

OPTICAL AND DIELECTRIC PROPERTIES OF MIXED LEAD HALIDES $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$

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Abstract : The determination of the static dielectric constant ϵ_s at low frequencies of the mixed lead halides $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$ vs. the composition x shows the existence of a discontinuity for the equimolar composition. A discontinuity is also observed for the same composition for the shift of the energetic position of the first excitonic reflectivity peak.

This discontinuity is interpreted in terms of the anionic substitution.

INTRODUCTION

The XRD studies¹ of the structure of mixed lead halides $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$ exhibit a discontinuity of the lattice parameters and the cell volume for the equimolar composition (PbClBr) : we observe two linear variations on both sides of this composition. This discontinuity can be explained by the preferential site occupancy also revealed by the XRD experiments.

Phase relationships in the system $\text{PbCl}_2\text{-PbBr}_2$

have been reported some time ago^{2,7} : complete mutual solid solubility exists in this system. All the solid solutions^{1,2,3} adopt the PbCl_2 -type orthorhombic symmetry, in which two non equivalent anion sites can be discerned. XRD experiments¹ show preferential site occupancy : an anion site (II) can accomodate larger ions than anion site (I). The anion array of the equimolar composition PbClBr is completely ordered with Cl in site (I) and Br in site (II). The same situation persists for the sites (I) when $0.5 < x < 1$ and for the sites (II) when $0 < x < 0.5$.

This preferential substitution involves a discontinuity of the physical properties for the equimolar composition, observed particularly in the study of the electric properties (ionic conductivity obtained by impedance diagram)^{4,5,6} and the thermodynamical properties (specific heat)⁷.

The aim of this paper is to show the existence of this discontinuity in the study of both the static dielectric constant and the optical reflexion.

EXPERIMENTAL

The Bridgman technique has been utilized to grow a variety of $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$ crystals. A full account of the employed starting materials and crystal growth conditions has been reported before^{1,6}. Microprobe analyses revealed the actual compositions to be close to the compositions of the starting mixtures. Here actual compositions are used. After cleaving the crystals perpendicular to the crystallographic b-axis, they were oriented by Laue diffraction, and subsequently cut along the a- and the c-axis. Surfaces were polished to optical finish. Sample surfaces were typically 0.1 to 0.3 cm², and sample thicknesses about 0.1 cm. For the electrical measurements graphite dag was

applied to sample surfaces as electrode contact material. The samples were placed between the platinum disk electrodes of a metal conductivity cell provided with resistive heating. As working atmosphere circulating purified nitrogen or argon was used. For the optical measurements, the wave vector q of the incident light was set parallel to the b -axis, and the polarization vector E parallel to a or c .

DIELECTRIC CONSTANT MEASUREMENTS

The determination of the static dielectric constant at low frequencies, for each composition and for each cristallographic axis, has been obtained from a Hewlett Packard impedance analyser (model 4192 A ; 5 Hz - 13 MHz) and a Solartron frequency response analyser (model 1172 ; 0.1 Hz - 10 kHz and model 1250 ; 10^{-2} Hz - 65 kHz).

The a.c. response^{4,5,6} data (impedance) in the complex plane is composed of several semi-circles. The high frequency semi-circle is the only one independent of the nature of the electrode and, therefore, it is representative of the bulk phenomena of the cristal.

The figure 1 presents the ϵ_s variation vs. the composition at $T = 553$ K, deduced from the a.c. response data measured along the b -axis.

In a first time, if we take into account the incertitude of the measurements, we can say that the value of the static dielectric constant ϵ_s , for the three ordered compound ($x=0, 0.5, 1$) is

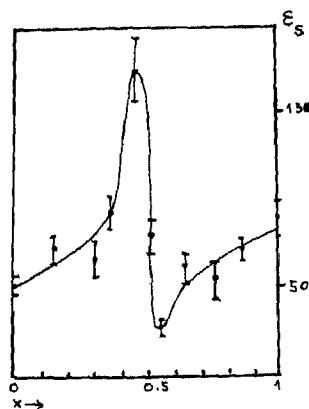


Figure 1 Static dielectric constant ϵ_s vs. composition

almost the same (50 to 75).

Moreover this value is very high for a solid.

For the intermediate compositions, we obtain two increasing variations in the two domains of substitution ($0 < x < 0.5$ and $0.5 < x < 1$), while the value of ϵ_s falls suddenly from 200 to 30 between these domains, on both sides of the equimolar composition.

This result can be attributed to an additional polarization due to the disorder induced by the substitution Cl/Br and Br/Cl (two anions of different sizes and polarizabilities) in each family of composition.

OPTICAL PROPERTIES

The reflectance spectra of single crystals of PbCl_2 and PbBr_2 exhibit at low temperatures several peaks which have been attributed to Frenkel excitons localized on the lead ion^{9,10,11,12}. Similarly, the first low energy peak observed in the reflectance spectra of single crystals of $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$ has recently been interpreted in the same terms¹³. Therefore, the energetical position of the peak is directly correlated to the mechanism of the anionic substitution Cl/Br.

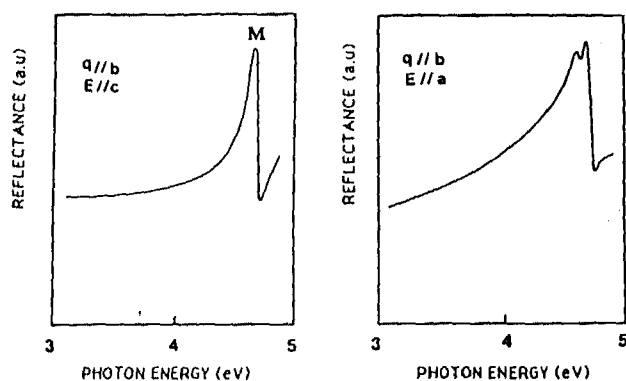


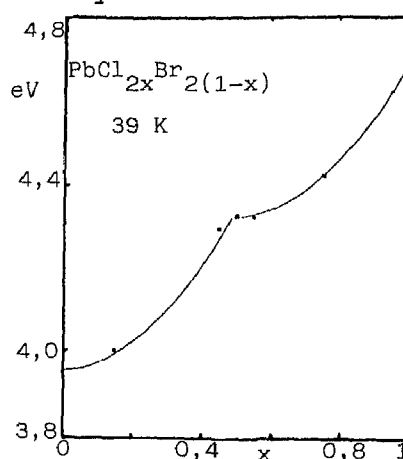
Figure 2 Reflectance spectra of single crystals of PbCl_2 at 39 K

The spectra under near-normal incidence are recorded by comparing the reflectivity of the sample to the one of a front metallic mirror.

For instance, the reflectivity spectrum of PbCl_2 measured at 39 K between 3.5 and 4.8 eV on a freshly cleaved surface is shown in figure 2. The spectrum displays a reflectivity maximum M at 4.69 eV followed by a minimum on the high energy side for the geometry q parallel to b and E parallel to c . This line shape is characteristic of an anomaly of reflectivity. However, we note that the maximum M is splitted in the other configuration q parallel to b and E parallel to a . The separation between the two maxima is about 74 meV. This splitting may be interpreted according to the lifting of the degeneracy of the excitonic state by the crystal field of Pb_2 ion.

The reflectance spectra of the other two more ordered compounds PbClBr and PbBr_2 are similar to that of PbCl_2 , whereas for the values of x equal or around 0.25 and 0.75 a single anomaly of reflectivity is only seen in both polarizations. In this last case, the line widths are broadened. Indeed the mixed lead halides crystals $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$ are isomorphic solid solutions and the symmetry C_s of the cationic site is only maintained for $x=0$, 0.5 and 1.

Figure 3 Composition dependence of the main reflectivity peak M ($q//b$, $E//c$) associated with the first exciton state for single crystals of $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$



The energy positions E (eV) of the reflectivity maximum M are plotted as a function of composition x in figure 3. The experimental data are fitted by the following equations :

for $0 \leq x \leq 0.5$

$$E(x) = 3.9572 + 0.00224x + 1.5009x^2 \text{ (eV)}$$

and for $0.5 \leq x \leq 1$

$$E(x) = 4.6188 - 1.25145x + 1.3229x^2 \text{ (eV)}$$

These two different relations show clearly the discontinuity in the composition range of the mixed lead halides solid solutions for $x=0.5$.

CONCLUSION

The determination of the static dielectric constant ϵ_s and the study of the reflectance spectra of the mixed lead halides $\text{PbCl}_{2x}\text{Br}_{2(1-x)}$ versus x confirm the existence of a discontinuity for the equimolar composition.

The mutual solid solubility of these compounds taking into account the preferential site occupancy, must be understood in terms of two families : one for the system $\text{PbBr}_2\text{-PbClBr}$ and another one for the system PbClBr-PbCl_2 .

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