

THE CRITICAL TEMPERATURE IN FLUORITE-TYPE SOLID SOLUTIONS

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The ionic conductivity of crystals of the fluorite-type solid solutions $Ba_{1-x}U_xF_{2+2x}$ ($0.005 \leq x \leq 0.15$), and $Pb_{1-x}U_xF_{2+2x}$ ($0 \leq x \leq 0.10$) has been studied up to high temperatures. The UF_4 dopant depresses the Faraday transition temperature T_c . At this temperature the conductivity is governed by ≈ 1 m/o extrinsic fluoride interstitials, which have mobilities of the order of ion mobilities in molten salts, a situation similar to that observed for the pure fluorites at much higher values of T_c . This is at variance with a critical defect model reported to account for the depression of T_c . Preliminary specific heat measurements reveal defect formation to be of minor importance.

La conductivité ionique de cristaux de solutions solides de type fluorure $Ba_{1-x}U_xF_{2+2x}$ ($0.005 \leq x \leq 0.15$), et $Pb_{1-x}U_xF_{2+2x}$ ($0 \leq x \leq 0.10$) a été étudiée jusqu'aux hautes températures. Le dopant UF_4 abaisse la température de transition de Faraday T_c . A cette température la conductivité est commandée par ≈ 1 m/o fluorures interstitiels extrinsèques, qui ont des mobilités de l'ion dans les sels fondus, situation similaire à celle observée pour les fluorures purs à de beaucoup plus hautes valeurs de T_c . Ceci est en contradiction avec un modèle de défaut critique tenant compte de l'abaissement de T_c . Les premières mesures de chaleur spécifique révélant que la formation de défauts est d'importance mineure.

1. Introduction

Metal halides with the fluorite (CaF_2) structure attain ionic conductivities of the order of ionic melts (10^{-10} Sm^{-1}) beyond a critical temperature T_c of about $0.8T_m$, where T_m is the melting point. Characteristic for these fluorites is the occurrence of a negative deviation from the conductivity Arrhenius relation at this so called Faraday transition. In addition, broad specific heat anomalies occur at temperatures T_λ (c_p maximum) $\approx T_c$. Both calorimetric measurements [1], and theoretical simulations [2] point to anti-Frenkel defect concentrations in pure fluorites in the range 2 to 10% at T_λ . Conductivity studies on pure fluorites reveal these defect concentrations to be only 0.5 to 2% at T_c [3]. For undoped fluorites T_c has been related with either a critical concentration of vacancies [2], or a critical mobility of the conducting species [3], this defect mobility being of the order of ion mobilities in molten salts.

Brillouin-scattering and microwave conductivity studies on YF_3 -doped CaF_2 and BaF_2 , and $GdCl_3$ -doped $SrCl_2$ reveal T_c to decrease with increasing solute content [4,5]. However, unambiguous values for T_c have not been obtained [5].

In this paper we present a detailed study of the temperature dependence of the ionic conductivity of the anion-excess solid solutions $Ba_{1-x}U_xF_{2+2x}$ ($0.005 \leq x \leq 0.15$), and $Pb_{1-x}U_xF_{2+2x}$ ($x \leq 0.10$). The results of preliminary specific heat measurements are also included. The depression of T_c and T_λ by the UF_4 content will be discussed in relation with a critical concentration, and a critical defect mobility model.

2. Experimental aspects

Single crystals of composition $Ba_{1-x}U_xF_{2+2x}$ were grown under vacuum (≈ 0.15 Pa) at about 1750 K by

the Bridgeman technique, using a radio-frequency induction furnace. Details of the growth method have been described before [6]. Single crystals of $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+2x}$ have been grown by the Bridgeman technique, or in a conventional zone-refining apparatus. Details of this method have been reported before [7]. Disks 1×10^{-3} to 1×10^{-2} m thick, and 8×10^{-3} m in diameter were cut from crystalline ingots, and polished to optical finish. The samples were provided with sputtered, or painted Pt electrodes [6], and loaded between Pt disks in a nickel conductivity cell.

The small-signal ac response of the cell was measured from 300 K to temperatures well beyond the critical temperature T_c . Especially around T_c temperature cycling was used to check the influence of inevitable oxygen contamination. Reproducible conductivity data could be obtained in a vacuum of about 10^{-2} Pa. In the frequency range 1×10^{-2} to 1×10^6 Hz use was made of a frequency response analyser (Solartron 1172, 1174). The specific heat measurements were performed on a Perkin Elmer DSC-2 differential scanning calorimeter. Sample weight varied from 1×10^{-5} to 1×10^{-4} kg.

3. Experimental results

Fig. 1 presents 3-D admittance spectra of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ ($x=0.05$ and 0.005) provided with ionically blocking Pt electrodes at temperatures below and above the critical temperature T_c . Fig. 2 presents the 3-D admittance spectra of $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+2x}$ ($x=0.10$ and 0.015) also for temperatures below and above the critical temperature. The solid solutions of other compositions exhibit similar admittance spectra. At moderate and high temperatures the system response indicates interfacial diffusion phenomena to occur. For fluorite-type solid solutions the effect of residual oxygen in interfacial processes has been emphasized before [7–9]. In fact, the system response can be modelled by a theoretical equivalent circuit, which takes the constant-phase-angle (CPA) impedance ($Z = K(i\omega)^{-\alpha}$), or finite-length Warburg effects, and adsorption and electrode reaction effects into account in an explicit manner [7–9]. However, the detailed analysis of the present admittance spectra by non-linear least-squares fitting to complex data [7] is beyond the scope of this paper, and shall be reported

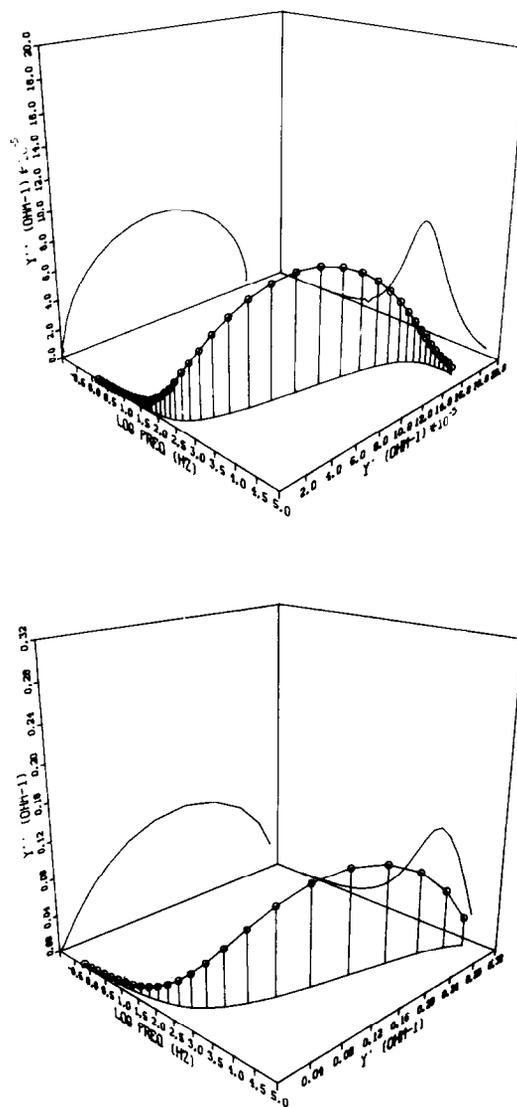


Fig. 1. 3-D admittance spectra of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$. Frequency range 0.3 Hz to 30 kHz. (a) $x=0.05$, $T=485$ K ($<T_c$); (b) $x=0.005$, $T=1255$ K ($>T_c$).

elsewhere. The spectra provide accurate values for the bulk ionic conductances, which can be used to obtain values for critical temperatures T_c . Fig. 3 presents the high-temperature ionic conductivity of several BaF_2 -based solid solutions. The temperature dependence of the ionic conductivity of the PbF_2 -based solid solutions is given in fig. 4.

Values for the critical temperatures T_c are gathered in table 1. It should be noted that the values

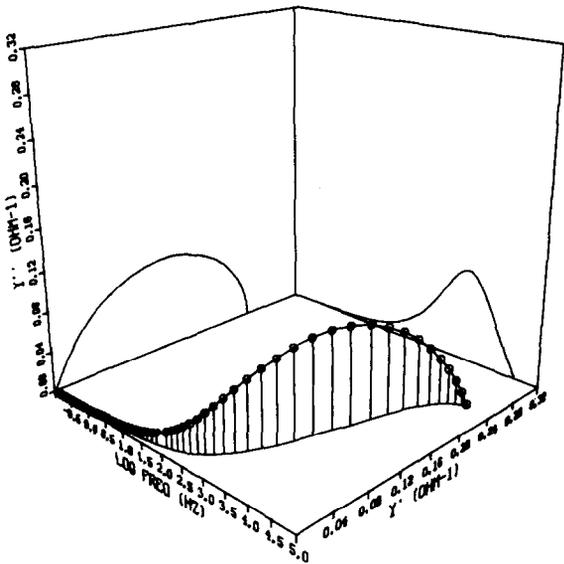
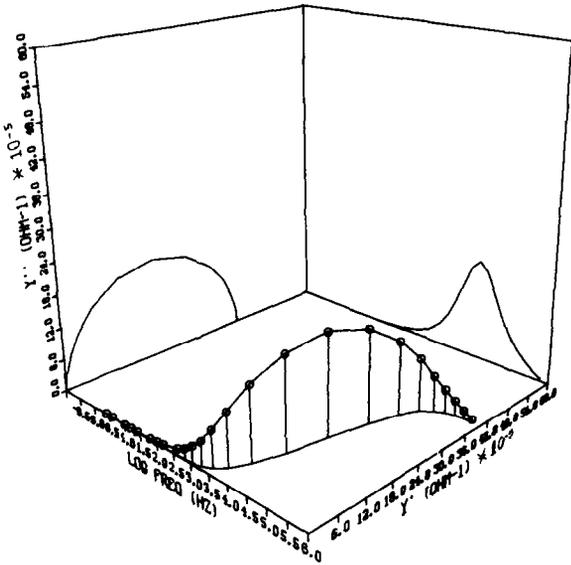


Fig. 2. 3-D admittance spectra of $Pb_{1-x}U_xF_{2+2x}$. Frequency range 0.3 Hz to 30 kHz. (a) $x=0.10$, $T=307\text{ K} (< T_c)$; (b) $x=0.015$, $T=773\text{ K} (> T_c)$.

for T_c given here represent those temperatures at which in the conductivity plots a negative deviation from Arrhenius behaviour starts to occur.

The results of the specific heat measurements are shown in fig. 5. It is clear that the heat content of the

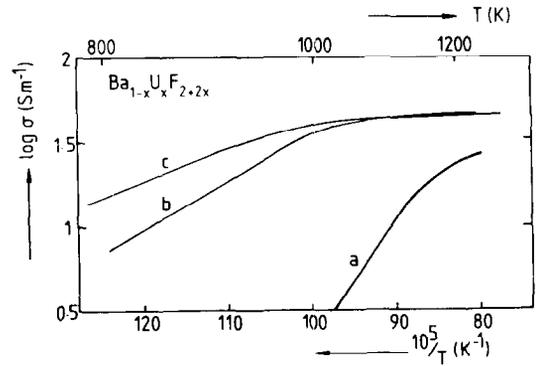


Fig. 3. The temperature dependence of the ionic conductivity of $Ba_{1-x}U_xF_{2+2x}$ solid solutions, plotted as $\log \sigma$ versus $10^5/T$. Temperature region 500–1000° C. (a) $x=0.005$; (b) $x=0.10$ and (c) $x=0.15$.

c_p -anomaly is an order of magnitude smaller in the solid solution $Pb_{0.9}U_{0.1}F_{2.2}$ as compared to undoped PbF_2 , i.e. $< 1\text{ kJ/mole}$ compared to 13.7 kJ/mole . Values for the temperature T_λ of the specific heat maximum are included in table 1. Both the critical temperatures T_c and T_λ decrease with increasing solute content. While the effect is small for the PbF_2 -based solid solutions, a maximum decrease of about 400° is achieved in the BaF_2 -based solid solutions. For these solid solutions the data indicate T_λ to level off at about 5 m/o UF_4 . In the range 5 to 15 m/o UF_4 T_c is found to decrease still 100° more before the 5 m/o UF_4 T_λ -value is reached.

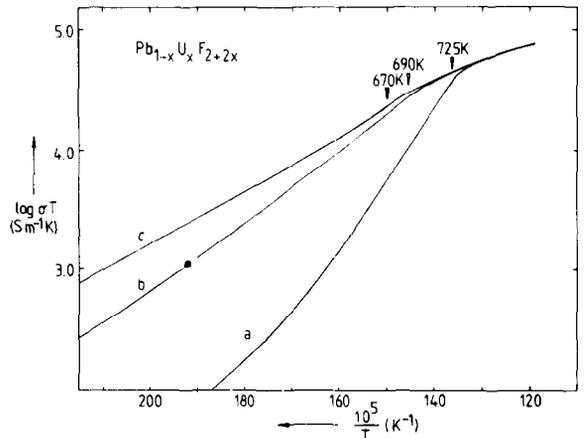


Fig. 4. The temperature dependence of the ionic conductivity of $Pb_{1-x}U_xF_{2+2x}$ solid solutions, plotted as $\log \sigma T$ versus $10^5/T$. (a) $x=0$; (b) $x=0.05$ and (c) $x=0.10$.

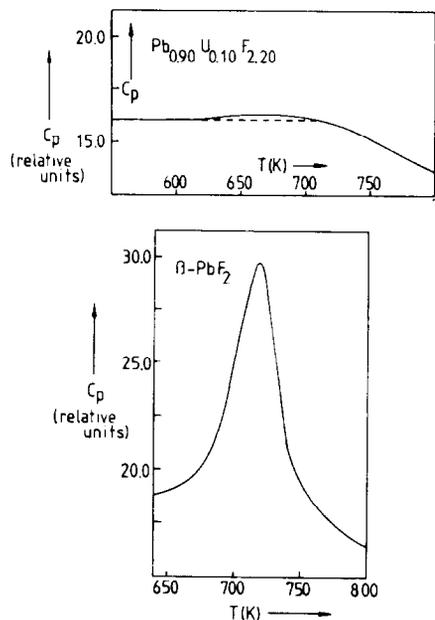


Fig. 5. Temperature dependence of the specific heat of β - PbF_2 and $\text{Pb}_{0.9}\text{U}_{0.1}\text{F}_{2.2}$. Both curves are on the same scale.

4. Discussion

The fluorite-type solid solutions $\text{Me}_{1-x}\text{Y}_x\text{F}_{2+x}$ ($\text{Me} = \text{Ca}, \text{Ba}$), $\text{Sr}_{1-x}\text{Gd}_x\text{Cl}_{2+x}$ [4,5], and the present solid solutions $\text{M}_{1-x}\text{U}_x\text{F}_{2+2x}$ ($\text{M} = \text{Ba}, \text{Pb}$) have in common that compared to the pure fluorites the Faraday transition occurs at lower temperatures. For dopant levels of about 9 m/o T_c decreases roughly 200° in $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$, and roughly 100° in $\text{Sr}_{1-x}\text{Gd}_x\text{Cl}_{2+x}$ [4,5]. An amount of 10 m/o UF_4 (20 m/o fluoride excess) causes T_c of BaF_2 to decrease with about 300° , and T_c of β - PbF_2 with about 50° . While the values for T_c could indicate that

the polarizability of the host lattice ions plays a role in the small depression of T_c of the solid solutions based on β - PbF_2 and SrCl_2 , we will focus the discussion on two effects, which have recently been proposed to result from extensive impurity defect clustering. Defect clustering is another common feature of these concentrated solid solutions, and the complex defect structure of the fluorite-type solid solutions with trivalent cationic dopants has been reviewed recently [11,12]. Wapenaar and Catlow [13,14] have studied the defect complexes in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ by computational methods and neutron scattering techniques. Although the defect structure of $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+2x}$ has not yet been studied, it is not unreasonable to assume that also in this material a variety of impurity defect complexes will exist. Hence, a substantial amount of the anion excess is bound, and not available for dc conduction in the fluorite-type solid solutions. Catlow et al. [4,5] have calculated that dopant-interstitial complexes will trap additional thermally generated interstitials to form negatively charged complexes in M^{3+} doped fluorites. There is no a priori reason why scavenging of fluoride interstitials by defect complexes in U^{4+} -doped fluorites shall not occur. This binding of thermally generated anion interstitials reduces the effective anti-Frenkel defect formation energy, and hence the temperature of the Faraday transition, provided that this transition can be associated with the generation of a critical concentration of anion vacancies, as has been proposed indeed by Catlow et al. [4,5]. In the calculations these authors used 3 and 7 m/o of anion vacancies to account for a decrease of T_c of about 100° in a solid solution for which the host lattice exhibits a Faraday transition at 1000 K and in which the binding energy for scavenged interstitials is 0.4 eV.

Several experimental observations seem to be in conflict with this model. This model assumes implicitly considerable thermal stability of impurity defect complexes. Recent conductivity studies on $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ [15] up to 1100 K indicate scavenged fluoride interstitials to dissociate from impurity defect complexes at temperatures well below T_c . The conductivity curves for $\text{Ca}_{1-x}\text{Y}_x\text{F}_{2+x}$ do not reveal an upward curvature, as one would expect when defect-defect interactions start to reduce the intrinsic defect formation energy.

The critical concentration concept applies to both pure and anion-excess fluorites. The present data for

Table 1

Values for the critical temperatures T_c and T_λ for some solid solutions $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+2x}$ and $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$

$\text{Pb}_{1-x}\text{U}_x\text{F}_{2+2x}$	T_c (K)	T_λ (K)	$\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$	T_c (K)	T_λ (K)
$x: 0$	725	720	$x: 0$	1250	1275
1×10^{-3}	720		5×10^{-3}	1140	
1.5×10^{-2}	700		5×10^{-2}	972	895
5×10^{-2}	690		1×10^{-1}	960	
1×10^{-1}	670	670	1.5×10^{-1}	860	885

$\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ reveal T_c to be 860 K for $x=0.15$. The experimental and theoretical value for an anti-Frenkel pair in BaF_2 is 1.90 eV [2]. With the critical concentration constraint one then obtains the value 1.31 eV for the anti-Frenkel pair formation enthalpy in $\text{Ba}_{0.85}\text{U}_{0.15}\text{F}_{2.30}$. Catlow et al. [2] have calculated the (anti-)Frenkel pair formation energy to be 1.0 eV for unit interstitial concentration with normal lattice parameter, and with an ordered arrangement of the defects. When lattice anharmonicity is simulated by expanding the lattice parameter of this hypothetical structure 3%, than the Frenkel pair formation energy is 1.2 eV. These energy values suggest indeed that the concentrated BaF_2 -based solid solutions will contain substantial thermal disorder. Yet the extrinsic conductivity of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ (fig. 3) does not reveal an upward curvature on approaching T_c . It is well known that impurity-interstitial complexes are stabilized by coupled-lattice-interstitial relaxations [16]; for instance, two $(\text{Y}_{\text{Ca}}\text{F}_i)^{\times}$ pairs can dimerize to form an aggregate which is stabilized by $\langle 111 \rangle$ displacements of two nearest lattice anions to form the so-called 222-cluster. The L-shaped $(\text{U}_{\text{Ba}}2\text{F}_i)'$ aggregate is stabilized by similar $\langle 111 \rangle$ displacements to form a 122-cluster [10,13]. Therefore, the question arises as to whether such highly disordered solid solutions can accommodate some 7 m/o thermal anion vacancies. The microwave conductivity of undoped SrCl_2 at 1000 K (T_c) equals that of $\text{Sr}_{0.912}\text{Gd}_{0.088}\text{F}_{2.088}$ at 880 K (T_c) [5]. The same holds approximately for the present BaF_2 and $\beta\text{-PbF}_2$ -based solid solutions. This in turn means that either the critical vacancy concentration has to increase with decreasing T_c to compensate for the lower mobility values, or that the mobility of the current carrying defects has to increase with increasing solute content.

Enhanced ionic motion has indeed been proposed to occur in the fluorite-type solid solutions [6,10]. Characteristic for concentrated solid solutions is an exponential increase of the ionic conductivity with x , while simultaneously the conductivity activation enthalpy decreases linearly. The present solid solutions do not behave differently. Fig. 6 presents the conductivity enthalpy data against the fluoride excess along with literature data. In fig. 7 the isothermal conductivity (500 K) is plotted against the conductivity activation enthalpy. The solid line represents literature data, and has a slope $0.434/kT$, which is the

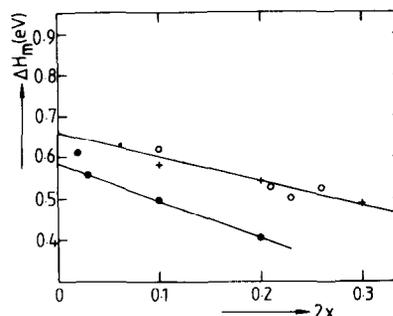


Fig. 6. The dependence of the conductivity activation enthalpy on the fluoride excess. (○) $\text{BaF}_2:\text{UF}_4:\text{CeF}_3$ (ref. [10]); (×) $\text{BaF}_2:\text{UF}_4$; (●) $\text{PbF}_2:\text{UF}_4$.

proportionality constant between $\log(\sigma T)$ and the enthalpy ΔH . In the enhanced ionic motion model [6,10] it is assumed that the mobility of a small and solute independent number of fluoride interstitials is determined by a distribution in the jump enthalpies, arising from the perturbations of the saddle point for interstitial migration by extended impurity defect complexes. With a Gaussian distribution one obtains

$$\sigma T = A_0 \exp\{-(kT)^{-1}[\overline{\Delta H_m} - (p^2/4kT)]\}, \quad (1)$$

where p stands for the width of the interaction energy distribution function, and $\overline{\Delta H_m}$ for the average activation enthalpy. p is proportional to the square root of the solute content, i.e. $p = C\sqrt{x}$ [10]. For the conduc-

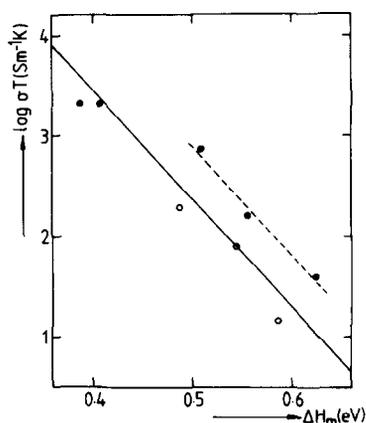


Fig. 7. Plot of the dependence of $\log \sigma T$ on the conductivity activation enthalpy at 500 K. (○) $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$, (●) $\text{Pb}_{1-x}\text{U}_x\text{F}_{2+2x}$. The solid line represents literature data for a variety of fluorite-type solid solutions, refs. [6,10].

tivity activation enthalpy

$$\Delta H = \overline{\Delta H_m}(-p^2/2kT) \quad (2)$$

is obtained from $\log \sigma T$ versus T^{-1} plots. A comparison of eqs. (1) and (2) gives for the measured value of the pre-exponential factor A :

$$\log A = \log A_0 - \frac{1}{9.2} \left(\frac{C}{kT} \right)^2 x. \quad (3)$$

The solid line in fig. 7 has been analysed in detail, and the data lead to the value 0.16 eV for C , and $5 \times 10^7 \text{ Sm}^{-1} \text{ K}$ for A_0 . ΔH_m has the value 0.714 eV [6]. In these solid solutions fast ionic conduction is due to ≈ 1 m/o fluoride interstitials. The present conductivity data indicate a similar free defect density to be present in $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ and $\text{Pb}_{0.9}\text{U}_{0.1}\text{F}_{2.2}$, while a larger free defect density seems to be present in the more dilute β - PbF_2 -based solid solutions. This deviation is currently being investigated. The extrinsic conductivity of $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ can now be used to calculate the mobility of the fluoride interstitials at T_c . For samples with $x=0.10$ and 0.15 we obtain $\approx 1 \times 10^{-6} \text{ m}^2/\text{Vs}$. For $\text{Pb}_{0.9}\text{U}_{0.1}\text{F}_{2.2}$ the fluoride interstitial mobility has the value $1.1 \times 10^{-6} \text{ m}^2/\text{Vs}$. The conductivity activation enthalpies for $\text{Ba}_{1-x}\text{U}_x\text{F}_{2+2x}$ are 0.542 eV ($x=0.10$), and 0.488 eV ($x=0.15$). The ratio between these activation enthalpies is equal to the ratio between the concomitant values for T_c , which follows from the usual Arrhenius relation with equal defect densities and conductivities (σT_c).

In pure BaF_2 and β - PbF_2 the concentration of fluoride interstitials is about 1 m/o, and about 0.5 m/o, respectively, at T_c , while the defect mobilities are comparable to ion mobilities in molten salts. In fact, for BaF_2 and β - PbF_2 mobility limits of $9 \times 10^{-7} \text{ m}^2/\text{Vs}$, and $1.5 \times 10^{-6} \text{ m}^2/\text{Vs}$, respectively, at T_c have been proposed [3]. It seems, therefore, that for both pure fluorites, and anion-excess fluorite-type solid solutions, the conductivity at T_c is governed by a relatively small defect density, together with liquid-like defect mobilities, a situation which favors the conductivity to level off. The preliminary specific heat data confirm that the thermal generation of defects in the solid solutions at T_c is not important. This is in line with the observation that T_c falls in the extrinsic

conductivity region. For the β - PbF_2 -based solid solutions, and to a lesser extent for the BaF_2 -based solid solutions, the extrinsic conductivity regions reveal an upward curvature. While this seems at first glance contradictory, it should be realized that the enhanced-ionic motion model itself introduces a temperature dependent pre-exponential factor as a consequence of the temperature dependence of the conductivity activation enthalpy, i.e. eqs. (1) and (2).

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