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STRUCTURE AND IONIC CONDUCTIVITY OF MIXED LEAD HALIDES $PbCl_{2x}Br_{2(1-x)}$. I.

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$PbCl_2$ and $PbBr_2$ show complete mutual solid solubility. The solid solutions $PbCl_{2x}Br_{2(1-x)}$ exhibit the $PbCl_2$-type orthorhombic symmetry. XRD measurements show preferential site occupancy. The ionic conductivity has been measured as a function of temperature and composition. The ionic conductivity of PbClBr in which the anion array is completely ordered, is slightly anisotropic. Homovalent anion doping causes the conductivity to decrease. The role of preferential site occupancy, and dopant induced lattice distortions on the number and mobility of the conducting defects is discussed.

1. INTRODUCTION

Phase relationships in the system $PbCl_2$-$PbBr_2$ have been reported some time ago (1,2). More recently, phase relationships in the systems $BaCl_2$-$BaBr_2$ (3), and PbX_2-PbI_2 (X = Cl,Br) (4) have been described in the literature. All the systems exhibit $PbCl_2$-type orthorhombic symmetry, but over different composition ranges.
Complete mutual solid solubility exists in the systems $BaCl_2$-$BaBr_2$, and $PbCl_2$-$PbBr_2$. In all the systems compositions occur which show anion ordering effects due to the size disparity between the different anions.
All the binary end members exhibit anion conductivity via a vacancy mechanism, and recently it has been shown by the present authors that preferential site occupancy and anion ordering effects decrease the electrical conductivity of solid solutions in the system $PbCl_2$-$PbBr_2$ (5). Homovalent ion doping induces substantial conductivity increases in several cation conducting Schottky or Frenkel type solid solutions based on alkali halides (6), respectively, silver halides (7,8).

In this paper we present for the solid solutions in the system $PbCl_2$-$PbBr_2$ quantitative information regarding structural and electrical properties in relation to the homovalent anion doping, and the anion distribution.

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2. EXPERIMENTAL ASPECTS

The preparation of the single crystals has been published elsewhere (5). The XRD measurements were taken on a CAD 4 ENRAF-NONIUS automatic diffractometer using CuKα or AgKα radiation from graphite monochromator. After absorption, following the empirical method proposed by Walker and Stuart (9) and Lorentz polarization corrections, all data were refined using a least-squares procedure (Shelx program) giving the complete matrix, anisotropic thermal vibration parameters, and site occupancy ratio. The temperature and composition dependence of the ionic conductivity of the solid solutions were studied by impedance spectroscopy using an automatic capacitance bridge (GR1680A), and a Solartron 1172 Frequency Response Analyser. Graphite dag was used as an electrode contact material.

3. RESULTS

The $PbCl_2$-type structure is observed throughout the entire system $PbCl_2$-$PbBr_2$. In this structure all the atoms occupy the fourfold special positions 4(c) of the space group D_{2h}^{16}-P_{nam}: they lie on a mirror plane, perpendicular to the short c-axis at z = ± 1/4. There are two non-equivalent anion sites in the $PbCl_2$-type structure. Anion site 2 can accommodate larger ions than anion site 1 (Figure 1).

The variation of the lattice parameters and cell volume versus the compositional parameter x has been reported (5).

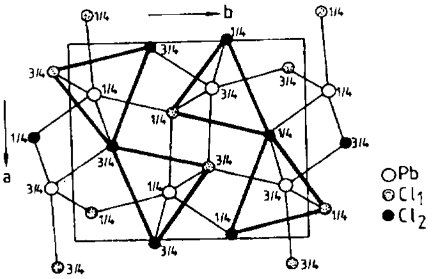

Figure 1. c-axis projection of the $PbCl_2$ structure.

The fractional atomic coordinates, site occupancy factor, and isotropic thermal parameters for these solid solutions will be reported in detail in part II (10).

The variations of the shortest interatomic distances with composition are given in Figure 2.

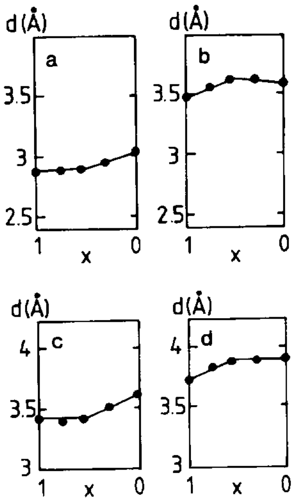

Figure 2: Variation of the shortest interatomic distances with composition.

a. $Pb-Cl_1$
b. $Pb-Cl_2$
c. Cl_1-Cl_1
d. Cl_2-Cl_2

The temperature and composition dependence of the ionic conductivity of several $PbCl_{2x}Br_{2(1-x)}$ crystals is presented in Figure 3.

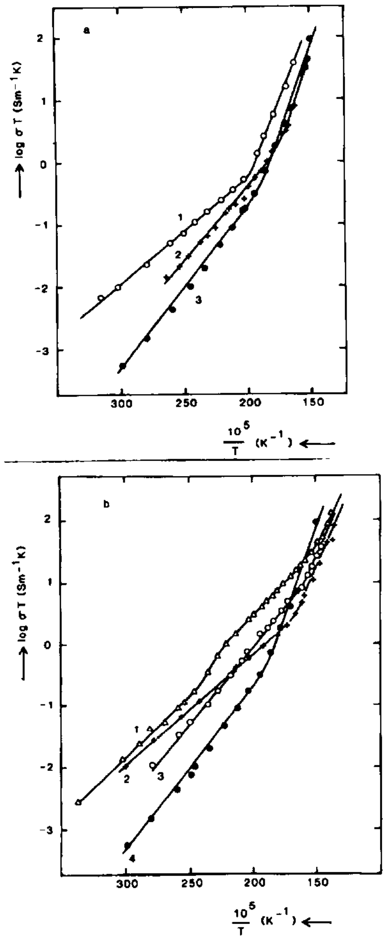

Figure 3: The ionic conductivity of $PbCl_{2x}Br_{2(1-x)}$ crystals measured along the b-axis.

a. x = 0(1), x = 0.3(2),
x = 0.5(3)
b. x = 0.75(1), x = 0.95(2),
x = 0.64(3), x = 0.5(4).

The composition dependence of the formation enthalpy and migration enthalpy is given in Figure 4. Details of the data analysis have been reported before (5).

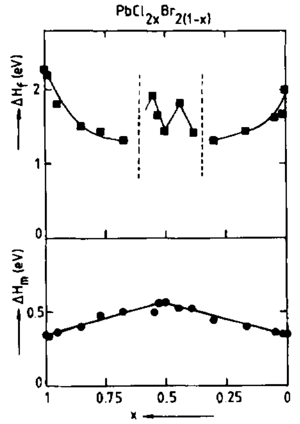

Figure 4: Variation of the formation enthalpy ΔH_f of Schottky defects, and migration enthalpy ΔH_m of anion vacancies in $PbCl_{2x}Br_{2(1-x)}$ with composition.

The ionic conductivity data reveal the conductivity of the equimolecular compound to be slightly anisotropic. In this ordered compound Cl^- ions occupy sites 1 and Br^- ions sites 2.(Figure 5)

DISCUSSION

All solid solutions adopt the orthorhombic $PbCl_2$ structure in which two anion sites can be discerned. Preferential anion site occupancy occurs. For $x > 0.5$ sites 1 remain completely occupied by Cl^- ions, while anion sites 2 are occupied by Cl^- and Br^- ions. The reversed situation is observed in solid solutions with $x < 0.5$. Here the anion sites 1 are occupied by Cl^- and Br^- ions, while

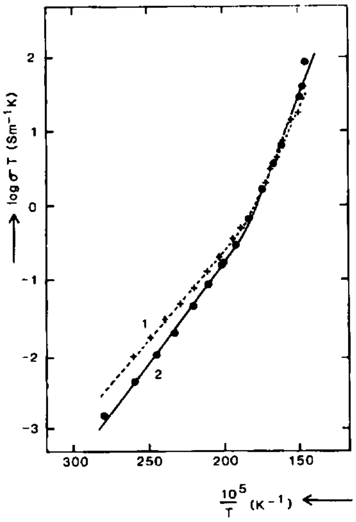

Figure 5: Temperature dependence of the ionic conductivity of PbClBr along the a-axis(1) and b-axis(2).

sites 2 remain occupied with Br^- ions. In the ordered array of the equimolecular composition sites 1 are occupied by Cl^-, and sites 2 by Br^- ions. These results are concordant with a structure in which site 2 can accommodate larger anions than site 1.

Conductivity isotherms reveal the ionic conductivity in the extrinsic region to decrease with increasing solute content. A minimum occurs around the equimolecular composition PbClBr. The intrinsic conductivity decreases in the sequence $PbBr_2 \rightarrow PbClBr \rightarrow PbCl_2$.

In the present solid solutions the anion vacancy migration enthalpy increases with increasing solute content, while the extrinsic conductivity isotherms reveal a minimum. Apart from several compositions around the equimolecular composition PbClBr, the defect formation enthalpy decreases with increasing solute content. The question, therefore, arises as to whether enhanced defect densities, or modified defect mobilities need to be taken into account. The anion vacancy mobility in the undoped end members reveal roughly $\mu_{V^\bullet_{Br}} \approx 10\ \mu_{V^\bullet_{Cl}}$ from room temperature up to about 630 K (11, 12). In the intrinsic region σ ($PbBr_2$) > σ (PbClBr) > σ ($PbCl_2$) with $\sigma(PbBr_2) \approx 10\ \sigma$ ($PbCl_2$). This implies that the defect densities in the pure end members are roughly equal. With regard to the minimum in the extrinsic conductivity isotherm, we must assume reduced defect mobilities to occur in the solid solutions, and hence slightly enhanced thermal defect densities. In addition, it seems likely that due to size disparity effects, and the local lattice distortions jumps represented by

$$Br^x_{Cl,1} + V^\bullet_{Cl,2} \rightarrow V^\bullet_{Cl,1} + Br_{Cl,2} \text{ and}$$

$$Cl^x_{Br,1} + V^\bullet_{Br,2} \rightarrow V^\bullet_{Br,1} + Cl^x_{Br,2} \text{ need}$$

not be taken into account.

Together with the preferential site occupancy, this may imply that preferential conduction pathways will develop with increasing solute content. This can be illustrated for the equimolecular compound PbClBr in which Br^- ions occupy sites 2, and Cl^- ions sites 1. By inspection of Figure 1, and ignoring for simplicity Cl^--Br^- ion exchange, one can envisage a continuous conduction pathway for Br^- ions along the a-axis. This would be concordant with σ (// a-axis) > σ (// b-axis) as found experimentally. Therefore, with increasing solute content the solute ions will be present more and more as pairs, and also in ordered PbClBr-type domains. It has been suggested before (7) that strain fields of pairs and domains may well produce effects on ΔH_f which differ from isolated solute ion effects. This may very well be the cause of the anomalous dependence of ΔH_f on x in the region $\sim 0.3 < x < \sim 0.7$. (viz. Figure 4). A detailed quantitative explanation of this anomalous behaviour has to await transference number data for chloride (t_{Cl}), and bromide ions (t_{Br}) as a function of composition. Such experiments are currently being undertaken.

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