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Comparison of superionic phases for some fluorine conducting materials

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Abstract

Impedance spectroscopy data for a several materials with high ionic conductivity in the temperature range 298–473 K were obtained and analyzed. Investigated systems included pure PbSnF_4 , KSn_2F_5 , RbSn_2F_5 and solid solutions based on PbSnF_4 and SnF_2 . The values of the dc conductivity and activation energies are estimated from the analysis of the conductivity spectra. The factors which influence on conductivity, phase transitions and activation energies in the given system have been established.

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1. Introduction

Solid state ionics mainly deals with the physics, chemistry and technological aspects of high ionic conduction in solids and has become a major area of research worldwide. The solids, exhibiting the high ionic conductivity are termed a superionic solids or solid electrolytes or fast ion conductors. Conductivity values of the most of superionic systems are not only closed to liquid electrolytes but remain stable over a fairly wide range of temperatures and there is a possibility of miniaturization for proper devices. For electrochemical device applications a solid electrolyte systems should possess the following properties [1-3]:

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- Ionic conductivity should be very high (approximately $10^{-4} - 10^{-1}$ S/cm) and electronic conductivity should be negligibly small ($<10^{-6}$ S/cm) at the ambient temperature.
- The activation energy should be very low (<0.5 eV).
- The primary charge carriers should be ions only, i.e. ionic transference number, $t_{\text{ion}} \cong 1$.

Fluoride ion conductors, which show the high value of ionic conductivity among the anionic conductors due to the small size of the anion, are found to be useful in following solid state ionic devices: solid state batteries, electrochromic devices, memory devices, solid state capacitors and gas sensors [1, 2].

2. Experiment

Polycrystalline samples were prepared by mixing stoichiometric amounts of the previously dried fluorides in a Nitrogen-filled dry box. These mixtures were then milled in vibrating mill and heated in quartz ampoule under vacuum at temperatures in the range 533–553 K for one hour. All compounds have been identified by X-ray diffraction method on the SMART 1000 CCD.

Two-terminal measurements of the ionic conductivity were performed using tablet-shaped samples (thickness 1–2 mm, diameter 13 mm) coated with conducting carbon paint DOTITE XC. A Solartron SI 1260 Impedance/Gain-Phase Analyzer with Dielectric Interface 1296 was used for obtaining the impedance measurements over the frequency range from 1 Hz to 7 MHz with logarithmic sweep 7 point per decade. All measurements were performed in a He inert atmosphere, in temperature range 296–473 K. Temperature monitoring was achieved using LakeShore 332 temperature controller with nickel-chromium thermocouple.

Activation energy E_a was calculated by means of the relation:

$$\sigma = A \exp(-E_a/kT),$$

where σ is dc conductivity calculated from real part of impedance spectra in Bode plot using equivalent circuit and counted including geometric factor, A is pre-exponential factor, k is Boltzmann constant and T is temperature in K [2].

3. Results and discussions

We found during investigation of $(1-x)\text{SnF}_2-x\text{MF}$ ($\text{M}=\text{Li}, \text{Rb}, \text{K}, \text{Cs}, \text{Na}; x=0.05, 0.07, 0.1$) the presence of a new phases: RbSn_2F_5 , KSn_2F_5 , CsSn_2F_5 , Cs_2SnF_6 and NaSn_2F_5 for respective doped elements [4,6, 7].

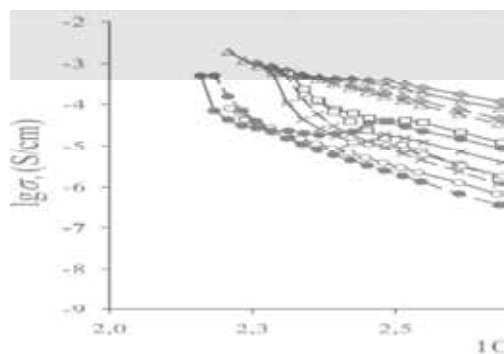


Fig. 1. Arrhenius plots of the $0.9\text{SnF}_2-0.1\text{MF}$ ($\text{M}=\text{Rb}, \text{K}, \text{Cs}, \text{Na}, \text{Li}$) in temperature range of 298–463 K

According to literature data RbSn_2F_5 and KSn_2F_5 phases have the highest ionic conductivity among other fluorides [5]. To compare these phases a pure one using mole ratio $x=33.3$ was synthesized.

Analysis of the experimental data (fig. 1) led us to conclude that the observed changes in conductivity and width of a hysteresis at all temperatures related with increasing ionic radius of dopant content ($\text{Li} \rightarrow \text{Cs}$). In addition a presence of high conductivity phases lead to increase total ionic conductivity of the system.

Any phases like in the system based on SnF_2 were not detected during investigation of $\text{PbSnF}_4\text{-MF}$ ($\text{M}=\text{Li}, \text{Cs}, \text{Rb}, \text{Ca}$). Doping has shown the positive influence on ionic movement only in case $(1-x)\text{PbSnF}_4\text{-xLiF}$ with $x=0.1, 0.05$. Addition of investigated fluorides with ionic radius more than Li (i.e. Ca) and variation of its concentration affects negatively on general electroconductivity but made the temperature dependence of conductivity more smoothness in some cases (fig. 2). It is explained by high polarization ability of the lithium ions.

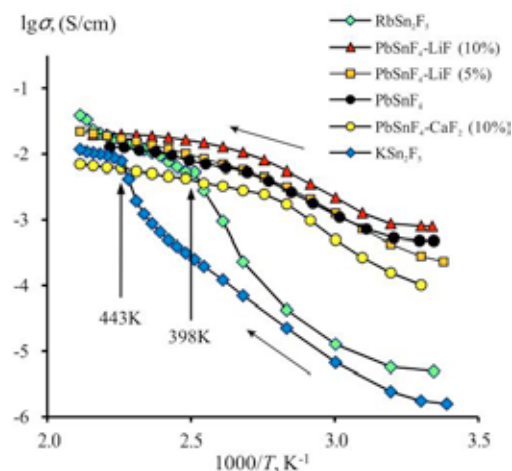


Fig. 2. Comparison of conductivity dependence versus temperature data of investigated superionic materials with indicated phase transition's temperatures for KSn_2F_5 and RbSn_2F_5

Following table presents the electrolytic properties of investigated materials, estimated from impedance spectra. Activation energies were calculated from linear segments of Arrhenius plots.

Table 1. Electrolytic properties of investigated materials

Sample	ΔT , K	E_a , eV	σ , S/cm at (T , K)
PbSnF_4	312–370	0.40 ± 0.01	$1.51 \cdot 10^{-3}$ (300)
	382–441	0.18 ± 0.01	$1.68 \cdot 10^{-2}$ (371)
			$4.01 \cdot 10^{-2}$ (451)
$\text{PbSnF}_4\text{-LiF}$ (10%)	313–383	0.44 ± 0.01	$1.26 \cdot 10^{-3}$ (300)
	373–433	0.18 ± 0.01	$3.43 \cdot 10^{-2}$ (373)
			$6.30 \cdot 10^{-2}$ (463)
$\text{PbSnF}_4\text{-RbF}$ (5%)	322–411	0.36 ± 0.01	$5.61 \cdot 10^{-4}$ (300)

<i>PbSnF₄-RbF (5%)</i>	411–451	0.24±0.01	5.61·10 ⁻⁴ (300)
			5.90·10 ⁻³ (373)
			2.87·10 ⁻² (451)
<i>PbSnF₄-CsF (15%)</i>	323–383	0.16±0.02	7.37·10 ⁻⁵ (297)
			3.30·10 ⁻³ (373)
			1.50·10 ⁻² (451)
<i>RbSn₂F₅</i>	373–433	0.34±0.03	1.57·10 ⁻⁵ (300)
			7.30·10 ⁻⁴ (373)
			7.44·10 ⁻² (463)
			1.25·10 ⁻¹ (473)
<i>KSn₂F₅</i>	443–473	0.22±0.02	5.04·10 ⁻⁶ (295)
			2.21·10 ⁻⁴ (371)
			3.29·10 ⁻² (463)
			3.73·10 ⁻² (473)

4. Conclusions

A group of perspective fluorine materials with high ionic conductivity were investigated. The electrophysical properties, behavior of ionic conductivity, phase transitions and activation energies in the given system have been established. It has been shown that these materials have a high ionic conductivity especially RbSn₂F₅ with $\sigma = 1.25 \cdot 10^{-1}$ S/cm at 473 K and 0.9PbSnF₄–0.1LiF with $\sigma = 6.3 \cdot 10^{-2}$ S/cm at 463 K.

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