STRUCTURE AND IONIC CONDUCTIVITY OF MIXED LEAD HALIDES
PbCl$_{2x}$Br$_2$(1-x). I.

M. LUMBERGAS
C.I.O.E.S., Laboratoire de Génie Physique, Université de Metz,
57045 Metz Cedex 1, France.

J. PROTAS, S. JEBBARI
Laboratoire de Cristallographie, Université de Nancy I,
P.O. Box 239, 54506 Vandoeuvre-les-Nancy, France.

G.J. DIRKSEN
Solid State Department, Utrecht University, P.O. Box 80.000,
3508 T.A. Utrecht, The Netherlands.

J. SCHOONMAN
Laboratory of Inorganic and Physical Chemistry, Delft University
of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands.

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.
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 (CH1680A), 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 $D_{2h}^{16}$ $P$nnm; they lie on a mirror plane, perpendicular to the short c-axis at $z = \pm 1/4$. 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.](image)

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.](image)

- 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](image)

**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](image)

**Figure 4:** Variation of the formation enthalpy $\Delta H_f$ of Schottky defects, and migration enthalpy $\Delta H_m$ 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
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 $\mu_{\text{Br}} \approx 10 \mu_{\text{Cl}}$ from room temperature up to about 630 K [11, 12]. In the intrinsic region $\sigma (\text{PbBr}_2) > \sigma (\text{PbClBr}) > \sigma (\text{PbCl}_2)$ with $\sigma (\text{PbBr}_2) \approx 10 \sigma (\text{PbCl}_2)$. 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

$$\text{Br}^X \rightarrow 1 + \text{V}^{-}_{\text{Cl}}, 2 \rightarrow \text{V}^{-}_{\text{Cl}}, 1 + \text{BrCl}, 2$$ and

$$\text{Cl}^X \rightarrow 1 + \text{V}_{\text{Br}}, 2 \rightarrow \text{V}_{\text{Br}}, 1 + \text{Cl}^X \rightarrow 2$$ 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 $\sigma (// a\text{-axis}) > \sigma (// b\text{-axis})$ 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 (1) that strain fields of pairs and domains may well produce effects on $\Delta H_f$ which differ from isolated solute ion effects. This may very well be the cause of the anomalous dependence of $\Delta H_f$ on $x$ in the region $0.3 < x < 0.7$. (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.

ACKNOWLEDGEMENTS

The authors are grateful to professor C. Carabatos, University of Metz, for critical discussions. One of the authors (M.L.) would like to thank professor G. Blasse, Utrecht University, for kind hospitality.

REFERENCES