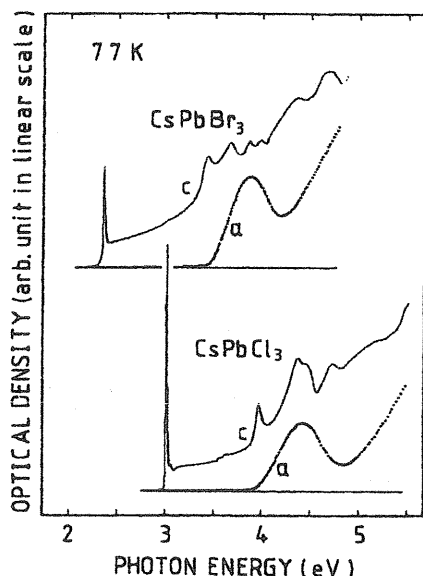


Fig. 2. Absorption spectra at 77 K near the fundamental edge of amorphous (curves a) and crystalline (curves c) films of CsPbX₃ (X = Br, Cl).

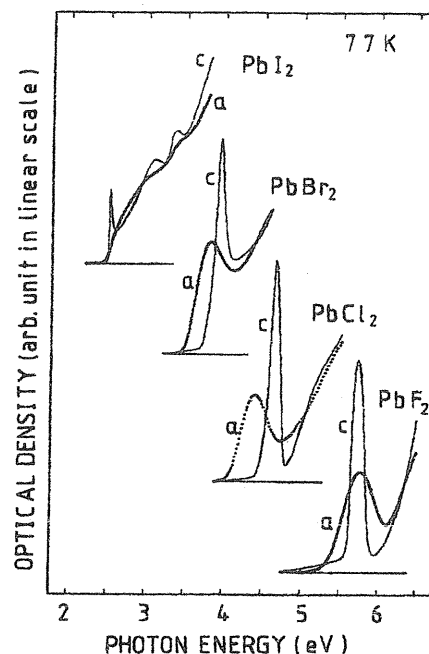


Fig. 3. Absorption spectra at 77 K near the fundamental edge of amorphous (curves a) and crystalline (curves c) films of PbX₂ (X = I, Br, Cl, F).

preparing the amorphous films are given, for example, in Ref. [11].

In TlX (Fig. 1) the spectra of the crystallized films have the features characteristic of orthorhombic TlI [4] for X = I and of sc (simple cubic) TlBr [5] and TlCl [5] for X = Br and Cl, respectively, all exhibiting the sharp direct-band-gap exciton peaks of the Wannier type. (Novel spectra measured on sc [18] or fcc [19] TlI and fcc TlBr and TlCl [20] are also reported in the literature). The figure demonstrates that these exciton peaks disappear when the compounds are amorphized. Further, the amorphization accompanies a considerable blue-shift of optical energy gap for TlBr and TlCl, both by about 0.5 eV.

The Wannier-exciton peaks of the crystallized (into slightly distorted perovskite structure) CsPbX₃ films (Fig. 2) are very sharp in feature. The full width at half maximum (FWHM) of the peaks is about 15 meV for both X = Br and Cl, which is much smaller than that observed for the "improved" films in [21] (where the FWHM at 77 K are of the order of 30 meV for both compounds), suggesting that the process of amorphization and subsequent heat treatment (annealing) is favorable for achieving high-quality polycrystalline films free from strains and/or lattice defects (this is particularly the case for CsPbCl₃ as seen from its very sharp exciton resonance). On the other hand, the amorphous films are characterized by the missing exciton peaks and the strongly reduced optical densities with the largely blue-shifted optical energy gaps by about 1 eV for both X = Br and Cl.

Spectral behavior in the amorphous versus crystalline states is somewhat different for PbX_2 (Fig. 3). Although, in PbI_2 , the Wannier-exciton peak, which is observed for the crystallized (into a layered structure) film, is missing in the amorphous film like in the cases of TlX and CsPbX_3 , the amorphous films of PbBr_2 , PbCl_2 and PbF_2 are characterized by the first absorption bands appearing as "amorphous counterparts" of the Frenkel-exciton peaks of the respective crystallized (into an orthorhombic structure) films.

3. Discussion

As demonstrated in Section 2, the cationic exciton absorption occurring on the $6s^2$ -ion sublattice ceases to occur by amorphization for the case of the Wannier exciton, while for the Frenkel exciton, amorphization leaves behind an alternative peak, the amorphous counterpart, in the absorption spectra of the compounds.

We have shown in Ref. [13] that in CsPbX_3 ($X = \text{Br}, \text{Cl}$) a considerable number of the one-electron states near the band edges, i.e. the $6s$ -like valence and $6p$ -like conduction states, are localized by amorphization. Since the Wannier exciton is a coupled effective mass state of valence (hole) and conduction (electron) states, the localization of the one-electron states is considered to make the Wannier exciton state unable to be formed in the amorphous CsPbX_3 . The missing exciton absorption in the amorphous state of TlX ($X = \text{I}, \text{Br}, \text{Cl}$) and PbI_2 may also be attributed to localization of the associated one-electron states. On the other hand, the Frenkel exciton for PbX_2 ($X = \text{Br}, \text{Cl}, \text{F}$) is basically an excitation of a single Pb^{2+} ion, which moves from ion to ion on the Pb^{2+} -ion sublattice. Such an excited state of the Pb^{2+} ion is also possible to occur in the amorphous PbX_2 , though it can no longer move. This corresponds to the amorphous counterpart of the exciton state.

It is interesting to note the fact that, as seen from Figs. 1–3, the first bands of both amorphous TlX and CsPbX_3 are very close in energy location to those (amorphous counterparts) of amorphous PbX_2 (such comparison is available for $X = \text{Br}$ and Cl), i.e. 4.3 and 4.4 eV for amorphous TlCl and CsPbCl_3 , respectively, as compared with 4.4 eV for amorphous PbCl_2 , and 3.9 eV for both amorphous TlBr and CsPbBr_3 , as compared with 3.7 eV for amorphous PbBr_2 . It is also noted that the optical energy gaps in the amorphous state are nearly the same for the three compounds (with the same X), i.e. 3.8, 3.9 and 4.0 eV for amorphous TlCl , CsPbCl_3 and PbCl_2 , respectively, and 3.4 eV for all the three amorphous bromides. These facts strongly suggest that the first bands of amorphous TlX , CsPbX_3 and PbX_2 are all of a nature of the same origin. In fact, the first band of amorphous CsPbX_3 has been assigned as due to localized Pb^{2+} -ion excitation (spin-orbit allowed transition to $^3\text{P}_1$ state, or transition from $6s$ to $6p_{1/2}$ states [13]). Therefore, it can be said that the $6s$ to $6p_{1/2}$ promotion energy is nearly the same for the three $6s^2$ ions embedded in the

different amorphous surroundings (but with the same nearest-neighbor halogen ion), leading to nearly the same energy location of the first band as well as nearly the same optical energy gap. The somewhat blue-shifted Frenkel-exciton peak compared to the amorphous-phase first band for PbX_2 is considered to be caused by the reduction of Coulomb and exchange interactions between the $6p_{1/2}$ electron and the $6s$ hole, since the electron and the hole have instantaneous opportunity to be more or less distant in position from each other in the exciton state.

Finally, we note that the common feature of the electronic states related to the $6s^2$ ion in the amorphous state disappears when they merge into extended states by crystallization. Their energetic dispersion in the Brillouin zone gives rise to band gaps smaller or larger than the amorphous-state optical energy gaps in the way strongly dependent on the resulting crystal structure probably due to a long-range nature of the ionic potential in the crystal. This is in great contrast to the case of covalent semiconductors, where the gross feature of the one-electron states is determined by the short-range order and is not largely dependent on the long-range order (therefore, both the amorphous and crystalline states exhibit nearly the same density-of-states function).

4. Conclusion

We have compared the absorption spectra near the fundamental edge of the amorphous and crystalline states of metal halides containing $6s^2$ cations (Tl^+ , Pb^{2+}) as a constituent, in order to investigate the effect of amorphization on the Wannier- and Frenkel-exciton transitions, both originating from $6s \rightarrow 6p$ transitions. By amorphization the Wannier-exciton peak disappears, whereas an alternative peak appears as an amorphous counterpart for the Frenkel exciton. The amorphous counterpart corresponds to a particular case of the localized $6s^2$ -ion excitation, which is commonly observed as the first band for all the amorphous states of the metal halides investigated.

Acknowledgements

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References

- [1] M.H. Cohen, in: D. Adler, B.B. Schwartz, M.C. Steele (Eds.), *Physical Properties of Amorphous Materials*, Plenum Press, New York, 1985, p. 343.
- [2] N.F. Mott, E.A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1979, p. 416.
- [3] J.H. Slowik, *Phys. Rev. B* 10 (1974) 416.

- [4] N. Ohno, K. Nakamura, Y. Nakai, J. Phys. Soc. Jpn. 55 (1986) 3659.
- [5] R.Z. Bachrach, F.G. Brown, Phys. Rev. B 1 (1970) 818.
- [6] I.P. Pashuk, N.S. Pidzyraido, M.G. Matsko, Soviet Phys.—Solid State 23 (1981) 1263.
- [7] I.Ch. Schlüter, M. Schlüter, Phys. Rev. B 9 (1974) 1652.
- [8] M. Fujita, M. Itoh, H. Nakagawa, M. Kitauro, D.L. Alov, J. Phys. Soc. Jpn. 67 (1998) 3320.
- [9] M. Fujita, H. Nakagawa, K. Fukui, H. Matsumoto, T. Miyanaga, M. Watanabe, J. Phys. Soc. Jpn. 60 (1991) 4393.
- [10] S. Kondo, M. Nakano, J. Phys. Soc. Jpn. 61 (1992) 3819.
- [11] S. Kondo, T. Itoh, T. Saito, M. Mekata, J. Phys. Soc. Jpn. 60 (1991) 2764.
- [12] S. Kondo, T. Itoh, T. Saito, M. Mekata, Solid State Commun. 78 (1991) 557.
- [13] S. Kondo, T. Sakai, H. Tanaka, T. Saito, Phys. Rev. B 58 (1998) 11401.
- [14] S. Kondo, M. Shiraki, T. Saito, Jpn. J. Appl. Phys. Part 1 31 (1992) 3399.
- [15] S. Kondo, T. Arakawa, T. Saito, Jpn. J. Appl. Phys. Part 1 32 (1993) 4611.
- [16] S. Kondo, H. Maruyama, T. Saito, Phys. Status Solidi A 147 (1995) 453.
- [17] S. Kondo, M. Itoh, T. Saito, Phys. Status Solidi A 154 (1996) 591.
- [18] A. Fujii, K. Takiyama, J. Nakahara, K. Kobayashi, J. Phys. Soc. Jpn. 42 (1977) 525.
- [19] K. Heidrich, W. Staude, J. Treusch, Solid State Commun. 16 (1975) 1043.
- [20] K. Heidrich, W. Staude, J. Treusch, Phys. Rev. Lett. 33 (1974) 1220.
- [21] D. Fröhlich, K. Heidrich, H. Künzel, B. Trendel, J. Treusch, J. Lum. 18/19 (1979) 385.