ELSEVIER

SciVerse ScienceDirect

Physics Procedia 23 (2012) 94 – 97

Physics Procedia

Asian School-Conference on Physics and Technology of Nanostructured Materials
(ASCO-NANOMAT 2011)

Comparison of superionic phases for some fluorine conducting materials

A.B. Podgorbunsky*, S.L. Sinebryukhov, S.V. Gnedenkov

Institute of Chemistry, 159 prospect 100-letiya Vladivostoku, Vladivostok 690022, Russia

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.

Keywords: impedance spectroscopy; superionic conductors; fluorine materials; anion conductivity

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]:

* Corresponding author. Tel.: +7-423-231-1889; fax: +7-423-231-2590.
E-mail address: defrag_2008@mail.ru.

doi:10.1016/j.phpro.2012.01.024

- 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, $t_{ion} \cong 1$.

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 milted 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 using 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)SnF_2-xMF (M=Li, Rb, K, Cs, 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].

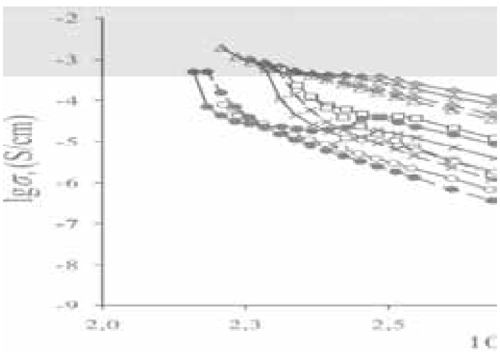

Fig. 1. Arrhenius plots of the 0.9SnF_2-0.1MF (M=Rb, K, Cs, Na, Li) in temperature range of 298–463 K

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 (Li → 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 $PbSnF_4$–MF (M=Li, Cs, Rb, Ca). Doping has shown the positive influence on ionic movement only in case (1-x)$PbSnF_4$–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.

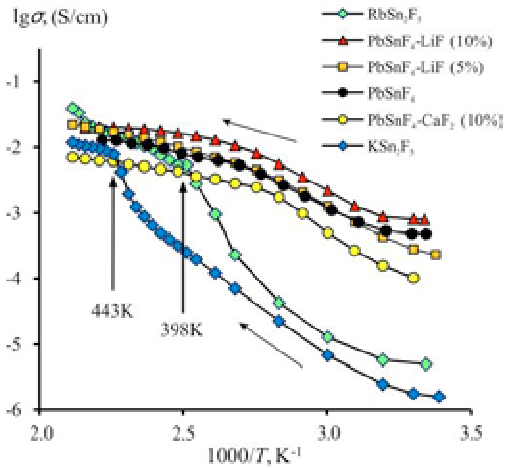

Fig. 2. Comparison of conductivity dependence versus temperature data of investigated superionic materials with indicated phase transition's temperatures for KSn2F5 and RbSn2F5

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	$1.51\cdot10^{-3}$ (300)
	382–441	0.18±0.01	$1.68\cdot10^{-2}$ (371)
			$4.01\cdot10^{-2}$ (451)
$PbSnF_4$-LiF (10%)	313–383	0.44±0.01	$1.26\cdot10^{-3}$ (300)
	373–433	0.18±0.01	$3.43\cdot10^{-2}$ (373)
			$6.30\cdot10^{-2}$ (463)
$PbSnF_4$-RbF (5%)	322–411	0.36±0.01	$5.61\cdot10^{-4}$ (300)

$PbSnF_4$-RbF (5%)	411–451	0.24±0.01	$5.61\cdot10^{-4}$ (300) $5.90\cdot10^{-3}$ (373) $2.87\cdot10^{-2}$ (451)
$PbSnF_4$-CsF (15%)	323–383 403–453	0.16±0.02 0.68±0.01	$7.37\cdot10^{-5}$ (297) $3.30\cdot10^{-3}$ (373) $1.50\cdot10^{-2}$ (451)
$RbSn_2F_5$	373–433	0.34±0.03	$1.57\cdot10^{-5}$ (300) $7.30\cdot10^{-4}$ (373) $7.44\cdot10^{-2}$ (463) $1.25\cdot10^{-1}$ (473)
KSn_2F_5	443–473	0.22±0.02	$5.04\cdot10^{-6}$ (295) $2.21\cdot10^{-4}$ (371) $3.29\cdot10^{-2}$ (463) $3.73\cdot10^{-2}$ (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 $RbSn_2F_5$ with $\sigma = 1.25\ 10^{-1}$ S/cm at 473 K and $0.9PbSnF_4$–0.1LiF with $\sigma = 6.3\ 10^{-2}$ S/cm at 463 K.

Acknowledgements

This work was supported by grant of Presidium FEB RAS № 12-III-B-04-041. Authors would like to thanks V.Ya. Kavun and V.K. Goncharuk for synthesis of fluorine materials and fruitful discussion of the obtained results.

References

[1] Agrawal R.C., Gupta R.K. Review Superionic solids: composite electrolyte phase – an overview. *J. Materials Science* 1999;**34**:1131-1162.

[2] Ivanov-Schitz A.K., Murin I.V. Solid State Ionic vol. 2. *SPb University press*, 2010.

[3] Ahmad M.M., Hefni M.A., Moharram A.H., Shurit G.M., Yamada K., Okuda T. Fluoride ion dynamics and relaxation in KSn_2F_5 studied by ^{19}F nuclear magnetic resonance and impedance spectroscopy. *J. Of Physics: Condensed Matter* 2003;**15**:5341-5352.

[4] Patro L.N., Hariharan K. Frequency dependent conduction characteristics of mechanochemically synthesized $NaSn_2F_5$. *J. Materials Science and Engineering* B 2009;**162**:173.

[5] Berastegui P., Hull S., Eriksson S.G. A high temperature superionic phase of $CsSn_2F_5$. *Journal of Solid State Chemistry* 2010;**183**:154-155.

[6] Yamada K., Ahmad M.M., Ohkia H., Okuda T., Ehrenbergb H., Fuess H. Structural phase transition of the two-dimensional fluoride ion conductor KSn_2F_5 studied by X-ray diffraction. *Solid State Ionics* 2004;**167**:301-307.

[7] Podgorbunsky A.B., Sinebrukhov S.L., Gnedenkov S.V., Goncharuk V.K., Kavun V.Ya., Usoltseva T.I. The influence of fluoride of first group elements on ionic conductivity in SnF_2-MF system. *Vestnik DVO RAN* 2010;**5**:12-17.