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Ionic conductivity in solid solutions of PbF_2 and YF_3

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Abstract

Ionic conductivity of a series of fluorite-type solid solutions $Pb_{1-x}Y_xF_{2+x}$ ($0.007 \leq x \leq 0.222$) has been measured in the frequency range 100 Hz – 3 MHz and in the temperature range 25–250°C under vacuum. The conductivity decreases and the activation energy increases gradually upon increasing the yttrium content up to ~ 4.5 mol % of Y^{3+} whereas, beyond that and up to 22 mol % of Y^{3+}, the ionic conductivity increases and the activation energy decreases. Thus two distinct regions in the general composition $Pb_{1-x}Y_xF_{2+x}$ could be delineated, in one the polarizability factor predominates over the number of extra-interstitial F anions and vice-versa in the other region. These results indicate the competing effects between the disorder caused by interstitial F anions and the polarizability of the host and guest cations. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

PbF_2 on heating undergoes an irreversible phase transition from orthorhombic (α) to cubic (β) form at about 315°C. The β-form can also be stabilized at room temperature on cooling. It was found that β-PbF_2 was more stable at room temperature and ambient pressure. However, a partial conversion of β-PbF_2 to α-PbF_2 was effected by pressing the material at above 30,000 PSI [1]. Obserschmidt et al. [2] investigated a systematic effect of hydrostatic pressure on the ionic conductivity and the phase transition in PbF_2.

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It was found that the transition temperature increases linearly with increasing pressure at higher temperature.

A comparison of the electrical properties of β-PbF_2 with other fluoride ion conductors such as CaF_2, BaF_2 shows that β-PbF_2 is a better ionic conductor, due to the high polarizability of the Pb^{2+} ions compared to that of Ca^{2+} and Ba^{2+} ions. The rare-earth trifluorides (e.g. Y^{3+}, La^{3+} etc.,) have reasonably high solubility in β-PbF_2. Hence, several studies have been made with an aim to enhance the conductivity by replacing a part of Pb^{2+} with other cations, while retaining the basic fluorite structure [3]. The substitution of Pb^{2+} with Y^{3+} increases the concentration of interstitial fluoride ions and thus resulting in an enhanced ionic conductivity [3-7]. Therefore, the aliovalently doped β-PbF_2 based solid solutions are perspective solid electrolyte with a fast fluoride ion conductivity at low and moderate temperatures as one can significantly alter the anionic sub-lattice. In view of this, Reau et. al., [3] investigated the ionic conductivity in the fluorite type solid solutions $Pb_{1-x}Y_xF_{2+x}$ ($0.02 \leq x \leq 0.30$) which were prepared by quenching from 820°C. We have investigated the ionic conductivity of the solid solutions $Pb_{1-x}Y_xF_{2+x}$ ($0.007 \leq x \leq 0.222$) prepared by short annealing (3 hours) at low temperature (~ 700°C) and slow cooling (@ 2°C/min.) to room temperature. This paper reports the correlation between composition, ranging from very low doping (0.7 mol %) to the maximum solubility (22 mol %) limit of Y^{3+} ion in β-PbF_2 and the activation energy and in-turn ionic conductivity.

2. Experimental

PbF_2 used was of spectroscopic grade. YF_3 was synthesized by the reaction between Y_2O_3 and NH_4HF_2 (in excess) at 350°C followed by drying at 250°C for 5 hours in an argon atmosphere. The solid solution of YF_3 and PbF_2 were synthesized by solid state reaction [8]. The required amounts of the constituents were mixed and pressed into 8 mm pellets. This pellet was wrapped in platinum foil and kept in a quartz tube that was evacuated (10^{-5} mbar) and sealed online. The sealed quartz tube along with the pellet was then heated at 700°C for three hours to facilitate the formation of solid solution. The samples were then slow cooled at a rate of 2°C/min. The products obtained were characterized by powder XRD using Ni-filtered Cu-Kα radiation.

Impedance measurements on the pressed pellets were carried out using Impedance/ Gain phase analyzer (HP 4194A) over the frequency range 100 Hz – 3 MHz, in the temperature range 25–250°C with the help of a high temperature-measuring cell [9] under vacuum of 10^{-5} mbar. The samples in the form of pellets were painted with graphite paste for better electrical contact. The silver paint was not suitable as it diffused into the sample during measurement. The samples were spring loaded between thick silver electrodes for impedance measurement. The studies were done during heating cycle with a rate of 1°C/min. The dc conductivity was derived from the impedance plot.

Table 1
Lattice parameter of various compositions

x	Composition (Pb_{1-x} Y_xF_{2+x})	a (Å)
x = 0.000	PbF_2	5.940 (1)
x = 0.007	$Pb_{0.993}$ $Y_{0.007}F_{2.007}$	5.936 (1)
x = 0.029	$Pb_{0.971}$ $Y_{0.029}F_{2.029}$	5.926 (1)
x = 0.044	$Pb_{0.956}$ $Y_{0.044}F_{2.044}$	5.919 (1)
x = 0.100	$Pb_{0.900}$ $Y_{0.100}F_{2.100}$	5.904 (1)
x = 0.154	$Pb_{0.846}$ $Y_{0.154}F_{2.154}$	5.871 (1)
x = 0.222	$Pb_{0.778}$ $Y_{0.222}F_{2.222}$	5.842 (1)

3. Results and discussion

Recently, the low temperature phase equilibria in PbF_2-YF_3 system was reported by Patwe et al., [9]. The composition with 22 mol % of YF_3 in PbF_2 was found to be the solubility limit for the solid solutions while retaining the fluorite structure. A number of ordered phases were also observed during the course of this work. The samples with the stoichiometric formula $Pb_{1-x}Y_xF_{2+x}$ ($0.0 \leq x \leq 0.222$) studied in the present investigation forms disordered fluorite-type solid solutions. The unit cell parameters for these samples are given in Table I. The fluorite unit cell parameters at the saturated solid solution (x = 0.222) is found to be 5.842(2) Å as against 5.940(1) Å for pure β-PbF_2. This is attributed to the difference in the ionic radii of the two ions (r_{Pb2+}=1.29 Å and r_{Y3+}=1.02 Å) in eight-fold coordination.[†]

In a conventional DC measurement on β-PbF_2 with silver as blocking electrodes, F anions encounter the problem of space charge polarization due to blocking at the sample and electrode interface. Thus the total measured resistance has the contributions from both the sample and the electrode. To extract the true resistance of the sample, one usually performs the measurements as a function of frequency. In such a case, the plot of $|Z'|$ vs $|Z''|$ (impedance plot) exhibits a semicircle due to the sample and a low frequency spike due to the electrode polarization. The resistance of the sample corresponds to the intercept of the semicircle with the spike. The dc conductivity (σ_{dc}) of the solid solutions $Pb_{1-x}Y_xF_{2+x}$ ($0.0 \leq x \leq 0.222$) is thus calculated from their true resistance extracted from the impedance plot. Fig. 1 presents the impedance plots for the solid solutions at 25°C. Fig. 2 shows the dc conductivity as a function of temperature, in the form of $\log\sigma_{dc}T$ vs 1000/T. It may be noticed from the Fig. 2 that at lower temperature, the ionic conductivity decreases considerably at low concentration of the Y^{3+} ions and increases gradually beyond ~ 4.5 mol % of Y^{3+} content. As we increase the temperature the difference in conductivity with yttrium content decreases. The conductivity data for all the samples are fitted to the Arrhenius equation:

$$\sigma_{dc} = (\sigma_o/T)*\exp(-E_\sigma/kT)$$

[†] VCH Periodic Table of Elements, Compiled by Fluck and Hermann.

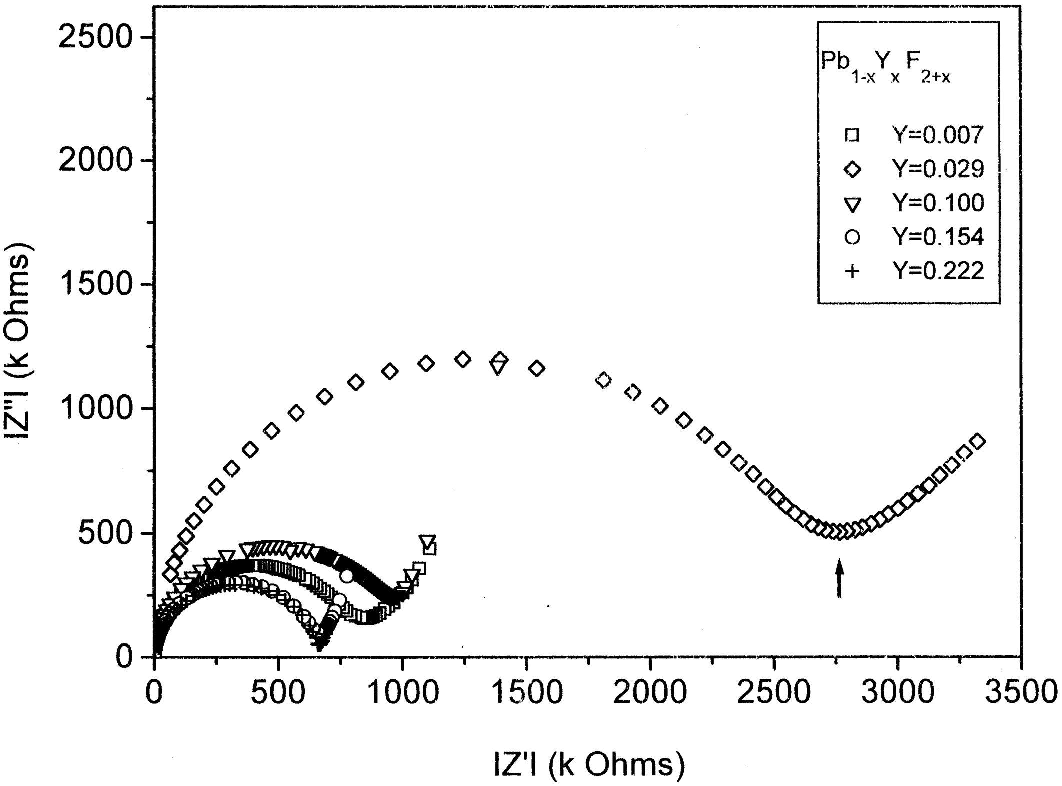

Fig. 1. Impedance plots at 25°C for the solid solutions $Pb_{1-x}Y_xF_{2+x}$. Arrow indicates true resistance.

where, E_σ is the activation energy for the dc conduction. The values of E_σ for the above samples as a function of composition are plotted in Fig. 3. The activation energy for the solid solution $Pb_{0.993}Y_{0.007}F_{2.007}$ is comparable to a value of 0.50 eV [1] reported for β-PbF_2. The ionic transport in all the above samples is mostly due to the extrinsic anion vacancies and interstitials.

The polarizability of Y^{3+} and Pb^{2+} are 1.5 $Å^3$ and (3.7 to 5) $Å^3$, respectively [10]. It is known that higher polarizability of the cation enhances the ionic conduction of anions, resulting in lower activation energy. It is seen clearly from Fig. 3 that with increasing yttrium content, the activation energy for dc conduction first increases and subsequently it decreases gradually. Thus there are two distinct regions in Fig. 3. In the first region, where the activation energy increases on increasing Y^{3+} content, the polarizability factor predominates over the number of extra-interstitial F anions which are rather insignificant. It is noted that the activation energy starts decreasing as a function of Y^{3+} content, after attaining a peak at the composition $Pb_{0.956}Y_{0.044}F_{2.044}$. This unusual observation can be attributed to the number of interstitial F-anions which predominates over the polarizability factor in this region. Thus the $Pb_{0.778}Y_{0.222}F_{2.222}$ shows the lowest activation energy in this system. Reau et al. [3], could not observe this peak in their plot of activation energy versus Y^{3+} content in $Pb_{1-x}Y_xF_{2+x}$ solid solutions. They performed the ionic conductivity measurements on the

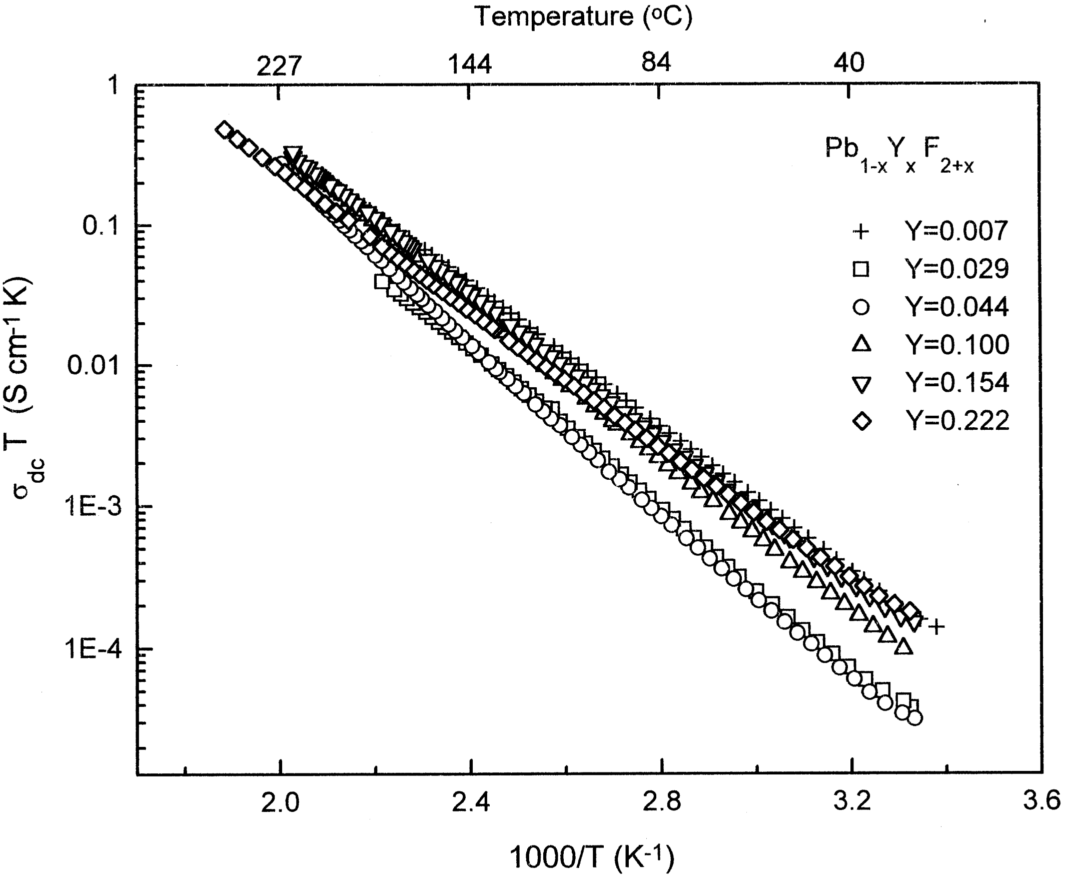

Fig. 2. dc conductivity as a function of temperature.

high temperature quenched samples as against low temperature-short annealed and slow cooled samples in the present investigation. The quenched samples are likely to have high disorder and slightly higher cell volume also, which might cause the compensation of polarizability factor. The slow cooled samples result in a better control over anionic sub-lattice and microstructure which must have facilitated an unequivocal delineation of two distinct regions, observed in the present investigations. It may be mentioned that the variations in σ_{dc} and E_σ in $Pb_{1-x}Y_xF_{2+x}$ system in our case are not as large as that in solid solutions $Pb_{1-x}M_xF_{2+x}$, where M is Bi, In and Sb [11,12] reported earlier. Probably, in these systems the polarizability factor did not play a crucial role.

4. Conclusions

The substitution of Y^{3+} in β-PbF_2 leads to a highly disordered cubic phase, resulting in an extra-interstitial F-anions. This should result in a gradual increase in conductivity and a

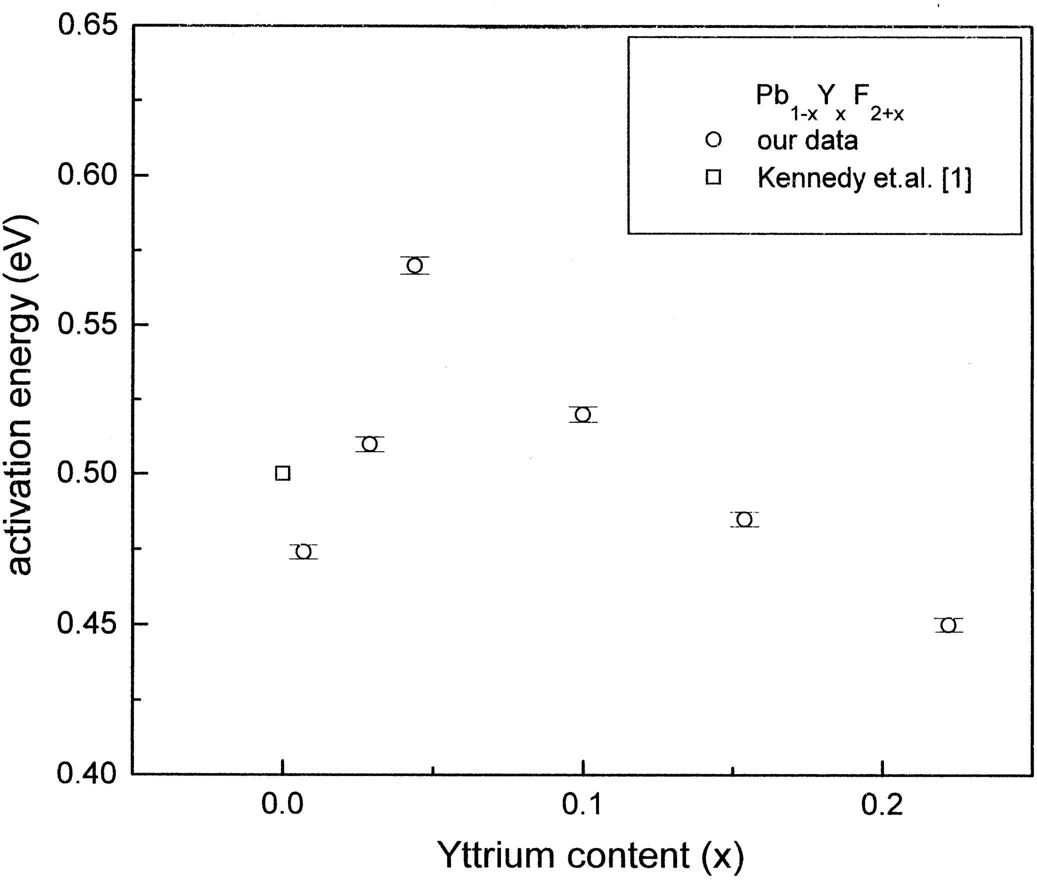

Fig. 3. Activation energy as a function of composition for the solid solutions $Pb_{1-x}Y_xF_{2+x}$.

decrease in activation energy with yttrium content. Contrary to this, in the present study it is found that at low concentrations of Y^{3+} the conductivity decreases and the activation energy increases. But beyond 4.5 mol % of Y^{3+} conductivity increases gradually and the activation energy decreases. These two distinct regions in the activation energy versus composition curve are explained based on the polarization factor and the extra-interstitial F anions. At higher content of Y^{3+} ($>$ 10 mol %) these two competing effects result in only a marginal variation in both conductivity and activation energy for $Pb_{1-x}Y_xF_{2+x}$ solid solutions, compared to other PbF_2-MF_3 (M = Bi, In and Sb) systems in which the extra-interstitial F-anions play a major role in enhancing the ionic conductivity.

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