X-RAY PHOTOELECTRON AND BROADBAND IMPEDANCE SPECTROSCOPY OF $\text{Li}_{1+4x} \text{Ti}_{2-x} (\text{PO}_4)_3$ SOLID ELECTROLYTE CERAMICS

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$\text{Li}_{1+4x} \text{Ti}_{2-x} (\text{PO}_4)_3$ (where $x = 0.2, 0.5$) compounds were synthesized by solid state reaction, and ceramics were sintered. The structure of compounds was studied by X-ray diffraction. Elemental compositions and binding energies of Ti 2p, P 2p, O 1s, and Li 1s core level at the surfaces of $\text{Li}_{1+4x} \text{Ti}_{2-x} (\text{PO}_4)_3$ ceramics were determined by energy dispersive X-ray spectrometer (EDX) and X-ray photoelectron spectroscopy (XPS). Impedance spectroscopy of the ceramics was performed in the frequency range of 10 Hz–1 MHz by the four-electrode method and in the frequency range of 1 MHz–3 GHz by the microwave impedance spectrometer. The measurements of electrical properties of the ceramics were carried out in the temperature interval of (300–700) K. The increase of the stoichiometric factor $x$ of the compounds leads to the increase of bulk conductivities and values of dielectric permittivity.

Keywords: XRD, SEM/EDX, XPS, ceramics, impedance spectroscopy, electric conductivity

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1. Introduction

A wide variety of Li$^+$ ion conducting compounds have been synthesized in the NASICON-type materials and are technologically important for applications as solid electrolytes for batteries and gas sensors $[1–4]$. The rhombohedral structured (space group R 3 c) $\text{LiTi}_2(\text{PO}_4)_3$ compound is a solid electrolyte with fast Li ion transport $[3–5]$. At room temperature the values of bulk and total conductivities were found to be $1 \cdot 10^{-2}$ S/m and $2 \cdot 10^{-3}$ S/m, respectively $[3]$. The bulk conductivity increase is a result from increase of Li$^+$ content in these compounds $[3]$. It makes them attractive materials for investigations of the dynamic properties associated with peculiarities of ionic migration. According to $[3, 4]$, in some NASICON-type compounds Li$^+$ ions occupy two different energy sites in the lattice what is typical of most NASICON conductors, but the results of nuclear magnetic resonance investigation have shown only one lithium site in the lattice $[7]$. High ionic conductivity of the above-mentioned NASICON-type structure solid electrolyte compounds stimulate further investigation of their electrical properties in the broadband frequency and temperature ranges and relationship between compositions and transport properties of the materials. For investigations, $\text{Li}_{1+4x} \text{Ti}_{2-x} (\text{PO}_4)_3$ (where
x = 0.2, 0.5) powders and ceramics were prepared. The results of the X-ray diffraction (XRD) study, scanning electron microscope with an attached energy dispersive X-ray spectrometer (SEM/EDX), X-ray photoelectron spectroscopy (XPS) of the surface of ceramics, and the results of investigation of the electrical properties of ceramics by impedance spectroscopy are presented.

2. Experiment

The stoichiometric mixture of Li$_4$CO$_3$ (purity 99.999%), extra pure NH$_4$H$_2$PO$_4$, and TiO$_2$ for the powder of Li$_{1+x}$Ti$_{2-x}$(PO$_4$)$_2$ (where x = 0.2, 0.5) synthesis was used. The powder was synthesized by solid state reaction. The mixture with stoichiometric amounts was placed into ethyl alcohol and milled for 8 hours in an agate mill. After milling, the mixture was heated for 20 h at the temperature $T = 723$ K. After heating, the mixture was placed into ethyl alcohol and this liquid was milled for 8 h in the planetary mill again. After this process the powder was heated for 8 h at $T = 1173$ K. The fine powder was dried at $T = 393$ K for 24 h. The structure parameters were obtained using the Brucker D8 Advance equipment at room temperature from the X-ray powder diffraction patterns in the region 20 = 6–80 degree, step 0.02 degree, time per step 1–8 sec, CuK$_\alpha$ radiation (40 kV, 40 mA). The lattice parameters were deduced by fitting the XRD patterns with software TOPAS v.4.1 and SCANIX v.2.16 (Matpol) [8]. SEM/EDX (TM3000, Hitachi) for analysis of chemical composition of investigated compounds was used. For investigation of SEM/EDX, XPS, and electrical properties the ceramic samples were sintered. The powder was uniaxially cold-pressed at 300 MPa. The sintering of Li$_{1+x}$Ti$_{2-x}$(PO$_4$)$_2$ ceramic samples with stoichiometric parameters x = 0.2, 0.5 were conducted in air at the temperature $T = 1363$ and 923 K, respectively. The sintering duration of ceramics was 1 h. The binding energies of the constituent elements of the surfaces of ceramics were examined by X-ray photoelectron spectroscopy as in [8] but the XPS was obtained by using Al K$_\alpha$ ($h\nu = 1486.6$ eV) radiation at an average of 30 scans with the step size of 0.05 eV. For the measurements of complex conductivity ($\sigma = \sigma' + i\sigma''$), complex specific electrical resistivity ($\rho = \rho' - i\rho''$), and complex dielectric permittivity ($\varepsilon = \varepsilon' - i\varepsilon''$) Pt electrodes were prepared. Pt paste from company GWENT was used. For measurements of electrical impedance in the frequency range of (10–1 · 10$^9$) Hz the four-probe method (as in [10]) was used. The measurements in the frequency range of (3 · 10$^3$–3 · 10$^5$) Hz were performed by the Agilent Network Analyzer E5062A connected to the coaxial line, part of the inner conductor of which was replaced by the sample. The impedance of the sample was calculated from the scattering parameters’ matrix of the two-port network as in [11].

3. Results and discussion

The amounts of up to 0.8 wt. % and 5 wt. % of LiTiPO$_4$ and Li$_4$(P$_2$O$_7$) in compounds with x = 0.2 and 0.5, respectively, were found. The amounts of impurities were estimated from intensities and their square analysis of XRD patterns. LiTiPO$_4$ and Li$_4$(P$_2$O$_7$) belong to the orthorhombic and triclinic symmetry group and are marked with asterisks on the XRD patterns in Fig. 1. At room temperature the Li$_{1+x}$Ti$_{2-x}$(PO$_4$)$_2$ (where x = 0.2, 0.5) compounds belong to the rhombohedral symmetry (space group R $\overline{3}$ c) with six formula units in the unit cell. In Table 1 the lattice a, c parameters, volume V, theoretical $d_0$ and relative $d_1$ densities of the ceramics are presented.

An increase of Li content leads to an increase of the volume of the lattice and decrease of the theoretical density of the compounds. This variation can be caused by the different values of the ionic radii of Li$^+$ and Ti$^{4+}$ ions. The ionic radii of Li$^+$ and Ti$^{4+}$ are 0.92 and 0.74 Å, respectively [12]. On the other hand, the analysis of XRD patterns shows the impurities of LiTiPO$_4$ and Li$_4$(P$_2$O$_7$), which can influence the above-mentioned parameters too. The SEM image of the surface of Li$_{1.1}$Ti$_{1.8}$(PO$_4$)$_2$ ceramics is presented in Fig. 2. The microstructure of both investigated ceramics is similar and their grain sizes vary in the range from 4 to 10 μm. Figure 3 shows EDX spectra for the grains of ceramics. The results of the investigation of elemental compositions showed a small amount of Al (0.585–0.457 wt. %, the error of this amount is found to be $\eta \pm 0.035–0.033$ wt. %) and Si (0.220–0.201 wt. %, $\eta \pm 0.32–0.031$ wt. %) impurities in the grains of the investigated ceramics (see the insertions of Fig. 3). These impurities could be from substrates which were used for the sintering of ceramics.
Table 1. Summary of X-ray diffraction results for Li\textsubscript{1+4}Ti\textsubscript{2-x}(PO\textsubscript{4})\textsubscript{3} (where x = 0.2, 0.5) compounds at room temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Lattice parameters</th>
<th>Formula units (Z)</th>
<th>Theoretical density (d_t), g/cm\textsuperscript{3}</th>
<th>Relative density (d_r), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li\textsubscript{1.8}Ti\textsubscript{1.8}(PO\textsubscript{4})\textsubscript{3}</td>
<td>R 3 c</td>
<td>8.5162(4)</td>
<td>20.8482(30)</td>
<td>1309.50</td>
<td>6 2.90</td>
</tr>
<tr>
<td>Li\textsubscript{1}Ti\textsubscript{1.5}(PO\textsubscript{4})\textsubscript{3}</td>
<td>R 3 c</td>
<td>8.5144(5)</td>
<td>20.8762(60)</td>
<td>1310.80</td>
<td>6 2.85</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of Li\textsubscript{1+4}Ti\textsubscript{2-x}(PO\textsubscript{4})\textsubscript{3} (where x = 0.2, 0.5) at room temperature.

Fig. 2. SEM image of Li\textsubscript{1}Ti\textsubscript{1.8}(PO\textsubscript{4})\textsubscript{3} ceramics surface.
To exclude any effects on the values of binding energies due to the charging of the sample during XPS analysis, all data were corrected by a linear shift such that the peak maximum of the C 1s binding energy of adventitious carbon corresponded to 284.6 eV. Ti 2p, P 2p, and O 1s core level XP spectra of Li$_{1+x}$Ti$_{2-x}$(PO$_4$)$_3$ (where $x$ = 0.2, 0.5) were fitted. Characteristic Ti 2p, P 2p, O 1s, and Li 1s core level XP spectra of Li$_{1+4x}$Ti$_{2-4x}$(PO$_4$)$_3$ (with $x$ = 0.2, 0.5) ceramics are shown in Fig. 4(a–d). The Ti 2p XP spectrum is shown in Fig. 4(a). The spectrum shows a double spin-orbit doublet of Ti 2p spectra as in...
The relative amounts of elements with different binding energies, spin-orbit doublets’ splitting energies of Ti 2p_{3/2} core level XP spectra for investigated ceramics are presented in Table 2. The spin-orbit doublets assembled two peaks at different binding energy. The lower energy peaks of Ti 2p_{3/2} spectra depend on stoichiometric parameters x of the investigated compounds and are in the range from 459.4 to 459.5 eV. The higher binding energy peaks are at 460.4 eV and do not depend on parameter x. The 2p_{3/2} peaks at a lower binding energy (see Table 2) can be associated with a lower oxidation state (Ti^{3+}). The peaks at a higher 2p_{3/2} binding energy can be associated with the Ti^{4+} valence state as in [14]. The results of the investigation of the Ti 2p core level XPS have shown that the increase of parameter x is associated with the increase of Ti^{4+} amount. So, a ratio Ti^{4+}/Ti^{3+} changes from 1.5 for a compound with x = 0.2 to 1.9 for a compound with x = 0.5. The binding energy splitting between lower and higher binding energy peaks is 5.6 and 5.7 eV, respectively. The authors of [13] reported that the binding energy splitting between Ti 2p_{3/2} and Ti 2p_{1/2} core level XPS was 5.4 eV. The P 2p core level XP spectra of Li_{1-x}Ti_{2-x}(PO_{4})_{3} (where x = 0.2, 0.5) ceramics deconvoluted into two peaks as shown in Fig. 4(b). The peaks at the binding energy of 132.5 eV (x = 0.2, 50.4 at. %), 132.5 eV (x = 0.5, 43.4 at. %), and 133.6 eV (x = 0.2, 49.6 at. %; x = 0.5, 56.6 at. %) (see Table 2) can be associated with dominated groups (PO_{4})^{3−} and (PO_{3})^{1−} as in [13]. This difference in binding energies comes from different bonds of phosphorus such as P–O–P (or double bond P=O) and P–O–Ti (or Li). The splitting energy of P 2p spectra is 1.0 eV and does not depend on parameter x.

Figure 4(c) shows the characteristic fitting patterns of O 1s core level XP spectra of Li_{1-x}Ti_{2-x}(PO_{4})_{3} (where x = 0.2, 0.5) ceramic surfaces. In the investigated compounds the O 1s spectrum has been deconvoluted into four peaks. The O 1s peak (see Table 2) at the binding energy of 531.1 eV (amount 55.1 at. % for x = 0.2) and the peak at the binding energy of 531.0 eV for compounds with parameters x = 0.5 can be attributed to the lattice oxygen and associated with groups (PO_{4})^{3−} and (PO_{3})^{1−} in the compounds. A small amount of O 1s peaks at the binding energy of 530.0 and 530.3 eV (8.2–8.5 at. %) can be attributed to oxygen forming relationships with the metal atoms, while other two O 1s peaks can be assigned to the oxygen in hydroxyl environment (OH) or CO as in ceramics [9, 10]. On the other hand, LiTiPO_{4}, Li_{2}(PO_{4}) exist in the investigated compounds as impurities, and these can influence the binding energies and amount of peaks.

The Li 1s signal is of very low intensity but in all investigated compounds only a single peak with the amount of 100 at. % was found (Table 2). These results can be assigned to the fact that in the lattice of the compounds one energy position for Li ions dominates. The binding energy of Li 1s core level XPS changed in the range from 55.3 to 55.0 eV and these results accord with [17]. A decrease of parameter x determines an increase of the binding energy of Li 1s core level XPS. It is reported in [13] that for the Li_{3}CoO_{4} composition the Li 1s single peak has been observed at 55.4 eV and their binding energy and the number of peaks depend on Li amount in the compound. The authors concluded that Li ions occupy two different positions. The results of the NMR study of LiTi_{2}Zr_{x}(PO_{4})_{3} composition have shown that Li ions occupy two different positions.

Table 2. Binding and splitting energies of Ti 2p, P 2p, O 1s, Li 1s core levels, amounts of peaks with certain binding energies and chi-square values in Li_{1-x}Ti_{2-x}(PO_{4})_{3} (where x = 0.2, 0.5) compounds.

<table>
<thead>
<tr>
<th>Core level</th>
<th>Binding energy E, eV</th>
<th>Splitting ΔE, eV</th>
<th>Amount, at. %</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti 2p_{3/2}</td>
<td>459.5</td>
<td>5.6</td>
<td>39.1</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>460.4</td>
<td>5.7</td>
<td>60.9</td>
<td></td>
</tr>
<tr>
<td>P 2p_{3/2}</td>
<td>132.7</td>
<td>1.0</td>
<td>50.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>133.6</td>
<td>1.0</td>
<td>49.6</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>530.3</td>
<td></td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>531.2</td>
<td></td>
<td>55.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>532.1</td>
<td></td>
<td>27.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>533.3</td>
<td></td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>Li 1s</td>
<td>55.5</td>
<td></td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>Li_{2}(PO_{4})</td>
<td>Li_{3}Ti_{2}(PO_{4})_{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti 2p_{3/2}</td>
<td>459.4</td>
<td>5.6</td>
<td>34.7</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>460.4</td>
<td>5.7</td>
<td>65.3</td>
<td></td>
</tr>
<tr>
<td>P 2p_{3/2}</td>
<td>132.5</td>
<td>1.0</td>
<td>43.4</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>133.6</td>
<td>1.0</td>
<td>56.6</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>530.0</td>
<td></td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>531.1</td>
<td></td>
<td>50.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>532.0</td>
<td></td>
<td>28.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>533.2</td>
<td></td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>Li 1s</td>
<td>55.0</td>
<td></td>
<td>100</td>
<td>0.2</td>
</tr>
</tbody>
</table>
in the lattice \[4\]. The results of NMR investigations of the NASICON-type framework structure \(\text{Li}_{1.3}\text{Al}_{0.15}\text{Y}_{0.15}\text{Ti}_{1.7}(\text{PO}_4)_3\) compound showed only one Li ion position in the lattice \[7\].

The characteristic frequency dependences of the real part of complex conductivity (\(\sigma'\)) of \(\text{Li}_{1+4x}\text{Ti}_{2-x}(\text{PO}_4)_3\) (where \(x = 0.2, 0.5\)) ceramics measured at the temperature \(T = 300\) K are shown in Fig. 5. In the frequency range from 10 Hz to 100 kHz the ceramics were investigated by the four-probe method, and in the microwave range the measurements were carried out by the coaxial technique. Two dispersion regions in \(\sigma'\) spectra for all investigated compounds were found. The low frequency dispersion range of \(\sigma'\) is caused by ion transport in grain boundary because high frequency range is attributed to ion transport in grain as in \[19–22\]. The processes are thermally activated and dispersion regions shift towards higher frequencies as temperature increases. This phenomenon is typical of relaxation-type dispersions. In Fig. 5 the characteristic frequency dependences of the real part of complex conductivity (\(\sigma'\)) of \(\text{Li}_3\text{Ti}_{1.5}(\text{PO}_4)_3\) ceramics measured at different temperatures are shown. The total conductivities (\(\sigma_{\text{tot}}\)) of the ceramics were derived from temperature dependences of the plateau of \(\sigma'\) (\(f\)) dependences and complex specific resistance \(\sigma''(\sigma')\) plots (see Fig. 7). The temperature dependences of bulk ionic conductivities \(\sigma_{\text{b}}\) have been found from complex plain plots of conductivity at different temperatures as shown in Fig. 8. The temperature dependences of \(\sigma_{\text{tot}}\) and \(\sigma_{\text{b}}\) of \(\text{Li}_{1+4x}\text{Ti}_{2-x}(\text{PO}_4)_3\) (where \(x = 0.2, 0.5\)) ceramic samples are shown in Fig. 8. The maximal value of \(\sigma_{\text{tot}}\) was found for a compound with parameter \(x = 0.5\). The increase of the parameter \(x\) leads to the increase of the value of \(\sigma_{\text{b}}\). The activation energies of \(\sigma_{\text{tot}}\) and \(\sigma_{\text{b}}\) were found from the slopes of the Arrhenius plots. From the maxima of \(\rho''(f)\) at different temperatures, the characteristic relaxation frequency \(f_{\text{b}}\) in the grain was determined as in \[23, 24\]. In Fig. 10 the characteristic frequency dependences of \(\rho''\) at the temperature of 300 K of \(\text{Li}_{1+4x}\text{Ti}_{2-x}(\text{PO}_4)_3\) (where \(x = 0.2, 0.5\)) compounds...
gated ceramics are similar to the activation energies of relaxation frequency, which can be attributed to mobility of Li\(^+\) ions, the concentration of charge carriers remains constant with changing temperature. The temperature dependences of the dielectric permittivity \(\varepsilon'\) were investigated at the frequency of 1 GHz. The values of \(\varepsilon'\) at the temperature of 300 K of Li\(_{1+4x}\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) ceramics where \(x = 0.2\) and 0.5 were found to be 9.69 and 10.82, respectively. These \(\varepsilon'\) values at room temperature are characteristic of NASICON-type compounds \([19, 25]\). For example, the values of dielectric permittivity of Li- conducting NASICON-type compounds Li\(_{1+4x}\)Y\(_{2-y}\)Ti\(_{2-y}\)(PO\(_4\))\(_3\) are shown. The relaxation frequency is thermally activated and increases with temperature according to the Arrhenius law: \(f_b = f_0 \exp(-\Delta E_f/kT)\), where \(f_0\) is an attempt frequency related to the lattice vibrations, \(\Delta E_f\) is the activation energy of \(f_b\), \(k\) is the Boltzmann constant. The activation energies \(\Delta E_f\) were calculated from the slopes of the Arrhenius plots of \(f_b\). Figure 11 shows the temperature dependences of \(f_b\). Table 3 summarizes our experimental results of the investigation of \(\sigma_{\text{tot}}, \sigma_b, \) their activation energies, and \(f_b\) and activation energy of characteristic relaxation frequency \(\Delta E_r\). The values of the activation energy of ionic conductivity in grains \(\Delta E_b\) and the activation energy of characteristic relaxation frequency \(\Delta E_r\) are similar. The activation energy \(\Delta E_r\) associates with the activation energy of mobility of charge carriers in grains. As we found that the values of activation energies of the bulk ionic conductivities of investi-

Fig. 8. Complex specific electrical conductivity plots of Li\(_{1+4x}\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) (where \(x = 0.2, 0.5\)) ceramics at temperature \(T = 300\) K.

Fig. 9. Arrhenius plots of total and bulk conductivities of Li\(_{1+4x}\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) (where \(x = 0.2, 0.5\)) ceramics.

Fig. 10. Frequency dependences of the imaginary part of complex resistivity of Li\(_{1+4x}\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) (where \(x = 0.2, 0.5\)) ceramics at the temperature \(T = 300\) K.

Fig. 11. Temperature dependences of relaxation frequency in the bulk of Li\(_{1+4x}\)Ti\(_{2-x}\)(PO\(_4\))\(_3\) (where \(x = 0.2, 0.5\)) ceramics.
Fig. 12. Frequency dependences of $\varepsilon'(f)$ for Li$_{1+x^4}$Ti$_{2-x^4}$(PO$_4$)$_3$ ceramics at the temperatures of 300 and 400 K.

Fig. 13. Temperature dependences of the real part of complex dielectric permittivity measured at 1 GHz frequency.

Table 3. $\sigma_\text{b}$ ($T = 300$ K), $\sigma_\text{tot}$ ($T = 380$ K), $f_\text{b}$ ($T = 300$ K) and their activation energies of Li$_{1+x^4}$Ti$_{2-x^4}$(PO$_4$)$_3$ (where $x = 0.2$, 0.5) samples.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_\text{b}$ S/m</th>
<th>$\Delta E_{\text{obs}}$ eV</th>
<th>$\sigma_\text{tot}$ S/m</th>
<th>$\Delta E_{\text{obs}}$ eV</th>
<th>$f_\text{b}$ MHz</th>
<th>$\Delta E_\text{f}$ eV</th>
<th>$\varepsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>{1.8}$Ti$</em>{1.8}$(PO$_4$)$_3$</td>
<td>0.0338</td>
<td>0.18</td>
<td>0.0073</td>
<td>0.31</td>
<td>34</td>
<td>0.21</td>
<td>9.69</td>
</tr>
<tr>
<td>Li$<em>{3}$Ti$</em>{1.5}$(PO$_4$)$_3$</td>
<td>0.0515</td>
<td>0.19</td>
<td>0.0146</td>
<td>0.30</td>
<td>70</td>
<td>0.22</td>
<td>10.82</td>
</tr>
</tbody>
</table>

(where $x$, $y = 0.3$, 0.4) were found to be $\varepsilon' = 10$ and increase with temperature [19]. This frequency at the temperature $T = 400$ K is higher than Maxwell relaxation frequency $f_\text{M} = \sigma_\text{b}/2\pi\varepsilon_\text{e} \varepsilon_0$ (where $\varepsilon_\text{e} = 8.85 \cdot 10^{-12}$ F/m is the dielectric constant of the vacuum). The frequency dependences of $\varepsilon'$ for Li$_{1+x^4}$Ti$_{2-x^4}$(PO$_4$)$_3$ (where $x = 0.2$, 0.5) ceramics at the temperatures of 300 and 400 K are shown in Fig. 12.

The results of the measurements of dependences $\varepsilon'(f)$ showed that the frequency of 1 GHz is higher than the frequency dispersion regions for both compounds. The calculated Maxwell relaxation frequency at temperature $T = 400$ K for compounds with $x = 0.2$ and 0.5 were found to be 332 and 426 MHz, respectively. The temperature dependences of $\varepsilon'$ of Li$_{1+x^4}$Ti$_{2-x^4}$(PO$_4$)$_3$ (where $x = 0.2$, 0.5) ceramics are shown in Fig. 13. The values $\varepsilon'$ at the temperature of 300 K of Li$_{1+x^4}$Ti$_{2-x^4}$(PO$_4$)$_3$ (where $x = 0.2$, 0.5) ceramics are summarized in Table 3 too. The increase of the values of $\varepsilon'$ with temperature of the investigated compounds can be caused by contribution of the migration polarization of lithium ions, vibration of the lattice, and electronic polarization.

4. Conclusions

The results of the XRD investigations from the powder showed that Li$_{1+x^4}$Ti$_{2-x^4}$(PO$_4$)$_3$ (where $x = 0.2$, 0.5) compounds belong to the rhombohedral symmetry (space group R3c). The Ti 2p core level XPS peaks at the binding energy in the range of 459.4 to 459.5 eV were associated with Ti$^{3+}$ oxidation states, and the peaks at the binding energy of 460.4 eV can be associated with the Ti$^{4+}$ valence state. In all the investigated compounds the O 1s spectrum has been deconvoluted into four peaks. It was ascertained that there are four different kinds of oxygen on the ceramics surface, including lattice oxygen, oxygen in the OH and CO groups. The deconvolution into two peaks of P 2p XP spectra in the investigated ceramics showed different amounts of P$^{5+}$ and P$^{3+}$ valence states. The splitting energy between P 2p$^3/2$ and P 2p$^1/2$ spectra is 1.0 eV and does not depend on parameter $x$. Only single peaks with the amount of 100 at. % in Li 1s core level XP spectra were found. Two relaxation dispersion regions of electrical properties are attributed to Li ion migration in grain.
boundary and bulk of the investigated ceramics. The activation energy of characteristic relaxation frequency correlates with the activation energy of bulk conductivity of the investigated compounds. The temperature dependence of bulk conductivity is related to the Li⁺ ion mobility, which increases as temperature increases.

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Santrauka

Li_{1+x}Ti_{2-x}(PO_4)_{3–x} (x = 0,2; 0,5) kietųjų elektrolitų milteliai buvo sintezuoti kietųjų kūnų reakcijos metodu. Kristalinė junginių struktūra tirta rentgeno spindulių difrakcijos metodas. Tyrimams naudotas Brucker D8 difraktometras bei CuKα spinduliui. Kristalinių gardeles sudaro šeši formulinių vienetai. (erdvinė simetrijos grupė R₃c). Jų elementariasias kristalines gardeles sudaro šeši formuliniai vienetai. Abiejų junginių spindulių difrakcijos metodu. Tyrimams naudotas keturių elektrodų metodas. Kristalinės gardeles sudaro šeši formuliniai vienetai. Abiejų junginių spindulių difrakcijos metodu. Tyrimams naudotas keturių elektrodų metodas.