Solid State Ionics 28–30 (1988) 1305–1309
North-Holland, Amsterdam

ELECTRICAL CONDUCTIVITY OF MIXED LEAD HALIDES $PbCl_{2x}Br_{2(1-x)}$

M. LUMBRERAS
C.L.O.E.S., Université de Metz, Supelec Technopole de Metz, 2, rue Edouard Belin, 57078 Metz Cedex 3, France

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

and

E.J.L. SCHOULER
Laboratoire du Ionique et d'Electrochemie du Solide, B.P. 75, 38402 St Martin d'Hères, France

Received 20 August 1987

The small signal ac response of $PbCl_{2x}Br_{2(1-x)}$ solid solution crystals has been studied as a function of temperature, crystallographic axes, and composition ($0 \leqslant x \leqslant 1$) over a wide range of frequencies. The frequency dispersion has been analysed using a computer program for non-linear least-squares fitting to complex data. The data can be fitted to one type of equivalent circuit for all crystallographic axes and studied temperatures. The composition and structural dependence of bulk ionic conductivity parameters have been analysed in detail. The intrinsic conductivity reveals the formation enthalpy of the Schottky defects to be orientation invariant. Transference number measurements indicate Br^- ions to be immobile in $PbCl_{1.98}Br_{0.02}$ and Cl^- ions to be mobile in $PbCl_{0.02}Br_{1.98}$.

1. Introduction

In a study of the ion dynamics of ternary lead halides $PbCl_{2x}Br_{2(1-x)}$ we have focussed attention on Raman spectroscopy and impedance spectroscopy. While the Raman study will be reported elsewhere [1], previous papers dealt with crystal growth, structural properties and ionic conductivity along the crystallographic *b*-axis [2]. A preliminary account of an impedance study on solid solution crystals along the *b*-axis has been presented only recently [3].

It is well established that $PbCl_2$ and $PbBr_2$ exhibit complete mutual solid solubility. The solid solution $PbCl_{2x}Br_{2(1-x)}$ show preferential site occupancy for Cl^- and Br^-, while the anion array of the equimolecular composition PbClBr is completely ordered [2]. As a result preferential conduction pathways develop in the solid solutions which lead to conduction anisotropy [2]. Schottky defects are assumed to predominate with anion vacancies constituting the more mobile species.

The present paper deals with small signal ac response measurements on single crystals of $PbCl_{2x}Br_{2(1-x)}$ in order to determine the anisotropy in the ionic conductivity parameters. Recorded immittance spectra were fitted to electrical equivalent circuits, comprising bulk and electrode interface phenomena.

In order to shed light on the conduction mechanism attempts have been made to measure transference numbers using PbX_2 ($X=Cl$, Br) as protective electrolytes.

2. Experimental aspects

2.1. Single crystals

The Bridgman technique has been utilized to grow a variety of $PbCl_{2x}Br_{2(1-x)}$ crystals. A full account of the employed starting materials and crystal growth

0 167-2738/88/$ 03.50

conditions has been reported before [1,2]. 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 cm^2, 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 [1].

2.2. Electrical measurements

Impedance or admittance spectra of the cells C|$PbCl_{2x}Br_{2(1-x)}$|C were investigated in the frequency region of 0.1 Hz to 13 MHz using a Hewlett Packard impedance analyser (model 4192A: 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).

Representative examples of the measurements have been analysed using a computer program for non-linear least-squares fitting to complex data. In the minimization procedure the method reported by Marquardt [4] was employed to fit simultaneously the real and imaginary parts of the recorded immittance data to appropriate equivalent circuits. Transference numbers were measured using the solid state electrolysis cell Pt|Y_1|Y_2|Y_3|Z_1|Z_2|Z_3|Y_4| |Y_5|Y_6|Pt where Y_i denotes a PbX_2 (X=Cl, Br, $t_X=1$) protective electrolyte crystal, and Z_i a solid solution crystal ($t_{Cl}+t_{Br}=1$) [5,6]. Usually currents of 0.4 to 0.5 mA were passed through the cell until about 10C of charge had been passed.

3. Results

The ac response data for the cells C|$PbCl_{2x}Br_{2(1-x)}$|C are presented in complex plane representations in which the imaginary part of the impedance or admittance is plotted against the real part. In the high-frequency domain, and for relatively low temperatures such impedance spectra comprise a semicircle which in several instances is slightly depressed. Fig. 1 presents impedance spectra at different temperatures for $PbCl_{1.36}Br_{0.64}$ (*a*-axis), and $PbCl_{0.37}Br_{1.63}$ (*c*-axis). These responses can be modelled with an equivalent circuit comprising a parallel (p) combination of a resistance and a capacitance, i.e. *R*Cp. Under the assumption that *R* represents the bulk ionic resistance (R_b) and *C* the high frequency geometric capacitance (C_g) the analysis of the temperature dependence of the resonance frequency $\omega_0[(R_bC_g)^{-1}=\sigma/\epsilon_0\epsilon_r$, where σ represents the specific ionic conductivity, ϵ_0 the permittivity of free space and ϵ_r the dielectric constant of the solid solution] leads to a value of the activation enthalpy similar to the conductivity activation enthalpy, thus confirming the high frequency response to be a bulk phenomenon [1].

Accurate R_b data have been obtained for all $PbCl_{2x}Br_{2(1-x)}$ solid solutions in all three crystallographic directions. The data, when presented in Arrhenius plots [2] of the temperature dependence of the ionic conductivity, yield thermodynamic parameters of the mobile species. Fig. 2 presents the composition dependence of the migration enthalpy along the *a*, *b* and *c*-axis as well as the composition dependence of the Schottky defect formation enthalpy. The composition dependence of the enthalpy of anion migration along the *a*-axis equals that along the *c*-axis. For migration along the *b*-axis the enthalpy increases starting from the binary compositions at $x=0$ and 1 to the equimolecular composition. As expected the formation enthalpy is invariant to the crystallographic direction. The scatter in the ΔH_f values is due partly to the scatter in the ΔH_m values because the intrinsic conductivity activation enthalpies represent $\frac{1}{2}\Delta H_f+\Delta H_m$. In addition, for *x* values in the range 0.3 to 0.7 intrinsic conductivity data could be obtained in only a limited temperature region.

At low and moderate frequencies (0.01 Hz–50 kHz) the immittance spectra reveal two depressed semicircles with overlapping relaxation times. All the spectra could be fitted to the equivalent circuit given in fig. 3. The impedance of the constant phase element *Q* is $Z_Q=k(i\omega)^{-\alpha}$. For Q_1, α values are about 0.5 indicating Q_1 to be a Warburg impedance. For Q_2

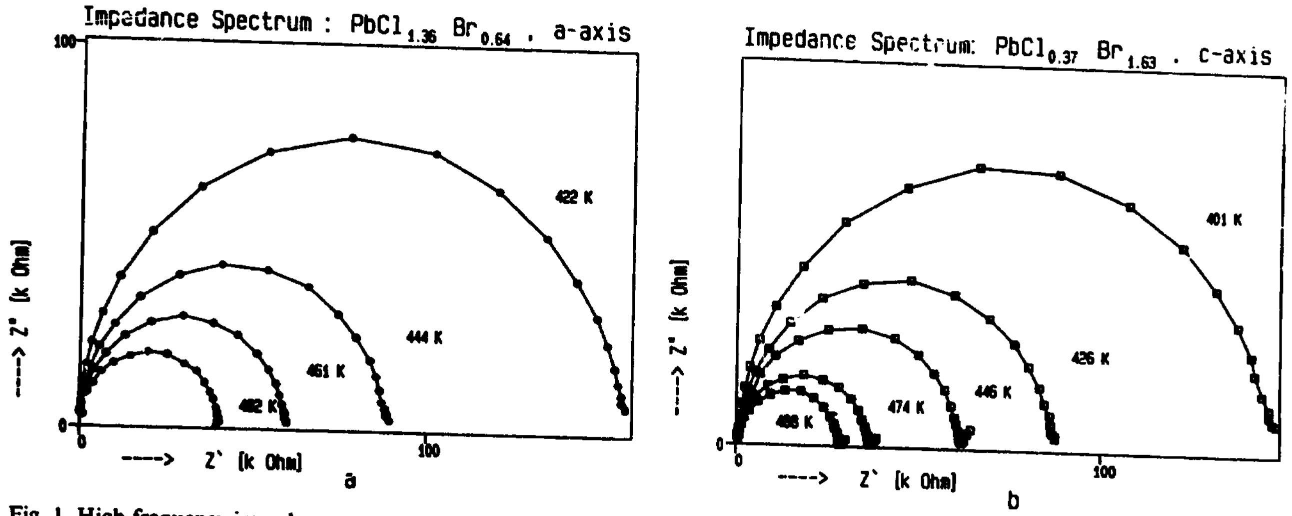

Fig. 1. High frequency impedance spectra of the cell C|PbCl$_{2x}$Br$_{2(1-x)}$|C (5 Hz–13 MHz) at different temperatures: (a) $x=0.68$, a-axis; (b) $x=1.85$, c-axis.

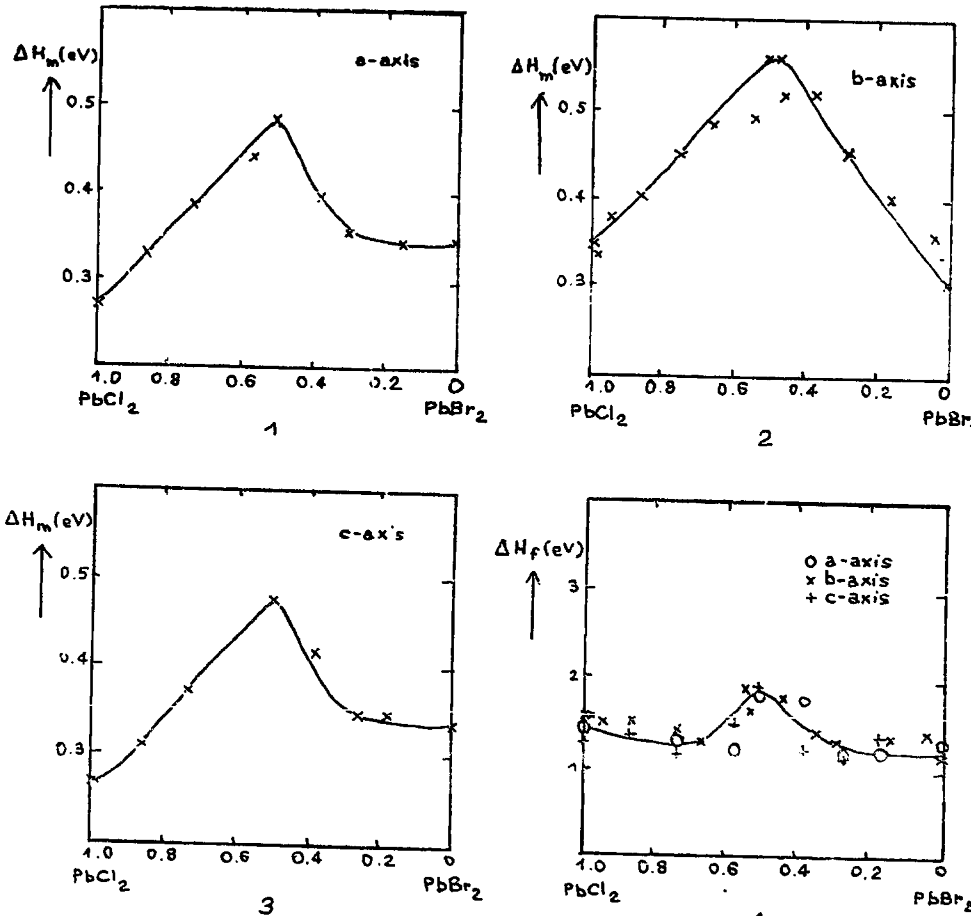

Fig. 2. Orientation dependence of the anion vacancy migration enthalpy, and Schottky defect formation enthalpy: 1–3, ΔH_m along a, b, respectively c-axis, 4, ΔH_f along a, b and c-axis.

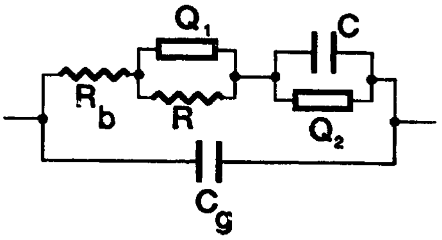

Fig. 3. Electrical equivalent circuit $Q_1RpCQ_2psR_bSC_gp$, used to model the impedance spectra. Q_1RpCQ_2ps represents the interfacial response (s=series, p=parallel).

α values are always much smaller than 0.5. A representative example of an experimental and calculated admittance and concomittant impedance spectrum is given in fig. 4.

Transference numbers have been measured for $PbCl_{0.02}Br_{1.98}$ with $PbCl_2$ as protective electrolyte, and $PbBr_{0.02}Cl_{1.98}$ with $PbBr_2$ as protective electrolyte. Crystals Z_1 and Y_3, as well as Z_3 and Y_4 could not always be separated. In these instances, weight changes of the two crystals were interpreted. For Z_1 and Y_3 and the $PbBr_2$-based solid solution we obtain $\Delta W(Z_1, Y_3) = t_{Br}(A_{Br} - A_{Cl})Q/F$ where A denotes atomic weight. Q the charge and F Faraday's constant. At 550 K and $Q = 12C$ we obtain $\Delta W(Z_1, Y_3) = 0.0046 \pm 0.0004$ g, and hence $t_{Br} = 0.83 \pm 0.07$. For the $PbCl_2$-based solid solution the analysis of Z_1 is in most cases feasible. Its weight change is $\Delta W(Z_1) = t_{Cl}A_{Cl}Q/F$. $\Delta W(Z_1)$ is equal to 0.0033 g at 552 K and $Q = 9.2$ C, and hence $t_{Cl} \sim 1$.

4. Discussion

The high-frequency small-signal ac response of the cells $C|PbCl_{2x}Br_{2(1-x)}|C$ provides bulk ionic conductivities, and hence can be used to evaluate accurately the orientation dependence of the defect migration enthalpies. Before discussing a conduction mechanism it is recalled that the crystallographic studies [2] have revealed that for $x > 0.5$ sites 1 in the $PbCl_2$-structure of the $PbCl_{2x}Br_{2(1-x)}$ solid solutions, i.e. fig. 5, remain completely occupied by Cl^- ions, while anion sites 2 are occupied by Cl^- and Br^- ions. The reversed situation is observed for $x < 0.5$. Here sites 1 are occupied by Cl^- and Br^-, while sites 2 remain occupied with Br^- ions. In addition, the present transference number measurements lend support to the assumption that in solid solutions with $x > 0.5$ bromide ions on sites 2 are virtually immobile, while for $x < 0.5$ chloride ions on sites 1 may exchange with bromide ion vacancies, and thus contribute to dc transport. The orientation dependence of ΔH_m reveals ΔH_m(∥ *a*-axis) $= \Delta H_m$(∥ *c*-axis). The composition independent behaviour for $x < 0.3$ can then be understood if conduction occurs via preferential pathways involving only sites 2 (see fig. 5). In the region x from 0 to 0.5 the shortest Cl_2–Cl_2 distances remain constant, while the shortest Cl_1–Cl_1 distances decrease [2], which is concordant with a composition invariant ΔH_m. However, for the more concentrated solid solutions in this region ($x > 0.3$) the over-all lattice contraction becomes substantial.

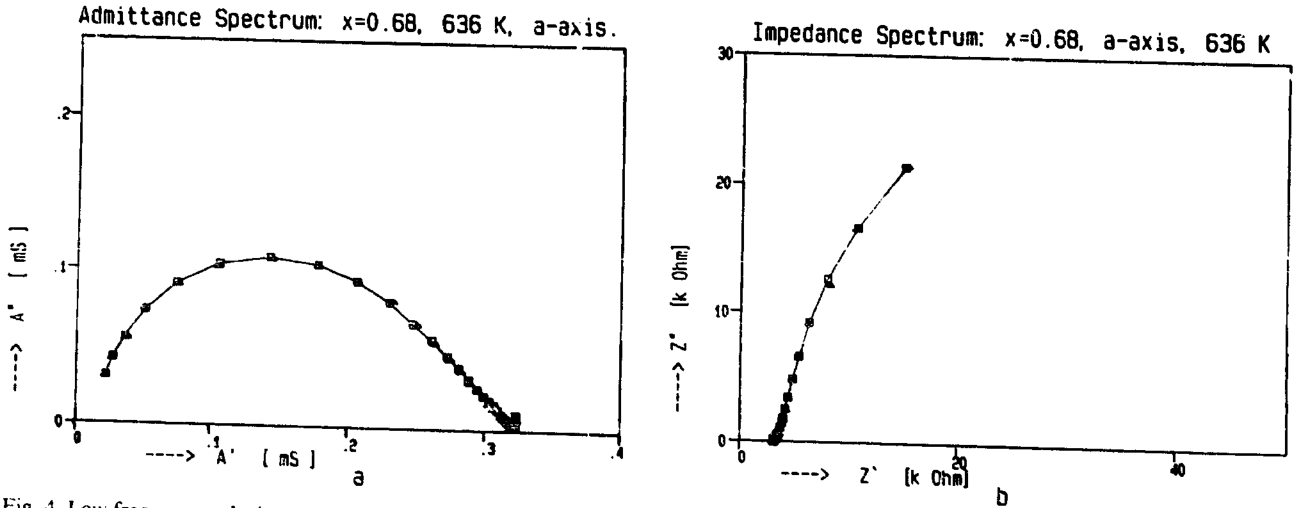

Fig. 4. Low frequency admittance (a) and impedance spectrum (b) of the cell $C|PbCl_{1.36}Br_{0.64}$(∥ *a*-axis)$|C(1{,}6 \times 10^{-2}$–10^5Hz); (△) experimental data, (□) fit results.

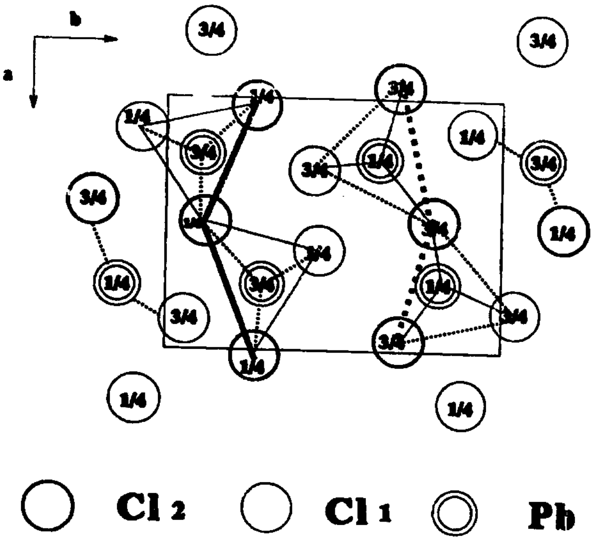

Fig. 5. The c-axis projection of the $PbCl_2$ structure: (○) Cl_2; (○) Cl_1; (◎) Pb.

As has been argued before [2], this leads, along with the preferential site occupancy, to distorted pathways which are reflected in increased jump barriers. Because the Cl_1–Cl_1 as well as the Pb–Cl_1 [2] distances decrease Cl^- diffusion over Br sites 1 requires an activation enthalpy which is assumed to be larger than that in undisturbed $PbCl_2$. Using the same rationale the migration enthalpy for chloride ion diffusion decreases from PbClBr ($x=0.5$) to $PbCl_2$ ($x=1$). For $x>0.5$ the lattice contraction is becoming less pronounced, while the shortest Cl_1–Cl_1 and Pb–Cl_1 distances are composition invariant, and Cl_2–Cl_2 distances decrease [2].

For conduction along the *b*-axis anion vacancy jumps involving sites 1 and 2 have to be considered. Because Br^- ions are virtually immobile in dilute solid solutions ($x>0.5$) sites 2 become effectively blocked. For $x<0.5$ Cl^- ions on sites 1 may contribute to the conduction, but, using above mentioned arguments, with large activation enthalpies. Hence activation enthalpies increase from $x=0$, or $x=1$ to the equimolecular composition at $x=0.5$. It should be borne in mind that in the interpretation of the transference number measurements it has been assumed that neither protective electrolyte reacts to form a solid solution at the interfaces Z_1/Y_3 and Z_3/Y_4, and that Br^- or Cl^- ions from Z_1 do not diffuse into $PbCl_2$, respectively, $PbBr_2$ protective electrolyte crystals Y_3.

Analysis of the low frequency immittance spectra reveals R_b and R to be of the same order of magnitude, Q_1, to represent practically a Warburg impedance, and Q_2 to be a distributed R, which may arise as a result of current in-homogeneities. Limited information on the temperature dependence of the interfacial circuit elements precludes a detailed analysis. However, we attribute the interfacial response as due to reaction products like $Pb(OH)_2$ and PbO which are present as dispersed phases in the surface layers of the crystals. These products can be formed, because the used graphite dag revealed the presence of a slight amount of ammonia. While more research is required to interpret this response quantitively, it is noted that this type of interfacial response did not occur when silver paints, not containing ammonia, were applied [3].

Acknowledgement

The authors are grateful to Prof. Dr. C. Carabatos (C.L.O.E.S.) for encouraging this research. They thank Robert Kalwij (T.U. Delft) for computational contributions.

References

[1] M. Lumbreras, Thése d'Etat (University of Metz, 1987).

[2] M. Lumbreras, J. Protas, S. Jebbari, G.J. Dirksen and J. Schoonman, Solid State Ionics 16 (1985) 195; 18/19 (1986) 1179; 20 (1986) 295.

[3] M. Lumbreras, J. Schoonman and E.J.L. Schouler, Cryst. Latt. Defects Amorph. Mat. 15 (1987) 211.

[4] Marquardt, J. Soc. Industr. Appl. Math. 11 (1963) 431.

[5] C. Tubandt, H. Reinhold and G. Liebold. Z. Anorg. Allg. Chem. 197 (1931) 225.

[6] A.F. Halff, Ionic Conductivity and Photoconductivity of the Ternary Lead Halides PbFCl and PbFBr, Ph.D. Thesis (University of Utrecht, 1978).