Lithuanian Journal of Physics, Vol. **47**, No. 3, pp. 315–319 (2007) doi:10.3952/lithjphys.47304

ELECTRICAL PROPERTIES OF MONAZITE-TYPE SUPERIONIC CERAMICS IN THE 10^6–$1.2{\cdot}10^9$ Hz FREQUENCY RANGE [*]

E. Kazakevičius [a], T. Šalkus [a], A. Kežionis [a], A. Dindune [b], Z. Kanepe [b], J. Ronis [b], and A.F. Orliukas [a]

[a] *Faculty of Physics, Vilnius University, Saulėtekio 9, LT-10222 Vilnius, Lithuania*
E-mail: tomas.salkus@ff.vu.lt
[b] *Institute of Inorganic Chemistry at the Riga Technical University, Miera 34, LV-2169 Salaspils, Latvia*

Received 11 June 2007

The high temperature solid electrolyte $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ compound was synthesized by a solid state reaction and studied by X-ray diffraction and IR spectroscopy. At room temperature the investigated compound has monazite-type structure and belong to monoclinic symmetry (space group $P2_1/n$) with four formula units in the lattice. The ceramic samples were sintered at 1273 K varrying the sintering duration. Complex impedance spectroscopy was performed in the frequency range from 10^6 to $1.2{\cdot}10^9$ Hz at temperatures ranging from 300 to 600 K. A relaxation dispersion related to the fast Li^+ ion transport was found. The results of the electrical measurements were compared to the ones of $Li_3Ce_2(PO_4)_3$ compound and it was shown that the partial isomorphous substitution of Ce^{3+} by Sc^{3+} leads to significantly higer ionic conductivity.

Keywords: ionic conductivity, permittivity, relaxation dispersion, synthesis, ceramic, sintering

PACS: 61.10.Nz, 66.30.Hs, 81.05.Je, 82.45.Yz

1. Introduction

Lithium ion solid electrolytes can be used for development of high energy batteries [1, 2] and sensitive CO_2 gas sensors [3, 4]. The compounds of $LiGe_2(PO_4)_3$, $LiTi_2(PO_4)_3$ with NASICON-type crystal structure are known as low temperature solid electrolytes with fast Li^+ ion transport [5–9]. The conductivity of the abovementioned compounds was improved by several orders of magnitude by partial substitution of Ge^{4+} and Ti^{4+} with Fe^{3+}, Sc^{3+}, Al^{3+}, Y^{3+}, B^{3+}, In^{3+}, Ga^{3+}, Cr^{3+} cations [10–17]. It was shown that conductivity of $Li_3Sc_2(PO_4)_3$ was increased by partial isomorphous substitution of triple valence Sc^{3+} by B^{3+} [18].

$Li_3Ce_2(PO_4)_3$ was also proved to be a Li^+ ion conductor, however, its conductivity at 600 K is only $2.4{\cdot}10^{-4}$ $S{\cdot}m^{-1}$ [19]. The XPS indicate that cerium exists as Ce(III) with no Ce(IV) in investigated crystals [19]. Authors of [20] reported the results of partial substitution of Ce^{3+} by Sc^{3+}, but there was a great deficiency of lithium (indicated as $\Box$ in the paper) in the obtained $Li_{1.3}\Box_{1.7}Sc_{0.3}Ce_{1.7}(PO_4)_3$ compound, which possibly caused the formation of PO_3^- groups in the material, lowering the sintering temperature of the ceramics, and the conductivity increase was not significant.

In this work a new compoud $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ was syntesized and studied by XRD, IR, and complex impedance spectroscopy.

2. Experimental

The powder of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ was synthesized from a mixture of CeO_2, Li_2CO_3 (of 99.999% purity), Sc_2O_3 (99.99%), and $NH_4H_2PO_4$ (extra pure) by solid state reaction. The mixture was milled as emulsion with ethyl alcohol in a planetary mill with one milling ball of 52 mm in diameter and then heated at 773 K for 3 h. Thereafter the mixture was milled, heated at 1173 K for 1 h, then milled and heated at 1173 K for 3 h again. Finally the mixture was milled for 8 h and dried at temperature 393 K for 24 h.

The structure parameters were obtained at room temperature from the X-ray powder diffraction patterns. The measurement was recorded with a step of 1 degree/min in the region of $2\Theta = 6$–80 degrees using Cu $K_\alpha 1$ radiation. The material was examined at the chemical bonding level by infrared (IR) spectroscopy (SPECORD).

---

[*] The report presented at the 37th Lithuanian National Physics Conference, 11–13 June 2007, Vilnius, Lithuania.

ISSN 1648-8504

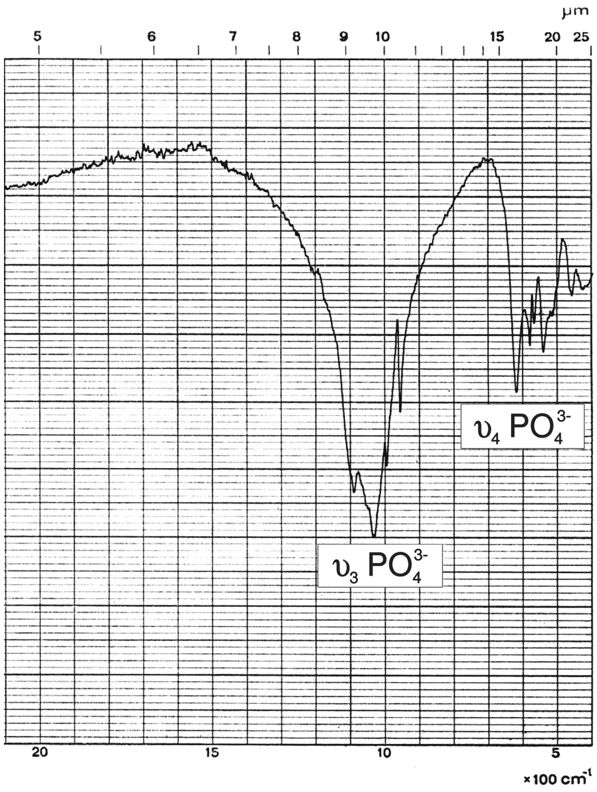

Fig. 1. IR spectrum of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ at room temperature.

The powder was uniaxially cold pressed at 300 MPa. The sintering of the ceramics was conducted in air at temperature 1273 K for 1 h and 5 h.

Complex conductivity $\tilde{\sigma} = \sigma' + \mathrm{i}\sigma''$, complex impedance $\tilde{Z} = Z' + \mathrm{i}Z''$, and complex dielectric permittivity $\tilde{\varepsilon} = \varepsilon' - \mathrm{i}\varepsilon''$ were measured on cooling the sample from 600 down to 300 K in the frequency range from 10^6 to $1.2{\cdot}10^9$ Hz by coaxial impedance spectrometer set-up [15]. Pt paste was used to form electrodes on the ceramic samples. The measurements were carried out in air.

3. Results and discussion

IR spectrum of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ is identical to $CePO_4$ spectrum [21] and is typical of orthophosphate compounds (Fig. 1). It shows very strong absorption bands belonging to ν_3 PO_4^{3-} vibrations (950–1090 cm^{-1}) and weaker bands assigned to ν_4 PO_4^{3-} (550–620 cm^{-1}) vibrations. The absorbtion bands which could be assigned to PO_3^- groups were not found.

The results of the X-ray diffraction study have shown that $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ powder is a single phase material. The compound has typical monazite-type structure of $CePO_4$ and belong to the monoclinic symmetry (space group $P2_1/n$) with four formula units in the lattice. The lattice parameters were found to be $a = 6.799(1)$ Å, $b = 7.023(1)$ Å, $c = 6.489(1)$ Å, $\beta = 103.465(14)°$, and the unit cell volume is $V = 300.38$ Å^3. The values of lattice parameters and the volume of the unit cell are bigger compared to $Li_3Ce_2(PO_4)_3$ material [19]. The theoretical density of the compound is $d_{\text{X-ray}} = 4.11$ g/cm^3. The densities of the ceramic samples reach about 90% of the theoretical density.

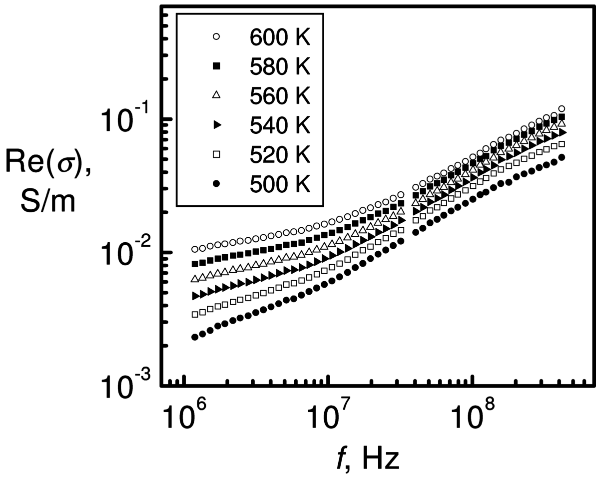

Fig. 2. Frequency dependences of the real part of conductivity of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics (sintering duration 5 h) measured at different temperatures.

The characteristic frequency dependences of the real part of $\tilde{\sigma}$ of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics sintered for 5 h and measured at different temperatures are shown in Fig. 2. A dispersion region was found in σ' spectra. The shift of the dispersion region towards higher frequencies with the increase of temperature is a typical peculiarity of relaxation process and this dispersion was attributed to the fast Li^+ ion motion in the investigated material. The temperature dependences of ionic conductivities (σ) of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics were derived from complex plots of $Z''(Z')$ at different temperatures as shown in Fig. 3. The temperature dependences of σ are shown in Fig. 4. The changes of σ with temperature have been described according to the Arrhenius law:

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right), \qquad (1)$$

where σ_0 is preexponential factor, ΔE is activation energy of ionic conductivity, k is Boltzmann's constant, T is temperature. The comparison of electrical parameters of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ and host compound $Li_3Ce_2(PO_4)_3$ [19] ceramics is presented in Table 1. The enhancement of conductivity of the investigated ce-

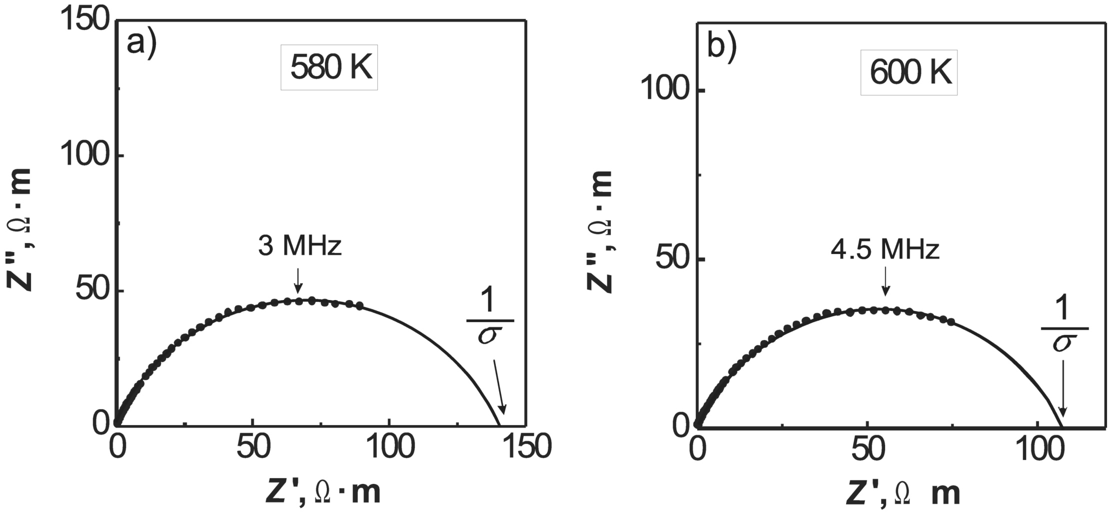

Fig. 3. Complex plane plots of impedance of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics sintered for 5 h measured at (a) 580 and (b) 600 K.

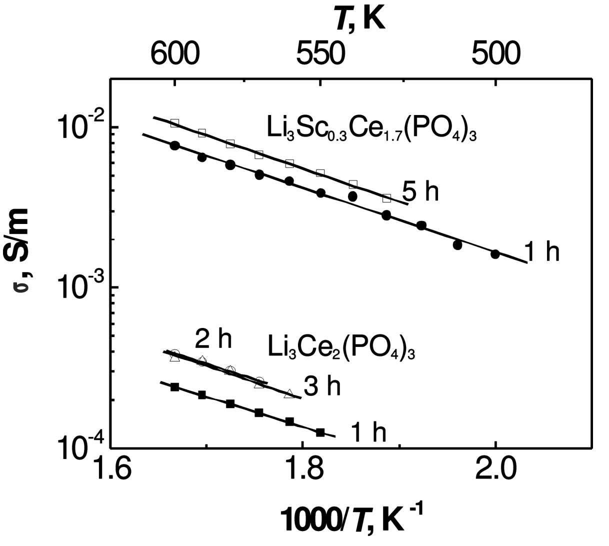

Fig. 4. Temperature dependences of conductivities of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ and $Li_3Ce_2(PO_4)_3$ [19] ceramics.

Table 1. Summary of electrical properties of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ and $Li_3Ce_2(PO_4)_3$ [19] ceramics sintered for different times (t_s).

Compound	t_s, h	σ, S/m (600 K)	ΔE, eV
$Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$	1	$7.7 \cdot 10^{-3}$	0.4
	5	$1.1 \cdot 10^{-2}$	0.41
	1	$2.4 \cdot 10^{-4}$	0.37
$Li_3Ce_2(PO_4)_3$	2	$3.9 \cdot 10^{-4}$	0.41
	3	$3.7 \cdot 10^{-4}$	0.39

ramics can be related to the expansion of the unit cell because of the partial substitution of Ce^{3+} cations by Sc^{3+}. We observe a slight increase of ionic conductivity of the ceramics sintered for a longer time, and this fact can be related to grain growth at the sintering temperature.

The temperature dependences of the real part of dielectric permittivity (ε') and dielectric losses ($\tan\delta = \varepsilon''/\varepsilon'$) were investigated at the frequency of 1 GHz. This frequency is higher than Maxwell relaxation frequency $f_M = \sigma/(\varepsilon'\varepsilon_0)$ (where $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m is dielectric constant of the vacuum). At 600 K temperature f_M of the ceramics sintered for 5 h was found to be 100.1 MHz. The temperature dependences of ε' and $\tan\delta$ of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics are shown in Fig. 5. The increase of the values of ε' with temperature of the investigated compound can be caused by contribution of the migration polarization of lithium ions, vibration of lattice, and electronic polarization. The increase of $\tan\delta$ with temperature is related to the contribution of conductivity in the investigated temperature region.

4. Conclusions

The solid electrolyte $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ compound has monazite-type structure and belongs to monoclinic symmetry (space group $P2_1/n$) with 4 formula units in the lattice. The obtained compound is a single phase material where phosphorus exists completely in the radical group PO_4^{3-}. The relaxation-type dispersion was found in the conductivity spectra and it was related to the lithium ion transport in the obtained ceramics. The conductivity of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ has higher values in the investigated temperature range compared to the host compound of $Li_3Ce_2(PO_4)_3$. At 600 K the value of ionic conductivity of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics, sintered for 5 h, was found to be $\sigma = 1.1 \cdot 10^{-2}$ S/m. The value of ε' at room temperature at 1 GHz frequency was found to be 9 and is caused by the polarization pro-

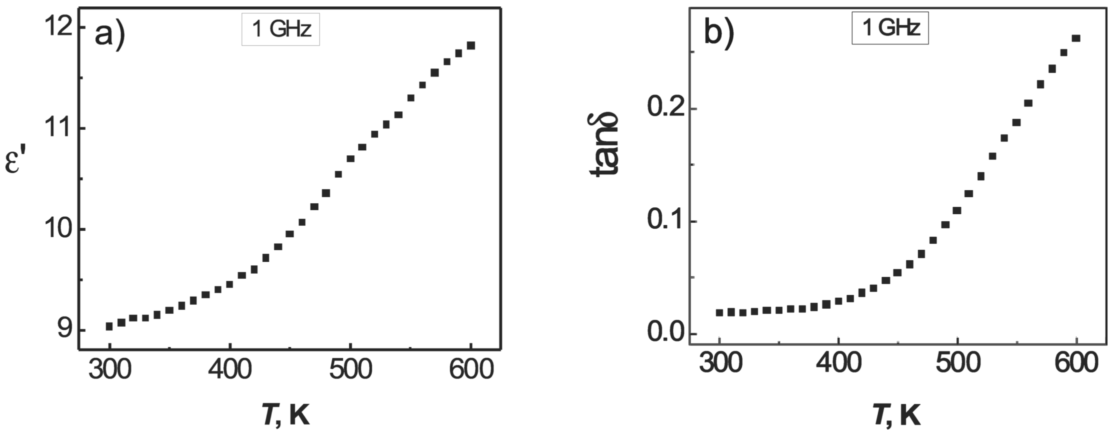

Fig. 5. Temperature dependences of (a) dielectric permittivity and (b) dielectric losses of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics measured at 1 GHz frequency.

cess due to migration of Li^+ ions, lattice vibrations, and electronic polarization.

References

[1] M. Broussely, J.P. Planckat, G. Rigobert, D. Virey, and G. Sarre, J. Power Sources **68**, 8–12 (1997).

[2] P. Birke, F. Salam, S. Doring, and W. Weppner, Solid State Ionics **118**, 149–158 (1999).

[3] W. Weppner, Ionics **5**, 355–359 (1999).

[4] A. Orliukas, J. Sinius, V. Kazlauskienė, and A. Kežionis, Mater. Sci. **8**, 65–67 (2002).

[5] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanoka, and G. Adachi, J. Electrochem. Soc. **137**, 1023–1027 (1990).

[6] S.-C. Li, J.-Y. Cai, and Z.-X. Lin, Solid State Ionics **28–30**, 1265–1270 (1988).

[7] Z.-X. Lin, H.-J. Yu, S.-C. Li, and S.-B. Tian, Solid State Ionics **31**, 91–94 (1988).

[8] M.A. Subramanian, R. Subramanian, and A. Clearfield, Solid State Ionics **18–19**, 562–569 (1986).

[9] S. Hamdoune, D. Tran Qui, and E.J.L. Schouler, Solid State Ionics **18–19**, 587–591 (1986).

[10] A. Dindune, Z. Kanepe, J. Ronis, E. Kazakevičius, A. Kežionis, and A. Orliukas, in: *Materials Engineering & Balttrib 2001, Materials of the Xth International Baltic Conference* (Riga Technical University, Riga, 2001) pp. 115–119 (2001).

[11] X.-X. Xu, Z.-Y. Wen, Z.-H. Gu, and Z.-X. Lin, Mater. Lett. **58**, 3428–3431 (2004).

[12] P. Maldonado-Manso, M.C. Martìn-Sedeño, S. Bruque, J. Sanz, and E.R. Losilla, Solid State Ionics **178**, 43–52 (2007).

[13] M. Cretin and P. Fabri, J. Eur. Ceram. Soc. **19**, 2931–2940 (1999).

[14] K. Arbi, M.G. Lazarraga, D. Ben Hassen Chehimi, M. Ayadi-Trabelsi, J.M. Rojo, and J. Sanz, Chem. Mater. **16**, 255–262 (2004).

[15] A.F. Orliukas, A. Kezionis, and E. Kazakevicius, Solid State Ionics **176**, 2037–2043 (2005).

[16] A.S. Best, M. Forsyth, and D.R. MacFarlane, Solid State Ionics **136–137**, 339–344 (2000).

[17] X. Xu, Z. Wen, J. Wu, and X. Yang, Solid State Ionics **178**, 29–34 (2007).

[18] A. Dindune, Z. Kanepe, J. Ronis, T. Salkus, A. Kezionis, E. Kazakevicius, and A.F. Orliukas, Phosphorus Res. Bull. **19**, 124–129 (2005).

[19] T. Salkus, A. Kezionis, A. Dindune, Z. Kanepe, J. Ronis, J. Miskinis, V. Kazlauskiene, L.J. Gauckler, U.P. Mucke, and A.F. Orliukas, J. Phys. Cond. Matter **19**, 106204-1–11 (2007).

[20] T. Šalkus, A. Dindune, Z. Kanepe, J. Ronis, A. Kežionis, E. Kazakevičius, L.J. Gauckler, U.P. Mucke, and A.F. Orliukas, Lithuanian J. Phys. **46**, 483–488 (2006).

[21] *Atlas Infrakrasnykh Spektrov Fosfatov. Ortofosfaty* (Nauka, Moscow, 1981) [in Russian].

MONAZITO GRUPĖS SUPERJONINIŲ KERAMIKŲ ELEKTRINĖS SAVYBĖS 10^6–1,2·10^9 Hz DAŽNIŲ RUOŽE

E. Kazakevičius [a], T. Šalkus [a], A. Kežionis [a], A. Dindune [b], Z. Kanepe [b], J. Ronis [b], A.F. Orliukas [a]

[a] *Vilniaus universiteto Fizikos fakultetas, Vilnius, Lietuva*
[b] *Rygos technikos universiteto Neorganinės chemijos institutas, Salaspilis, Latvija*

Santrauka

$Li_3Sc_{0,3}Ce_{1,7}(PO_4)_3$ junginys buvo susintetintas kietųjų fazių reakcijų metodu. Jo kristalinė sandara ištirta esant kambario temperatūrai Rentgeno spindulių difrakcijos nuo miltelių metodu. Nustatyta, kad tirtasis junginys priklauso monoklininei singonijai (erdvinė simetrijos grupė $P2_1/n$), o jo elementariojoje kristalinėje gardelėje yra 4 formuliniai vienetai. IR spektroskopijos metodu parodyta, kad fosforas šioje medžiagoje egzistuoja tik PO_4^{3-} grupėje. Buvo pagamintos tų kietųjų elektrolitų keramikos. Keramikų elektrinės savybės buvo tirtos impedanso spektroskopijos metodu, matuojant jų pilnutinę varžą, kompleksinį laidį ir kompleksinę dielektrinę skvarbą 10^6–1,2·10^9 Hz dažnio elektriniame lauke 300–600 K temperatūros intervale. Tirtose keramikose stebima relaksacinio tipo elektrinių parametrų dispersija, susijusi su Li^+ jonų pernaša. Išmatuotas jonų laidis tirtose keramikose yra maždaug 1,5 eilės didesnis, palyginus su $Li_3Ce_2(PO_4)_3$, o nedidelis laidžio padidėjimas padidinus keramikos kepinimo trukmę yra siejamas su kristalitų augimu kepinimo temperatūroje. Kai $T = 600$ K, keramikos, kurios kepinimo trukmė buvo 5 h, laidis $\sigma = 1{,}1\cdot10^{-2}$ S/m. Didėjant temperatūrai, keramikų ε' ir $\tan\delta$ didėja. Keramikų ε' dydį lemia ličio jonų migracinė, joninė tamprioji bei elektroninė poliarizacijos. Matuotų kietųjų elektrolitų dielektriniai nuostoliai yra dėl jų joninio laidumo kaitos.