ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 4. 2004

Synthesys and Electrical Properties of $Li_{1+x}Zr_{2-2x}Al_xTi_x(PO_4)_3$ Superionic Ceramics

Edvardas KAZAKEVIČIUS[1*], Antanas Feliksas ORLIUKAS[1], Algimantas KEŽIONIS[1], Laurynas JUCIUS[1], Antonija DINDUNE[2], Zaiga KANEPE[2], Janis RONIS[2]

[1] *Faculty of Physics, Vilnius University, Sauletekio al. 9, 10222, Vilnius, Lithuania*
[2] *Institute of Inorganic Chemistry, Riga Technical University, Miera str.34, LV-2169 Salaspils, Latvia*

Received 30 August 2004; accepted 12 October 2004

The compounds of the system $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ (where x = 0.1 – 0.3) were synthesized by a solid state reaction. The chemical composition and structure of the powder were studied by chemical analysis and X-ray diffraction. The ceramic samples were sintered and their electrical properties were investigated by complex impedance spectroscopy in the frequency range 1.0×10^6 Hz – 1.2×10^9 Hz and temperature range 300 – 600 K. Two relaxation dispersions related to the fast Li^+ ion transport in bulk and grain boundaries were found. The activation energy of the temperature dependent conductivity and relaxation frequency in bulk were obtained from the slops of Arrhenius plots. The values of the activation energy related to the bulk ionic conductivity and relaxation frequency in bulk were found to be very similar in each of the investigated materials. That can be attributed to the fact that the temperature dependences of bulk conductivity are caused only by the mobility of the fast Li^+ ions, while a number of charge carriers remains constant with temperature.

Keywords: Li ion solid electrolytes; ceramics; X-ray diffraction; high frequency impedance spectroscopy.

INTRODUCTION

The solid electrolyte with fast Li^+ ion transport emerget as attractive materials for applications in CO_2 gas sensors [1] and solid electrolyte batteries [2]. In present work we investigate Li^+ ion conductors based on $LiZr_2(PO_4)_3$ compound. The X-ray pattern of $LiZr_2(PO_4)_3$, prepared at (1323 – 1373) K, was highly distorted from rombohedral and possibly had a triclinic cell [3]. The results of X-ray diffraction from the powder study have shown that $LiZr_2(PO_4)_3$ belongs to rombohedral symmetry (lattice parameters a = 8.860 Å and c = 22.13 Å) [4]. At temperature (1423 – 1473) K sintered $LiZr_2(PO_4)_3$ pellets have a low conductivity (at room temperature the value of the ionic conductivity (σ) is lower than 10^{-7} S/m) [4]. The partial substitution of Zr^{4+} by Ti^{4+} and Sc^{3+} ions in the $LiZr_2(PO_4)_3$ compound causes the increase of the ionic conductivity and at room temperature the value of σ of $Li_{1.2}Sc_{0.2}Zr_{0.2}$ $Ti_{1.6}(PO_4)_3$ compound was found to be 1.2×10^{-2}S/m and its activation energy (ΔE) was 0.33 eV [4]. High ionic conductivity of substituted $LiZr_2(PO_4)_3$ compound stimulates further investigations of the electrical properties and peculiarities of ionic transport in a wide frequency range.

In the present work we report the conditions for the synthesis of the $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ (where x = 0.1 – 0.3) powder, sintering of the ceramic samples and the results of our investigations of X-ray diffraction from the powder, electrical properties of the ceramics in the frequency range from 10^6 Hz to 1.2×10^9 Hz and in the temperature range 300 – 600 K.

EXPERIMENTAL PROCEDURE

The powder of $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ (where x = = 0.1 – 0.3) has been synthesized from mixture of ZrO_2 (plasma synthesized nanodispersed powder), $Al_2O_3\cdot 2.5\,H_2O$ (99.9 %), Li_2CO_3 (99.999 %), TiO_2 and $NH_4H_2PO_4$ (extra pure) by solid-phase reaction. The mixture was heated for 20 h at a temperature T = 723 K, then milled in a planetary mill for 12 h. Obtained powder was heated for 8 h at T = 1273 K. After heating the powder was milled in a planetary mill for 8 h. The millings were carried out in ethyl alcohol. The final fine powder was dried at T = 393 K for 24 h. The average size of the powder grains was found to be ~1 μm. The structure parameters were obtained from the X-ray powder diffraction patterns in the region of $2\theta = 6 - 80$ degree with step of 1 degree/min measured at room temperature using $CuK_{\alpha 1}$ radiation. The results of chemical analysis have shown that in so synthesized compounds Al deviation is (Al = x – □, where □ = 0.03 – 0.09). The powder was uniaxially cold pressed at 300 MPa, and then sintered into the ceramic samples at T = 1673 K. The sintering was conducted in air for 1 h. The measurements of complex conductivity ($\tilde{\sigma} = \sigma' + \sigma''$), complex impedance ($\tilde{Z} = Z' + iZ''$), complex dielectric permittivity ($\tilde{\varepsilon} = \varepsilon' - i\varepsilon''$) were performed in a frequency range from 10^6 Hz to 1.2×10^9 Hz by coaxial impedance spectrometer set-up [5].

RESULTS AND DISCUSSION

The compounds of the $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ system were obtained by the substitution ($Zr^{4+} \rightarrow$ $\rightarrow Ti^{4+} + Al^{3+} + Li^+$) in $LiZr_2(PO_4)_3$. The results of the X-ray diffraction study have shown that $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ powder with x = 0.1, 0.2 and 0.3 are mainly single phase materials and belong to the rhombohedral symmetry (space group $R\bar{3}c$) with six formula units in the unit cell. A small amount of ZrP_2O_2 was detected in samples as impurities. The lattice parameters, unit cell volume and theoretical density of the compounds are presented in Table 1. The densities of the ceramics were found to be (80 – 85) % of theoretical density of the compounds.

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[*] Corresponding author. Tel.: +370-5-2366064; fax: +370-5-2366081.
E-mail address: *edvardas.kazakevicius@ff.vu.lt* (E. Kazakevičius)

Table 1. X-ray diffraction results of $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ compounds (where x = 0 – 0.3)

Compound	Lattice parameter, (Å)	Unit cell volume V, (Å^3)	Density d, (g/cm^3)
$LiZr_2(PO_4)_3$ [3]	$a = 8.8077$, $c = 22.715$	1526.05	3.10
$Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$	$a = 8.848(6)$, $c = 22.071(24)$	1496.46	3.09
$Li_{1.2}Zr_{1.6}Ti_{0.2}Al_{0.14}\square_{0.06}(PO_4)_3$	$a = 8.840(6)$, $c = 22.032(33)$	1490.96	3.03
$Li_{1.3}Zr_{1.4}Ti_{0.3}Al_{0.21}\square_{0.09}(PO_4)_3$	$a = 8.824(6)$, $c = 21.980(26)$	1482.08	2.98

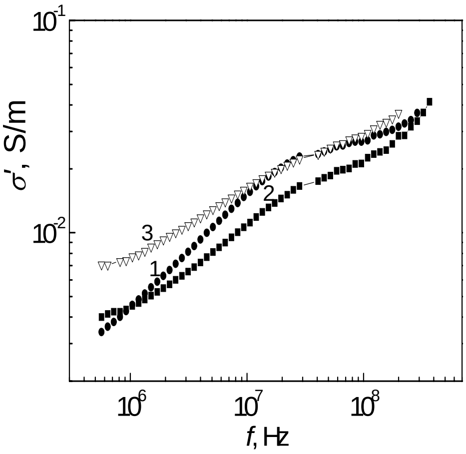

Fig. 1. Frequency dependences of σ' at $T = 370$ K:
$Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$ (1),
$Li_{1.2}Zr_{1.6}Ti_{0.2}Al_{0.14}\square_{0.06}(PO_4)_3$ (2),
$Li_{1.3}Zr_{1.4}Ti_{0.3}Al_{0.21}\square_{0.09}(PO_4)_3$ (3)

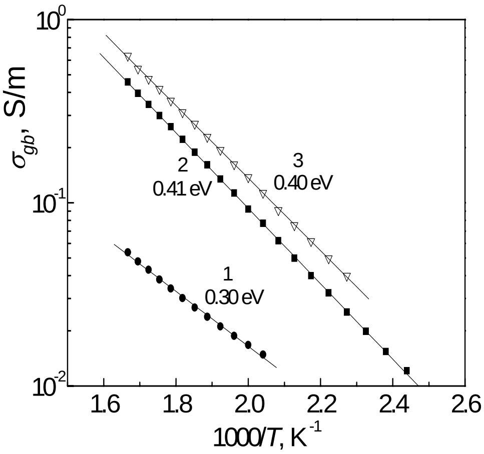

Fig. 3. Temperature dependences of σ_{gb}:
$Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$ (1),
$Li_{1.2}Zr_{1.6}Ti_{0.2}Al_{0.14}\square_{0.06}(PO_4)_3$ (2),
$Li_{1.3}Zr_{1.4}Ti_{0.3}Al_{0.21}\square_{0.09}(PO_4)_3$ (3)

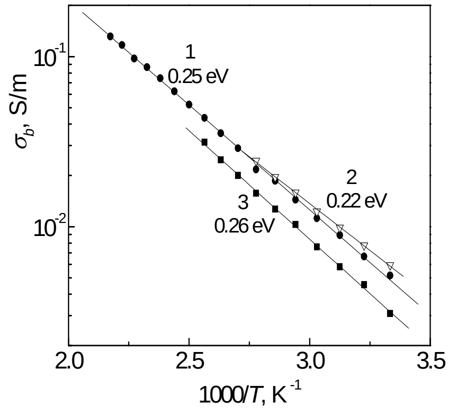

Fig. 2. Temperature dependences of σ_b:
$Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$ (1),
$Li_{1.2}Zr_{1.6}Ti_{0.2}Al_{0.14}\square_{0.06}(PO_4)_3$ (2),
$Li_{1.3}Zr_{1.4}Ti_{0.3}Al_{0.21}\square_{0.09}(PO_4)_3$ (3)

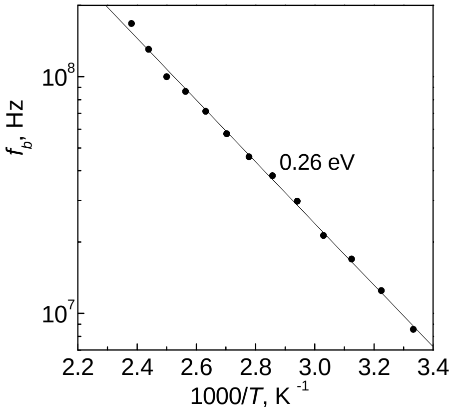

Fig. 4. Temperature dependence of the relaxation frequency f_b of the bulk conductivity of $Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$ compound.

Table 2. The values of σ_b, ΔE_b (at temperature $T = 300$ K) and σ_{gb}, ΔE_{gb} (at temperature $T = 500$ K) of the $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ compounds

Compound	σ_b, S·m^{-1}	ΔE_b, eV	σ_{gb}, S/m	ΔE_{gb}, eV
$Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$	$5.3\cdot10^{-3}$	0.25	$1.7\cdot10^{-2}$	0.30
$Li_{1.2}Zr_{1.6}Ti_{0.2}Al_{0.14}\square_{0.06}(PO_4)_3$	$3.4\cdot10^{-3}$	0.26	0.13	0.41
$Li_{1.3}Zr_{1.4}Ti_{0.3}Al_{0.21}\square_{0.09}(PO_4)_3$	$6.1\cdot10^{-3}$	0.22	0.17	0.40

The substitution of Zr^{4+} by Ti^{4+} and Al^{3+}in $LiZr_2(PO_4)_3$ causes the decrease of the cell parameters a, b, V and the density reduction of the compound. These variations are caused by the different value of the atomic radius of Zr, Ti and Al atoms. The atomic radius of Zr, Ti and of Al atoms are 1.6, 1.47 and 1.43 Å respectively [6].

The impedance investigation of the ionic conductors in the wide frequency range has an advantage, because it allows to separate charge transport processes in bulk and grain boundaries of the ceramics in a wide temperature range. The characteristic frequency dependences of the real part of $\tilde{\sigma}$ of $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ ceramics with different stoichiometric factor x at temperature $T = 370$ K are shown in Fig. 1. Two dispersion regions were found in the σ' spectra for all investigated samples. The dispersions are related to ion transport in the bulk and grain boundaries of the ceramics. Both dispersion processes are thermally activated and shift toward higher frequencies with increase of the temperature. The temperature dependences of the bulk (σ_b) and grain boundaries (σ_{gb}) conductivities of the ceramics were derived from the complex plots of $Z''(Z')$ and $\sigma''(\sigma')$ at different temperatures. The temperature dependences of σ_b and σ_{gb} of the $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ ceramic samples with different x are shown in Fig. 2 and Fig. 3 respectively. The activation energies of σ_b and of σ_{gb} were found from the slopes of the Arrhenius plots.

Varying x of the compounds affects the values of $\sigma_{gb,}$ σ_b and their activation energies ΔE_b and of ΔE_{gb} respectively. The increase of Li content in the $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ compounds leads to the increase of the values of σ_{gb} and decrease of ΔE_b. The results of the investigation of σ_{gb}, σ_b, ΔE_{gb} and ΔE_b of the compounds with different x are summarized in Table 2.

The characteristic frequencies of the relaxation processes in the bulk (f_b) of the compounds were obtained from the maximum of $Z''(f)$ curve at different temperature. The frequency of the relaxation dispersion exponentially increases with temperature. The typical temperature dependence of f_b of $Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$ compound is shown in Fig. 4.

The activation energies of f_b (ΔE_f) in $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$ compounds with different stoichiometric factor x were obtained from Arrhenius plots. The results of the investigation of $f_b(T)$ show, that values of ΔE_f coincide with values of ΔE_b for all compounds. This fact can be attributed to the temperature dependence of σ_b caused only by the mobility of the fast Li^+ ions, while number of charge carriers remains constant with temperature. Such ion transport features are dominant in the compounds with lithium [7, 8], sodium [9] fast ionic transport and oxygen solid electrolytes [10, 11].

CONCLUSIONS

The solid electrolyte $Li_{1.1}Zr_{1.8}Ti_{0.1}Al_{0.07}\square_{0.03}(PO_4)_3$, $Li_{1.2}Zr_{1.6}Ti_{0.2}Al_{0.14}\square_{0.06}(PO_4)_3$, $Li_{1.3}Zr_{1.4}Ti_{0.3}Al_{0.21}\square_{0.09}(PO_4)_3$ compounds have been synthesized by solid phase reactions and studied by the X-ray powder diffraction. The ceramics of the compounds were sintered in air for 1 h at temperature $T = 1673$ K and electrical properties of the ceramics were investigated by complex impedance spectroscopy in the frequency range from 10^6 to 1.2×10^9 Hz and in the temperature range from 300 to 600 K. Two regions of the impedance dispersion are analyzed in terms of the fast Li^+ ions transport in the bulk and grain boundaries of the ceramic samples. The temperature dependences of the bulk conductivity and relaxation frequency in the bulk have possessed by the same value of the activation energy. That suggests that fast Li^+ ion transport in the bulk of the compounds may be described mainly by the temperature dependent mobility, while concentration of mobile ions remains constant with temperature.

Acknowledgment

The Lithuanian State Science and Education Foundation supported this work under grant "Investigation of superionic conductors and solid state batteries".

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