Synthesy and Electrical Properties of Li$_{1+x}$Zr$_{2-2x}$Ti$_3$(PO$_4$)$_3$ Superionic Ceramics

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Received 30 August 2004; accepted 12 October 2004

The compounds of the system Li$_{1+x}$Zr$_{2-2x}$Ti$_3$(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 $1.0 \times 10^6$ Hz – $1.2 \times 10^9$ 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 slopes 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 emerge 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 rhombohedral 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 rhombohedral 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 ($\sigma$) 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 $\sigma$ of Li$_{1.2}$Sc$_{0.8}$Zr$_{0.2}$ Ti$_{1.2}$(PO$_4$)$_3$ compound was found to be 1.2×10$^{-7}$ S/m and its activation energy ($\Delta E$) 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$_3$(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 $1.2 \times 10^9$ Hz and in the temperature range 300 – 600 K.

EXPERIMENTAL PROCEDURE

The powder of Li$_{1+x}$Zr$_{2-2x}$Ti$_3$(PO$_4$)$_3$ (where $x = 0.1 – 0.3$) has been synthesized from mixture of ZrO$_2$ (plasma synthesized nanodispersed powder), Al$_2$O$_3$ $2.5$ H$_2$O ($99.9$ %), Li$_2$CO$_3$ ($99.999$ %), TiO$_2$ and NH$_4$H$_2$PO$_4$ (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 2θ = 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 ( $\bar{\sigma} = \sigma' + i\sigma''$ ), complex impedance ($\bar{Z} = Z' + iZ''$), complex dielectric permittivity ( $\bar{\varepsilon} = \varepsilon' - i\varepsilon''$ ) were performed in a frequency range from $10^6$ Hz to $1.2 \times 10^9$ Hz by coaxial impedance spectrometer set-up [5].

RESULTS AND DISCUSSION

The compounds of the Li$_{1+x}$Zr$_{2-2x}$Ti$_3$(PO$_4$)$_3$ system were obtained by the substitution (Zr$^{4+} \rightarrow Ti^{4+}$ + 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$_3$(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 $\overline{R}$3c) with six formula units in the unit cell. A small amount of Zr$_2$P$_2$O$_7$ 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.
Table 1. X-ray diffraction results of \( \text{Li}_{1-x} \text{Zr}_{2x} \text{Ti}_x \text{Al}_x (\text{PO}_4)_3 \) compounds (where \( x = 0 - 0.3 \))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameter, (Å)</th>
<th>Unit cell volume, ( V ), (Å(^3))</th>
<th>Density, (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LiZr}_2(\text{PO}_4)_3 ) [3]</td>
<td>( a = 8.8077, c = 22.715 )</td>
<td>1526.05</td>
<td>3.10</td>
</tr>
<tr>
<td>( \text{Li}<em>1 \text{Zr}</em>{1.8} \text{Ti}<em>0.2 \text{Al}</em>{0.07} \text{Li}_{0.03} (\text{PO}_4)_3 )</td>
<td>( a = 8.848(6), c = 22.071(24) )</td>
<td>1496.46</td>
<td>3.09</td>
</tr>
<tr>
<td>( \text{Li}<em>1 \text{Zr}</em>{1.6} \text{Ti}<em>0.4 \text{Al}</em>{0.14} \text{Li}_{0.06} (\text{PO}_4)_3 )</td>
<td>( a = 8.840(6), c = 22.032(33) )</td>
<td>1490.96</td>
<td>3.03</td>
</tr>
<tr>
<td>( \text{Li}<em>1 \text{Zr}</em>{1.4} \text{Ti}<em>0.6 \text{Al}</em>{0.21} \text{Li}_{0.09} (\text{PO}_4)_3 )</td>
<td>( a = 8.824(6), c = 21.980(26) )</td>
<td>1482.08</td>
<td>2.98</td>
</tr>
</tbody>
</table>

Fig. 1. Frequency dependences of \( \sigma' \) at \( T = 370 \) K:
\( \text{Li}_1 \text{Zr}_{1.8} \text{Ti}_0.2 \text{Al}_{0.07} \text{Li}_{0.03} (\text{PO}_4)_3 \) (1),
\( \text{Li}_1 \text{Zr}_{1.6} \text{Ti}_0.4 \text{Al}_{0.14} \text{Li}_{0.06} (\text{PO}_4)_3 \) (2),
\( \text{Li}_1 \text{Zr}_{1.4} \text{Ti}_0.6 \text{Al}_{0.21} \text{Li}_{0.09} (\text{PO}_4)_3 \) (3)

Fig. 2. Temperature dependences of \( \sigma_b \) of the bulk conductivity of \( \text{Li}_1 \text{Zr}_{1.8} \text{Ti}_0.2 \text{Al}_{0.07} \text{Li}_{0.03} (\text{PO}_4)_3 \) compound.

Fig. 3. Temperature dependences of \( \sigma_{gb} \) of \( \text{Li}_1 \text{Zr}_{1.8} \text{Ti}_0.2 \text{Al}_{0.07} \text{Li}_{0.03} (\text{PO}_4)_3 \) (1),
\( \text{Li}_1 \text{Zr}_{1.6} \text{Ti}_0.4 \text{Al}_{0.14} \text{Li}_{0.06} (\text{PO}_4)_3 \) (2),
\( \text{Li}_1 \text{Zr}_{1.4} \text{Ti}_0.6 \text{Al}_{0.21} \text{Li}_{0.09} (\text{PO}_4)_3 \) (3)

Fig. 4. Temperature dependence of the relaxation frequency \( f_b \) of \( \text{Li}_1 \text{Zr}_{1.8} \text{Ti}_0.2 \text{Al}_x (\text{PO}_4)_3 \) compounds.

Table 2. The values of \( \sigma_b, \Delta E_b \) (at temperature \( T = 300 \) K) and \( \sigma_{gb}, \Delta E_{gb} \) (at temperature \( T = 500 \) K) of \( \text{Li}_1 \text{Zr}_{1.8} \text{Ti}_0.2 \text{Al}_x (\text{PO}_4)_3 \) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \sigma_b ), S/m</th>
<th>( \Delta E_b ), eV</th>
<th>( \sigma_{gb} ), S/m</th>
<th>( \Delta E_{gb} ), eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}<em>1 \text{Zr}</em>{1.8} \text{Ti}<em>0.2 \text{Al}</em>{0.07} \text{Li}_{0.03} (\text{PO}_4)_3 )</td>
<td>( 5.3 \times 10^{-3} )</td>
<td>0.25</td>
<td>1.7 \times 10^{-2}</td>
<td>0.30</td>
</tr>
<tr>
<td>( \text{Li}<em>1 \text{Zr}</em>{1.8} \text{Ti}<em>0.2 \text{Al}</em>{0.14} \text{Li}_{0.06} (\text{PO}_4)_3 )</td>
<td>( 3.4 \times 10^{-3} )</td>
<td>0.26</td>
<td>0.13</td>
<td>0.41</td>
</tr>
<tr>
<td>( \text{Li}<em>1 \text{Zr}</em>{1.8} \text{Ti}<em>0.2 \text{Al}</em>{0.21} \text{Li}_{0.09} (\text{PO}_4)_3 )</td>
<td>( 6.1 \times 10^{-3} )</td>
<td>0.22</td>
<td>0.17</td>
<td>0.40</td>
</tr>
</tbody>
</table>
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 $\sigma$ of Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(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 $\sigma'$ 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 ($\sigma_b$) and grain boundaries ($\sigma_g$) conductivities of the ceramics were derived from the complex plots of $\sigma$($\sigma'$) at different temperatures. The temperature dependences of $\sigma_b$ and $\sigma_g$ of the Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(PO$_4$)$_3$ ceramic samples with different $x$ are shown in Fig. 2 and Fig. 3 respectively. The activation energies of $\sigma_b$ and of $\sigma_{gb}$ were found from the slopes of the Arrhenius plots.

Varying $x$ of the compounds affects the values of $\sigma_{gb}$, $\sigma_b$ and their activation energies $\Delta E_{gb}$ and of $\Delta E_b$ respectively. The increase of Li content in the Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(PO$_4$)$_3$ compounds leads to the increase of the values of $\sigma_{gb}$ and decrease of $\Delta E_b$. The results of the investigation of $\sigma_{gb}$, $\Delta E_{gb}$ and $\Delta E_b$ 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 $\sigma'$($f$) curve at different temperature. The frequency of the relaxation dispersion exponentially increases with temperature. The typical temperature dependence of $f_b$ of Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(PO$_4$)$_3$ compound is shown in Fig. 4.

The activation energies of $f_b$($\Delta E_b$) in Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(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 $\Delta E_b$ coincide with values of $\Delta E_b$ for all compounds. This fact can be attributed to the temperature dependence of $\sigma_b$ 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$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(PO$_4$)$_3$, Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(PO$_4$)$_3$, Li$_{1+x}$Zr$_{2-2x}$Ti$_x$Al$_x$(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 $1.2\times10^5$ 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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