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Anisotropic Conductivity of PbFCl

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Single crystals of undoped PbFCl have been grown. The ionic conductivity of these crystals has been measured parallel and perpendicular to the crystallographic *c*-axis, and has been compared with the ionic conductivity of undoped β-PbF_2 and $PbCl_2$ single crystals.

According to Greenwood the crystal structures involved favour the presence of anion Frenkel defects. In spite of the fact that conductivity experiments on undoped materials are not conclusive, the present results, together with structural considerations, favour the presence of Schottky defects.

Introduction

It is well known that $PbCl_2$ is an anionic conductor up to its melting point (*1–3*). Lead ion and chloride ion vacancies (V''_{Pb} and $V^{\cdot}_{Cl}$, respectively) are considered to be the only intrinsic point defects in lead chloride. In the conductivity experiments the displacement of the chloride ion vacancies is measured. Both the migration- and formation-enthalpy for the chloride ion vacancy and one set of Schottky defects, respectively, are isotropic within the experimental error.

Cubic lead fluoride exhibits as most compounds having the fluorite structure anionic Frenkel defect conduction.

The compound PbFCl can be prepared by melting an equimolar mixture of lead fluoride and lead chloride. PbFCl has a layered tetragonal structure. The unit cell consists of plane sheets perpendicular to the crystallographic *c*-axis with layer sequence (*4*) (Fig. 1):

FPbClClPbF

In spite of the fact that the lead ion is smaller than the chloride ion, the smaller coordination number of the anions favours according to Greenwood (*5*) the presence of Frenkel defects in the anion sublattice of this structure.

In literature scarce attention has been devoted to the electrical conductivity of this type of mixed lead halides. In this paper we report upon the crystal growth and ionic conductivity of undoped PbFCl. The results are compared with the ionic conductivity of undoped lead chloride, and cubic lead fluoride. As can be expected in this layer type

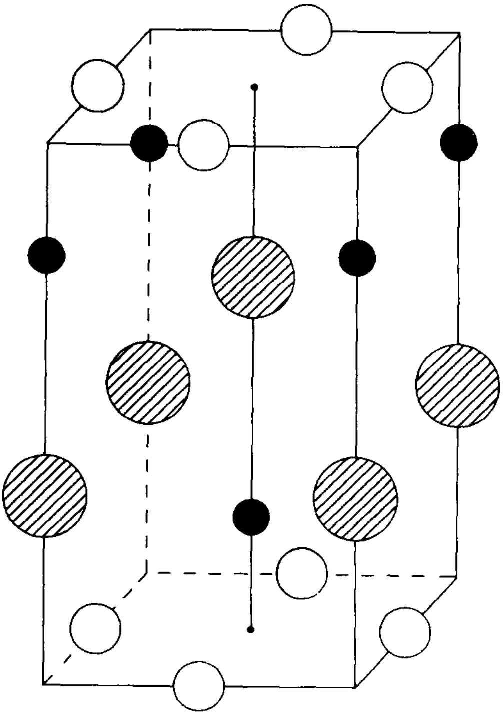

FIG. 1. Crystal structure of PbFCl: open circles F, black circles Pb, hatched circles Cl.

structure the ionic conductivity is highly anisotropic.

Experimental Procedure

Preparation of Crystals

As starting materials $PbCl_2$ of "Bakers Analyzed" grade and PbF_2 of "Ultra Pure" grade (Merck) were used. The lead fluoride was not further purified, whereas the lead chloride was subjected to a zone-refining procedure as described by Willemsen (*6*). Stoichiometric amounts of PbF_2 and $PbCl_2$ were thoroughly mixed. The mixture, placed in a platinum boat in a zone-refining equipment, was dried for 24 h at about 350°C under a gentle stream of dried oxygen-free nitrogen. The temperature of the furnace around the zone-refining equipment was subsequently raised to 650°C, at which temperature the mixture, being molten, reacted giving PbFCl. After 30 h the temperature was lowered to about 525°C.

According to Anosov and Patsukova (*7*) the dissociation of PbFCl into PbF_2 and $PbCl_2$ amounts to 32% at its melting point (601°C). For this reason the reaction product was subjected to a zone-levelling procedure before zone refining. Both procedures were carried out with a rate of 1 cm/h under purified nitrogen. In order to grow single crystals the last zone pass was carried out at a rate of 0.1 cm/h. The furnace was then cooled steadily to room temperature over a period of 24 h.

TABLE I

IMPURITY CONTENT (IN PPM) OF TWO PIECES OF UNDOPED PbFCl, CLEAVED FROM DIFFERENT PARTS OF THE ZONE-REFINED INGOT[a]

Impurity	PbFCl	PbFCl
Fe	$\leqslant 2$	$\leqslant 2$
Ni	$\leqslant 5$	$\leqslant 5$
Tl	42	48
Cu	$\leqslant 5$	$\leqslant 5$
Mn	$\leqslant 0.5$	$\leqslant 0.5$
Co	$\leqslant 1$	$\leqslant 1$
Bi	25	19
Ag	7	10
V	$\leqslant 10$	$\leqslant 10$

[a] Thanks are due to Mr. G. P. M. van den Heuvel for carrying out the spectrochemical analysis.

The single crystals which were used in the conductivity experiments had surface areas between 0.3 and 0.7 cm^2, and a thickness between 0.1 and 0.3 cm. They could be readily cleaved from the crystalline parts of the ingots. The samples were checked by X-ray analysis (*4*). It was confirmed that cleavage occurred perpendicular to the *c*-axis. Results of chemical analysis are given in Table I.

The preparation of the lead chloride single crystals used in this study has been described elsewhere (*6*). The single crystal specimens of β-PbF_2 were kindly placed at our disposal by Dr. E. E. Schneider of the University of Newcastle upon Tyne. These crystals have been grown by Gulton Industries from BDH zone-refined Optran material.

Conductivity Experiments

The crystals were springloaded between two platinum electrodes in a conductivity cell which was basically of the same type described before (*8*). Ohmic contacts between the crystal and the platinum electrodes were established by means of colloidal graphite (Aquadag). The conductivities were measured with an automatic capacitance bridge assembly (General Radio 1680A). The temperature of the crystals was measured with a Chromel–Alumel thermocouple, using a method described previously (*9*). Purified nitrogen was circulated through the cell throughout the measurements. Ure (*10*) has measured strong polarization effects in his ac-conductivity study of CaF_2, using among other things colloidal graphite paint.

Aquadag did not cause polarization effects at the frequencies used (400 c/s and 1 kc/s) neither on β-PbF_2 nor on $PbCl_2$ or PbFCl. The use of Leitsilber as an electrode paint on $PbCl_2$ and PbFCl was omitted during the experiments, since strong hysteresis occurred on warming and cooling due to reaction of the paint with the crystals: incorporation of silver occurred which enhanced the conductivity in both crystals.

Experimental Results

In Fig. 2 we have plotted the ionic conductivity as $\log\sigma T$ vs $1/T$ for undoped β-PbF_2, undoped $PbCl_2$, and undoped PbFCl. For PbFCl we have measured the conductivity parallel as well as

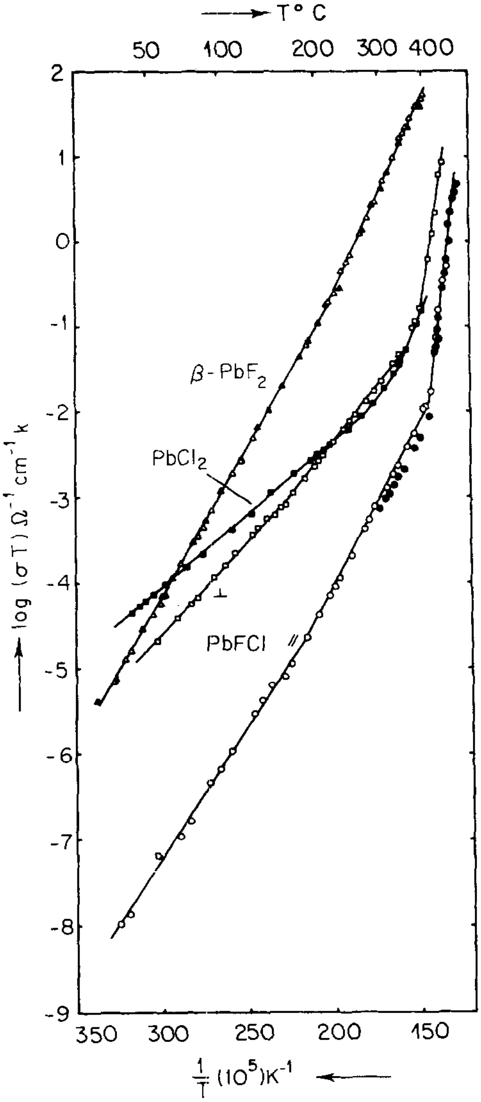

FIG. 2. The ionic conductivity, plotted as logσT vs $1/T$, of undoped β-PbF_2, $PbCl_2$, PbFCl (⊥ c-axis) and PbFCl (// c-axis).

perpendicular to the c-axis. In the temperature region involved the curves for both β-PbF_2 and $PbCl_2$ show one knee, whereas three distinct regions are observable in the curves for PbFCl. The heat effects are summarized in Table II.

For $PbCl_2$, ΔH_1 corresponds to the activation enthalpy of motion, ΔH_m, of a chloride ion vacancy, whereas ΔH_2 equals $\Delta H_m + \frac{1}{3}\Delta H_f$, giving for the formation enthalpy, ΔH_f, of a Schottky-defect trio the value 1.95 eV. Both values are in agreement with the values reported in literature.

The melting point of β-PbF_2 is 822 ± 2°C (*11*).

TABLE II

HEAT EFFECTS IN β-PbF_2, $PbCl_2$, AND PbFCl

Crystal	ΔH_1 (eV)	ΔH_2 (eV)	ΔH_3 (eV)
β-PbF_2	0.70	1.05	
$PbCl_2$	0.34	0.99	
PbFCl (// c-axis)	0.58	0.74	3.3
PbFCl (⊥ c-axis)	0.40	0.46	2.8

Since the conductivity of the undoped β-PbF_2 crystals was measured in the temperature region 25–400°C it is questionable whether the conductivity above the knee represents intrinsic conduction. Ure (*10*) has measured for $\Delta H_m(V_F^{\cdot})$ in CaF_2 in the temperature region 200–600°C values in between 0.87 and 0.52 eV, for $\Delta H_m(F_i')$ the value 1.65 eV, and for the formation enthalpy of the anionic Frenkel defects the value 2.82 eV. Since mass-spectrographic analysis of PbF_2 as given by the manufacturer shows among other things the presence of 40 ppm Cs and 20 ppm Li, which implies $[V_F^{\cdot}] > [F_i']$,* we may safely interpret ΔH_1 as the migrating enthalpy of fluoride ion vacancies. The influence of migrating interstitial fluoride ions in the conductivity above the knee needs further attention but seems reasonable if compared with the results reported for CaF_2 (*10*). Since in a zone-refined ingot the remaining impurity content is not uniformly dispersed, extrinsic conductivities of undoped material are found in a wide conductivity range. The first and second region in the conductivity plot of PbFCl are dependent on the remaining impurity content, whereas the high temperature region turned out to be independent of impurities. Apart from the conductivity mechanism we can conclude from Table II that $[\Delta H_3\text{-}(\Delta H_1 + \Delta H_2)]$ has the value 1.98 // and 1.94 eV ⊥ c-axis, which suggests a heat effect due to defect formation. The anisotropic conduction of PbFCl indicates an anisotropic jump probability for the predominant mobile defects.

Discussion

Crystal Structure

The unit cell as given in Fig. 1 contains two formula units. The cell dimensions have been

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* Here and throughout this paper the defect notation of Kröger is used (*19*).

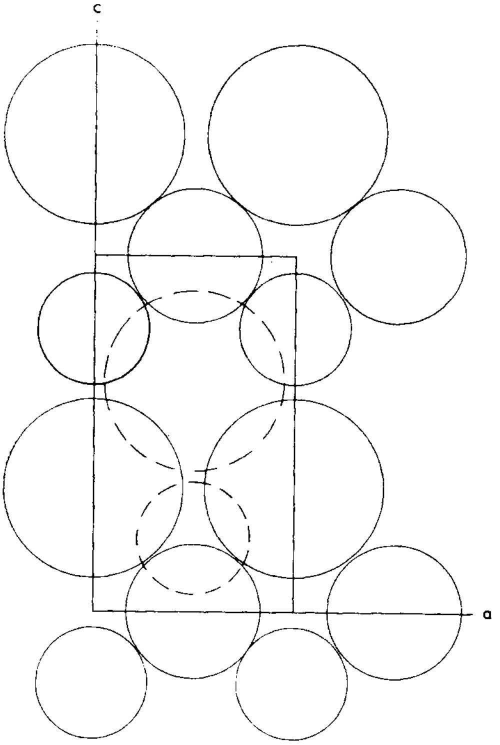

FIG. 3. Part of the crystal structure of PbFCl: ions drawn with full lines lie in the front plane of the unit cell (see Fig. 1.); ions drawn with broken lines lie midway the unit cell.

determined by Nieuwenkamp and Bijvoet (*4*), and were found to be a = 4.09 Å and c = 7.59 Å. The positions of the fluoride ions are $0\frac{1}{2}0$ and $\frac{1}{2}00$. Those of the lead and chloride ions are $00\bar{u}$, $\frac{1}{2}\frac{1}{2}u$, and $00\bar{w}$, $\frac{1}{2}\frac{1}{2}w$, respectively, with $u = 0.205$ and $w = 0.65$. The lead ions are surrounded by four fluoride ions at equal distance (2.52 Å), and five chloride ions, four of which are at equal distance (3.07 Å) and one at a distance of 3.21 Å. The symmetry of the fluoride ions around the lead ions (PbFPb layer) is very similar to that of the fluorite modification of PbF_2. In PbFCl, however, the chloride ion at $\frac{1}{2}\frac{1}{2}w$ reduces the interstitial space in the Pb layer compared with the space available in the identical Pb layer in β-PbF_2: The reduction amounts to about 30% (Fig. 3). The centres of the largest interstitial sites available in PbFCl are found at positions $00v$, $\frac{1}{2}\frac{1}{2}\bar{v}$ with v = 0.038. These interstitial spaces in PbFCl allow ions with radius of 0.45 Å.

In lead chloride De Vries (*12*) reported for the maximum available interstitial space the value 0.7 Å. The available space in β-PbF_2 at the centre of the cube formed by F^- ions allows ions with a radius of 0.61 Å. The radii of the ions involved are 1.26 Å (Pb^{2+} in 8 coordination), 1.32 Å (Pb^{2+} in 9 coordination), 1.36 Å (F^-), and 1.81 Å (Cl^-) (*5*).

Defect Structure

It was mentioned in the introduction that the structures involved all favour Frenkel defects in the anion sublattice, since the anions have a smaller coordination number (*5*). Indeed, anionic Frenkel defects are dominant in cubic PbF_2. According to Barsis and Taylor (*13*) the results on pure and doped lead chloride may be interpreted by accepting mobile anion vacancies and immobile interstitial chloride ions. Bradley *et al.* (*14*) even accept the presence of interstitial chloride ions using the argument given by Greenwood (*5*). In our opinion it is well established that the intrinsic defects in lead chloride are of the Schottky type. Direct evidence for a vacancy mechanism has been obtained from Br-tracer diffusion experiments for $PbBr_2$ (*9*), a substance in which the mass transport is identical to that in $PbCl_2$. Because of this similarity we tentatively assume identical mass-transport processes in PbFCl and PbFBr. It is known that PbFBr shows anionic conduction (*15*). In the temperature region 250–300°C the transport numbers turned out to be constant (*15*): $t_{F^-} = 1 - t_{Br^-} = 0.87$. Mixed anionic conduction in PbFCl implies that intrinsic point defects occurring in the lead ion sublattice only, may be neglected. We have, therefore, to make a choice between the following Schottky mechanism:

$$\begin{aligned} &\mathrm{PbFCl} \rightleftharpoons V''_{\mathrm{Pb}} + 2V^{\cdot}_{\mathrm{F}}, && K_{\mathrm{SF}} \\ &\mathrm{PbFCl} \rightleftharpoons V''_{\mathrm{Pb}} + 2V^{\cdot}_{\mathrm{Cl}}, && K_{\mathrm{SCl}} \\ &\mathrm{PbFCl} \rightleftharpoons V''_{\mathrm{Pb}} + V^{\cdot}_{\mathrm{F}} + V^{\cdot}_{\mathrm{Cl}}, && K_{\mathrm{S}} \\ \text{with}\quad & K_{\mathrm{S}} = (K_{\mathrm{SF}} \cdot K_{\mathrm{SCl}})^{\frac{1}{2}}, \end{aligned}$$

or a Frenkel mechanism in both the fluoride and chloride sublattice, i.e.

$$\begin{aligned} &\mathrm{PbFCl} \rightleftharpoons \mathrm{F}'_{\mathrm{i}} + V^{\cdot}_{\mathrm{F}}, && K_{\mathrm{FF}} \\ &\mathrm{PbFCl} \rightleftharpoons \mathrm{Cl}'_{\mathrm{i}} + V^{\cdot}_{\mathrm{Cl}}, && K_{\mathrm{FCl}} \end{aligned}$$

As compared with the situation in cubic PbF_2 we might expect interstitial fluoride ions in PbFCl but then these ions will be rather immobile. As compared with the $PbCl_2$ type structure the occurrence of Cl'_i ions in PbFCl is less probable, especially F'_i ions should be present. The heat effects summarized in Table II lead together with the structural considerations to a preference for Schottky defects, in spite of the smaller coordination number of the anions. With respect to the situation in PbFBr it is likely to correlate ΔH_1 with fluoride ion vacancy migration and ΔH_2 with mixed anionic conduction via vacancies. From Table II it was concluded that $[\Delta H_3 - (\Delta H_1 + \Delta H_2)] = n\Delta H_f = 1.98\,\text{eV}\,(1.94\,\text{eV})$, where n depends on the defect mechanism involved.

Recently, several authors (*16–18*) have introduced general empirical relations correlating melting temperatures, T_m, with formation enthalpies, ΔH_f:

Schottky defects only (*16, 17*):

$$\Delta H_f(\text{eV}) = 2.14 \times 10^{-3}\, T_m(K) \qquad (1)$$

Both Schottky and Frenkel disorder (*18*):

$$\Delta H_f(\text{eV}) = 3.47 \times 10^{-3}\, T_m(K) - 1.08 \qquad (2)$$

For compounds showing Frenkel disorder literature values for ΔH_f lead to a rough relation, represented by (3):

Frenkel defects only:

$$\Delta H_f = 1.2 \times 10^{-3}\, T_m + 0.34 \qquad (3)$$

Relation (1) gives for ΔH_f(PbFCl) the value 1.87 eV, relation (2) 1.95 eV and relation (3) 1.3 eV. A Schottky as well as a Frenkel mechanism demands for n a value larger than 1, which leads to the conclusion that at higher temperatures a model based only on mobile $V_F^{\bullet}$ and $V_{Cl}^{\bullet}$ (Scottky) is inadequate. Further results on both pure and doped PbFCl and PbFBr single crystals will be published in due course.

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