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Ionic transport studies in $Sn_{(1-x)}K_xF_{(2-x)}$ type solid electrolytes

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ABSTRACT

The ionic conductivity of $Sn_{(1-x)}K_xF_{(2-x)}$ systems has been investigated as a function of composition and temperature using complex impedance spectroscopy. These materials have been prepared by normal solid state reaction method and characterized through XRD and DSC. The highest conducting sample has been prepared through mechanochemical synthesis technique in addition to solid state reaction method. The universal scaling behavior of the real and imaginary part of the impedance including complex impedance plots indicating temperature independent relaxation behavior has been demonstrated. This result is further supported by the scaling behavior of the real part of the conductivity.

1. Introduction

Fluoride ion conducting materials are subject of long term investigation due to their promising applications in solid state ionic devices [1]. The motivation behind the present work on SnF_2 based systems is due to their high ionic conductivity value at room temperature and wide applications in chemical sensors [2]. Earlier reports on SnF_2-MF (M: Na, K, Rb, Cs, Tl and NH_4) systems had shown the existence of two kinds of compounds MSn_2F_5 and $MSnF_3$, out of which MSn_2F_5 is the best conducting one [3]. SnF_2 exists in three polymorphic forms (α, β and γ). Among these α-SnF_2 (monoclinic) is known to be stable at room temperature. It transforms to γ-SnF_2 (tetragonal) in the temperature range 413–453 K, which is stable up to the melting temperature (488 K) and upon cooling γ-SnF_2 transforms to β-SnF_2 (orthorhombic) at 340 K. β and γ phases of SnF_2 are mainly meta-stable at $T \leq 340$ K and $340 < T < 413$ K respectively and transforms back to α-phase by applying a small pressure [4]. KSn_2F_5 exhibits a superionic phase transition around 428 K associated with the reduction of the unit cell from $Z = 3$ to $Z = 1$ [5]. The present work is in continuation of our earlier work on ac conductivity and scaling studies of polycrystalline SnF_2 [6]. In this paper, we present the results obtained from the systematic investigation of (i) SnF_2 doped with KF of various concentrations ($0 \leq x \leq 0.1$), (ii) KSn_2F_5 ($x = 0.33$) and (iii) $KSnF_3$ ($x = 0.5$), using X-ray diffraction (XRD), differential scanning calorimetry (DSC), high resolution TEM (HR-TEM) and impedance spectroscopy. The conductivity of the present investigated materials has been studied as a function of composition, temperature and frequency. In addition, the sample KSn_2F_5 has also been prepared through mechanochemical synthesis technique (ball milling) along with the conventional solid state reaction method. This method has been known to produce ultra-fine powders, good for achieving high ionic conductivity and thus enhancing a good contact with electrode materials for solid state ionic devices. A comparative investigation of conduction characteristics of the same compound prepared by both the methods has been attempted. Further, in-depth analysis of the impedance data of KSn_2F_5 system has been undertaken to throw light on the dynamics of the fluoride ion transport.

In the case of ionic conductors, impedance data (Z^*) have been analyzed under conductivity, permittivity and modulus formalisms over a wide range of both frequencies and temperatures, to throw light on the relaxation properties of the material. Scaling studies are important in any physical measurement to get the common underlying behavior. In general, electrical conductivity (σ) and modulus (M^*) scaling studies have been adopted in the literature to show the temperature independent relaxation behavior [7]. For a given material, both σ and M^* spectra measured at various temperatures can be scaled to collapse into a single master curve [8]. The ac conductivity obtained at various temperatures follows a scaling law of the form:

$$\frac{\sigma}{\sigma_{dc}} = F\left(\frac{f}{f_0}\right) \quad (1)$$

Here f_0 is the characteristic frequency and F is the scaling function independent of temperature. Roling et al. have taken $\sigma_{dc}T$ as the scaling parameter for the frequency axis for the investigation of the temperature dependent conductivity scaling studies of sodium borate glass systems [9]. Later, others have extended the above scaling approach with parameters such as $\sigma_{dc}/(\varepsilon_0\Delta\varepsilon)$, where

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$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ representing the increase in the dielectric permittivity due to ionic relaxation and the hopping frequency, f_h in different glass systems [10,11]. The three scaling parameters, $\sigma_{dc}T$, $\sigma_{dc}/(\varepsilon_0\Delta\varepsilon)$ and f_h are correlated by the modified Nernst–Einstein relation [12]. In the case of fast ion conductors, most of the universal scaling work mainly focuses on the scaling of the conductivity and modulus data. However, the scaling of the fundamental impedance data is not reported. The advantage of studying the latter is that the scaling involves the dataset directly obtained from the impedance analyzer rather than the derived parameters (σ and M^*). In this regard, the present work also attempts at the scaling behavior of both real and imaginary part of impedance in addition to complex impedance plots of KSn_2F_5 at various temperatures.

2. Experimental details

$Sn_{(1-x)}K_xF_{(2-x)}$ systems were prepared at 523 K in the nitrogen (N_2, 99.999%) atmosphere by solid state reaction technique. For the preparation of KSn_2F_5 ($x = 0.33$) through mechanochemical synthesis technique, a high-energy planetary ball mill (*Insmart Systems*) operating at 300 rpm was used for 10 h keeping the weight ratio of the balls to materials as 10:1. The particle size of the mechanochemically synthesized sample was calculated using HR-TEM. XRD measurements were carried out using X-ray diffractometer (PANalytical X'pert PRO) with CuKα radiation ($\lambda = 1.5418$ Å). The samples were scanned in the 2θ range of 10–90°, at a step size of 0.016. Density measurements were carried out using Archimedes principle with xylene as the immersion liquid. DSC measurements were done using DSC200 PC-PHOX (NETSCH) instrument with a heating rate of 5 K/min. For the conductivity measurements, the samples were first pelletized with a diameter of 12 mm using die-plunger and then sintered at 423 K in the nitrogen atmosphere. Both the faces of the pellet serving as the electrodes were smeared with silver powder. Then the pellet was mounted in between finely polished silver electrode discs of the conductivity cell. In order to ensure good electrode–electrolyte contact, the electrodes were pressed by applying constant spring load. The sample was heated from outside by means of an external heater kept coaxially with the sample holder and the temperature of the sample was monitored by using chromel–alumel thermocouple positioned very close to the sample with an accuracy of ±1 K. All the measurements were carried out in nitrogen atmosphere. The ac impedance data for all the samples were obtained using HP4192A impedance analyzer over the temperature range of 313–473 K.

3. Results and discussion

3.1. XRD and DSC studies

XRD patterns of $Sn_{(1-x)}K_xF_{(2-x)}$ systems are displayed in Fig. 1. All the peaks could be indexed with respect to the relevant crystal structure. However, for clarity, the indexing has been displayed for only prominent peaks. XRD results indicate that SnF_2 doped with KF concentrations up to 10 mol% ($x = 0.1$) exhibit similar pattern as that of SnF_2. It is also seen that the highest intensity peak of SnF_2 (1 1 2) shows a significant shift with increase in KF dopant concentrations indicating that the dopant ions had been incorporated in the SnF_2 lattice rather than adhering as an absorbing species. However the presence of a small peak corresponding to KSn_2F_5 (spotted as * mark in Fig. 1) in the case of doped samples has not been ruled out. The lattice parameter values for un-doped SnF_2 are found to be; $a = 12.64$ Å, $b = 4.90$ Å and $c = 13.72$ Å, which increases with increase in KF dopant concentrations. Typically for 10 mol% KF doped SnF_2 sample, the lattice parameters are;

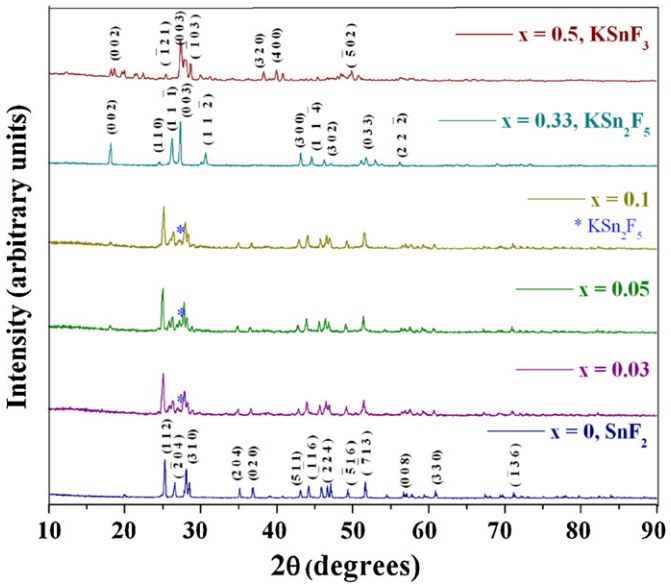

Fig. 1. XRD pattern of $Sn_{(1-x)}K_xF_{(2-x)}$ ($0 \le x \le 0.5$) systems, (a) $x = 0$, SnF_2, (b) $x = 0.03$, (c) $x = 0.05$, (d) $x = 0.1$, (e) $x = 0.33$, KSn_2F_5, and (f) $x = 0.5$, $KSnF_3$.

$a = 12.84$ Å, $b = 4.91$ Å and $c = 13.79$ Å. The increase in lattice parameters with increase in KF dopant concentrations can be possibly due to larger size of K^+ ion compared to the size of the Sn^{2+}cation.

Further, for the case of $x = 0.33$ and $x = 0.5$, the data is in agreement with the standard JCPDS values confirming the formation of KSn_2F_5 and $KSnF_3$ respectively. DSC spectra of $Sn_{(1-x)}K_xF_{(2-x)}$ systems are shown in Fig. 2. Features of DSC traces of the doped samples are similar to that of un-doped SnF_2 indicating an endothermic peak around 429 K due to α to γ phase transition and a peak at 493 K corresponding to the melting temperature of SnF_2. Further, DSC result of KSn_2F_5 shows an endothermic peak indicative of a phase transition at 430 K (Fig. 2(c)) in agreement with the literature [5].

3.2. Conductivity studies

The composition dependent transport parameters for $Sn_{(1-x)}K_xF_{(2-x)}$ systems are given in Table 1. It is clear from the table that (i) the conductivity of SnF_2 increases with increase in KF concentration up to $x = 0.1$, without any change in the structure of SnF_2. (ii) The sample KSn_2F_5 ($x = 0.33$) shows maximum

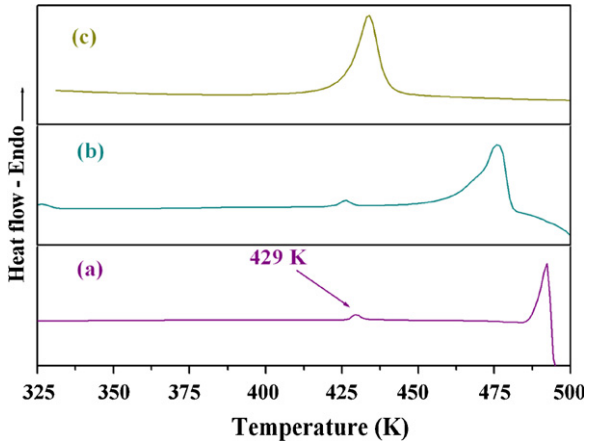

Fig. 2. DSC spectra of (a) SnF_2, (b) $0.9SnF_2$–0.1KF, and (c) KSn_2F_5.