

## CRYSTAL GROWTH AND CHARACTERIZATION OF MIXED LEAD HALIDES $PbCl_{2x}Br_{2(1-x)}$

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Single crystals of  $PbCl_2$ -type solid solutions  $PbCl_{2x}Br_{2(1-x)}$  have been grown using the Bridgeman technique. XRD measurements reveal preferential site occupancy for Cl and Br, while the anion array of  $PbClBr$  is completely ordered. The temperature and composition dependence of the ionic conductivity of the solid solution crystals have been studied. While cation conducting Schottky- or Frenkel-type solid solutions obtained by homovalent anion doping reveal substantial conductivity enhancements, the present anion conducting Schottky-type solid solutions exhibit the opposite effect. This will be discussed in relation to the ordering effects, and homovalent dopant induced lattice distortions on the number and mobility of the conducting defects.

### 1. INTRODUCTION

Lead chloride and lead bromide exhibit Schottky disorder, and anion conductivity (1-4). Their optical, photochemical, photoelectrical, and electrical properties have been described, but little formation is available for the mixed lead halides. Lead chloride and lead bromide show complete mutual solid solubility (5). The solid solutions in the system  $PbCl_2$ - $PbBr_2$  evidence  $PbCl_2$ -type orthorhombic symmetry (5,6).

The present study was undertaken to elucidate relations between structural, optical and electrical properties of single crystals of solid solutions in the system  $PbCl_2$ - $PbBr_2$ .

Usually cation conducting Schottky or Frenkel-type solid solutions obtained by homovalent anion doping reveal substantial conductivity

enhancements, e.g.  $KCl_xBr_{1-x}$  (7),  $AgCl_xBr_{1-x}$  (8), and  $AgBr_xI_{1-x}$  (9). The present solid solutions differ in that they exhibit anion conductivity. In this paper we report structural and electrical properties in relation to the homovalent anion doping.

### 2. EXPERIMENTAL ASPECTS

Single crystals of  $PbCl_{2x}Br_{2(1-x)}$  ( $0 \leq x \leq 1$ ) were grown by the Bridgeman technique using zone-refined  $PbBr_2$  (10) and  $PbCl_2$  (11). Before crystal growth, appropriate proportions of the reactants were pre-melted in a bromide ambient. Chemical compositions were obtained from microprobe analysis (Camebax) with pure  $PbCl_2$  and  $PbBr_2$  as reference. To avoid evaporation of chlorine and bromine from the sample the X-ray

beam was defocussed on a  $5\mu \times 5\mu$  squared surface. The wave lengths used are:

$$\lambda_{K\alpha_1 Cl} = 4.7278\text{\AA}$$

$$\lambda_{L\alpha_1 Br} = 8.3746\text{\AA}$$

$$\lambda_{M\alpha_1 Pb} = 5.286\text{\AA}$$

XRD measurements were taken on a CAD4 Enraf-Nonius automatic diffractometer using  $CuK_{\alpha}$  radiation from graphite monochromator. 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 Analyzer. Graphite-dag was employed as electrode contact material. An ambient of dry oxygen-free nitrogen was used. Purification was achieved with a BTS (BASF) catalyst, and a molecular sieve trap (Union Carbide).

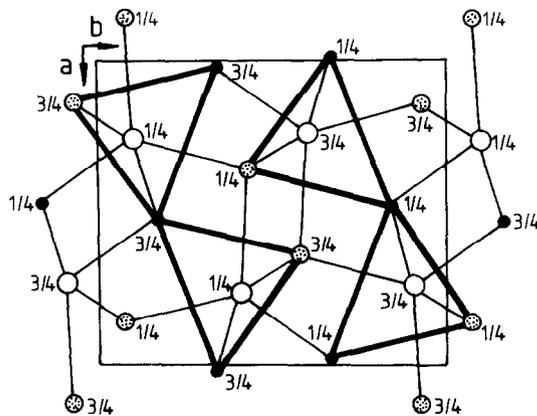
3. RESULTS

Microprobe analysis results are gathered in Table 1. The data reveal the actual compositions to be close to the composition of the reactant mixtures. XRD measurements reveal the solid solutions to have the  $PbCl_2$ -type structure (6,13). In this structure all atoms occupy the fourfold special positions (4c) of the space group  $D_{2h}^{16}P_{nam}$ : they lie on mirror planes, perpendicular to the short c-axis at  $z = \pm \frac{1}{4}$ . There are two non-equivalent sites in the anion array (12,13). Fig. 1 presents a c-axis projection of the unit cell of  $PbCl_2$ .

The variation of the lattice parameters and cell volumes with composition is presented in Fig. 2. These results are concordant with literature data reported for  $PbCl_2$ -type solid solutions in the system  $BaCl_2$ - $BaBr_2$ . In this system anion ordering occurs(14). In the present system the more pronounced discontinuity of the lattice in the b and c direction can be under-

TABLE 1  
Compositions of the  $PbCl_{2x}Br_{2(1-x)}$  crystals

COMPOSITION OF STARTING MIXTURES (%)		COMPOSITION OF SINGLE CRYSTALS (%)	
Cl	Br	Cl	Br
100	0	-	-
99	1	99.05	0.95
95	5	94.72	5.27
85	15	84.45	15.55
75	25	75.99	23.98
55	45	55.44	44.56
50	50	53.63	46.37
45	55	44.42	55.58
27	73	30.07	69.93
15	85	16.68	83.32
5	95	5.16	94.84
1	99	1.52	98.48
0	100	-	-



○ Pb  
⊙ Cl(1)  
● Cl(2)

FIGURE 1  
The c-axis projection of the  $PbCl_2$  structure

stood in terms of preferential occupancy of anion sites.

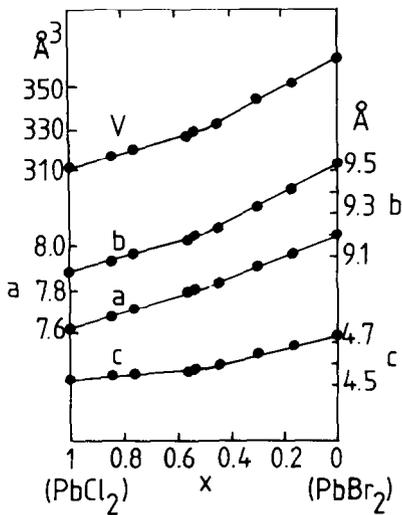


FIGURE 2

Lattice parameters and cell volumes of  $PbCl_{2x}Br_{2(1-x)}$  crystals

Preliminary results confirm anion ordering to occur also in the present solid solutions. In  $PbCl_{1.46}Br_{0.54}$  anion sites (1) are occupied by chloride ions, while anion sites (2) are occupied by chloride and bromide ions. The reverse situation is observed in  $PbCl_{0.5}Br_{1.5}$ . Here anion sites (1) are occupied by chloride and bromide ions. In this solid solution anion site (2) is occupied by a bromide ion. In  $PbClBr$  anion site (1) is occupied by a chloride ion, and anion site (2) by a bromide ion, indicating a completely ordered structure. The temperature and composition dependence of the bulk ionic conductivity of several  $PbCl_{2x}Br_{2(1-x)}$  crystals is presented in Figures 3 and 4. The conductivity values are reproducible on thermal cycling. The conductivity isotherms in the extrinsic region reveal the ionic conductivity of the solid solutions to decrease with increasing solute content. A minimum occurs around the equimolecular composition  $PbClBr$ . If we assume Schottky disorder to also prevail in the solid solutions, and the chloride ion vacancy  $V_{Cl}^{\cdot}$  to be the mobile species

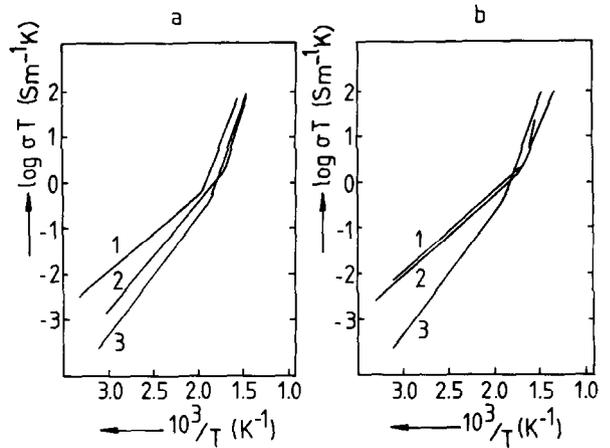


FIGURE 3

Temperature dependence of the ionic conductivity of  $PbCl_{2x}Br_{2(1-x)}$  crystals

3-a. x=0 (1), x=0.3 (2), x=0.5 (3)  
 3-b. x=0.95 (1), x=1 (2), x=0.5 (3)

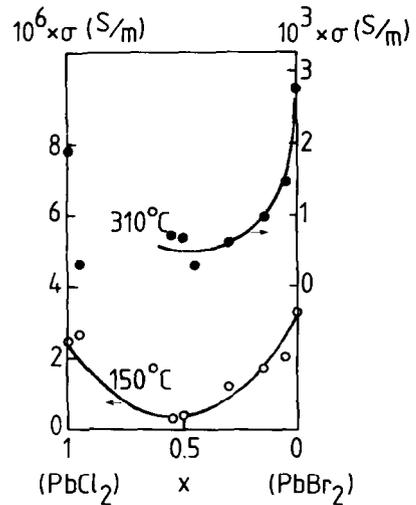


FIGURE 4

Conductivity isotherms of  $PbCl_{2x}Br_{2(1-x)}$  crystals

in  $PbCl_{2x}Br_{2(1-x)}$  for  $x > 0.5$ , and the bromide ion vacancy  $V_{Br}^{\cdot}$  the mobile species for  $x < 0.5$ .

the intrinsic conductivity region can be analysed to yield  $\Delta H_f/3$ . If anion vacancies are distributed over  $Cl_{Cl}^X$  and  $Br_{Cl}^X$  sites, or  $Br_{Br}^X$  and  $Cl_{Br}^X$  sites the intrinsic region also yields  $\Delta H_f/3$ . The composition dependence of the formation enthalpy  $\Delta H_f$ , and migration enthalpy  $\Delta H_m$  is given in Figure 5.

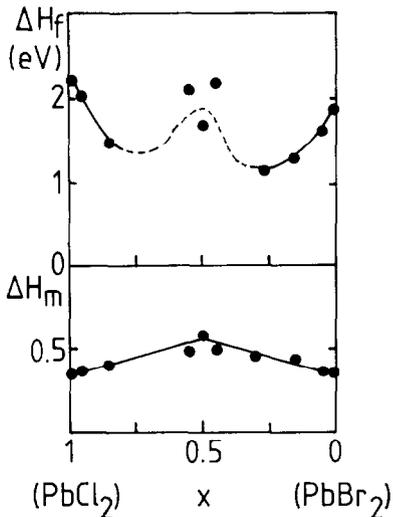


FIGURE 5

Variation of the formation and migration enthalpy of Schottky defects in  $PbCl_{2x}Br_{2(1-x)}$  crystals vs. composition

#### 4. DISCUSSION

Optically clear single crystals of the solid solutions  $PbCl_{2x}Br_{2(1-x)}$  can be grown with the Bridgeman technique. Close agreement between initial and final composition is found. The reported data here are based on the actual compositions. Usually cation conducting Schottky or Frenkel-type solid solutions obtained by homovalent anion doping reveal substantial conductivity enhancements, e.g.  $KCl_xBr_{1-x}$  and  $AgCl_xBr_{1-x}$ . In addition, a decrease in the melting point is observed. The host lattice of these solid solutions is subject to strain of a

magnitude dependent on  $1 - \frac{r_{Cl}}{r_{Br}}$ . The main factor for the enhancements in ionic conductivity, and the decrease in melting point are elastic displacements, due to the difference in anion size, i.e.  $r_{Br} > r_{Cl}$ . It appears that the present anion conducting Schottky-type solid solutions exhibit the opposite behaviour. The thermal diagram of the  $PbCl_2$ - $PbBr_2$  system is linear. For Schottky-type solid electrolytes a linear correlation exists between defect formation enthalpy and melting point, i.e.

$$\Delta H_f(\text{eV}) = 2.14 \times 10^{-3} T_m(\text{K}).$$

Hence, a linear composition dependence of the formation enthalpy is to be expected in contrast to experimental observation. Similar elastic displacements occur in the present  $PbCl_2$ -type solid solutions. However, these solid solutions are different in that the mobile species constitute anion vacancies. In addition to elastic displacements homovalent anion doping will introduce sites in the anion array, which will not easily exchange with anion vacancies. This effect, and a strain-induced modification of the anion vacancy mobility will lower the ionic conductivity.  $PbClBr$  seems to adopt a completely ordered  $PbCl_2$ -type structure. Low ionic conductivity values, and a large migration enthalpy are then to be expected<sup>(15)</sup>.

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