Effect of Nb substitution on structural, electrical and electrochemical properties of LiTi$_2$(PO$_4$)$_3$ as electrolyte materials for lithium ion batteries

M. Koteswara Rao*, K. Vijaya Babu*, V. Veeraiah* and K. Samatha*

*Department of Physics, Andhra University, Visakhapatnam, India; *Advanced Analytical Laboratory, Andhra University, Visakhapatnam, India

ABSTRACT

The NASICON (Na Super Ionic CONductors)-type materials are good ionic conductors when serving as solid electrolytes for lithium–ion batteries. In this paper, Nb-doped LiTi$_2$(PO$_4$)$_3$ has been synthesized by solid-state reaction method and the structural, vibrational and dielectric studies are systematically investigated. The X-ray diffraction conforms that the Nb-doped LiTi$_2$(PO$_4$)$_3$ compound has NASICON structure, i.e. rhombohedral with space group R-3c. The average crystallite size and lattice constant are increased with dopant concentration. The grain sizes of the synthesized compounds are investigated by scanning electron microscope and it is found to be in the range of 5 μm. From Fourier-transform infrared spectroscopy spectra, stretching vibrations of P-O-P bond are identified in the region of 700–750 cm$^{-1}$. AC electrical study is carried out by exploiting the impedance and dielectric spectroscopy. The activation energy increases with dopant concentration since ion diffusion becomes easy as the volume fraction of the grain increases. Non-Debye behavior of conductivity relaxation is reflected in the modulus analysis.

1. Introduction

Solid-state ionics provides scientific support for a wide variety of advanced electrochemical devices such as batteries, fuel cells, chemical sensors, gas separation membranes and ionic switches. Numerous solids with high ionic conductivity at room temperature are extensively used in technological applications and are named as fast ionic conductors. One of the applications of fast ionic conductors is used as electrolytes in battery applications; hence the fast ionic conductors are also referred as solid electrolytes. Solid electrolytes are having some advantages in electrochemical devices against the liquid electrolytes such as longer life, high energy density, less possibility of leakage, chemical stability, etc. Solid electrolytes are first discussed by Faraday at the end of the nineteenth century. Generally, these solid electrolyte materials are commonly featured as (1) crystal bonding is ionic in nature, (2) electrical conductivity is high ($10^{-1}$ to $10^{-4}$ S/cm), (3) principle charge carriers are ions, (4) the electronic conductivity is negligible, (5) low activation energy for ion migration and (6) special crystal structure with open tunnels or channels through which the mobile ions move. Aono et al. and Good Enough et al. reported in 1976 a high ionic conducting skeleton structure having polyhedral units popularly known as NASICON (Na Super Ionic CONductors) [1,2]. The NASICON structure consists of a rigid (immobile) sub-array (sub-lattice) of ions which render a large number of three dimensionally connected interstitial sites suitable for long range motion of small monovalent cations. Since 1970, a good number of studies focusing on the synthesis and characterization of solid electrolytes appeared. Search for the lithium–ion conductors is motivated by the small ionic radii of lithium–ion by its lower weight, easy of handling and its potential use in high energy density batteries. Li$_2$SiO$_4$, LiZr$_2$(PO$_4$)$_3$ and LiTi$_2$(PO$_4$)$_3$ are some of the earliest solid electrolytes which show high ionic conductivity and have been the subject of many interesting properties. Understanding of the structure, morphology and ion conduction in solid electrolyte materials is a challenge one. Among the various types of solid electrolytes, the NASICON-type materials have shown interesting features such as remarkable structure, good chemical stability, electrical and electrochemical properties and a promising material for solid electrolyte. In the present paper, we focused on structural, morphological, electrical and electrochemical properties of Nb-doped LiTi$_2$(PO$_4$)$_3$ and the results are systematically discussed. From these studies, we report the high conductivity NASICON-type solid electrolyte material at x = 0 is $2.0715 \times 10^{-6}$ which is in good agreement with previous result [3–8].

2. Result and discussion

2.1. Thermogravimetric/Differential thermal analysis (TG/DTA)

The quantitative analysis of thermal reactions that are accompanied by mass changes such as evaporation,
decomposition, gas absorption and dehydration of the LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ with (x = 0.05, 0.075, 0.1 and 0.15) is done by TG/DTA. Figure 1 shows the TG/DTA profiles of the synthesized precursor powder sample. From TG curve, we notice that there are two main weight losses in the measured region, the first loss is located from the room temperature to 194°C, with a total weight loss of 1.3% which is due to the evaporation of water and it is supported by the DTA curve showing an exothermic peak at 191°C [9]. The second weight loss is about 21% in the range from 194°C to 470°C indicating the evaporation of CO$_2$ and NH$_3$ gases and also residual organic compounds. The endothermic peak at 374°C in DTA curve shows the decomposition of NH$_4$H$_2$PO$_4$. Formation of the LiTi$_2$(PO$_4$)$_3$ takes place at 500°C and beyond which there is no weight loss in the TG curve; from the TG curve, it is realized that with such losses, the sample weight will be only 78% and it is found to be satisfactorily matching with the calculated value of 77.73%. The prevailing difference of 1.27% may be due to certain impurities in the precursor powder. A broad exothermic peak in the DTA curve at 447°C shows the crystallization trend in LiTi$_2$(PO$_4$)$_3$ solid electrolyte material [10,11].

2.2. X-ray diffraction (XRD)
XRD is used to obtain the information about structure composition and state of the polycrystalline materials. The XRD is unique for every crystalline substance and the line position in the diffraction depends on the unit cell size, types of atoms, arrangement in the crystals. So, a sample can be confirmed from its unique powder pattern which can be obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction file [12].

Figure 2 shows the XRD pattern of LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ (x = 0.05, 0.075, 0.1 and 0.15) solid electrolyte materials prepared at 1100°C for 4 h. All the materials belong to the NASICON-type structure and it crystallizes in the rhombohedral system (R-3c). The calculated lattice parameters, cell volume, crystallite size

![Figure 1](image1.png)

Figure 1. TG/DTA curves for LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$(x = 0, 0.05, 0.075).
are listed in Table 1. From the XRD pattern, it is found that all peaks could be indexed to a single phase of ordered NASICON-type structure belonging to the rhombohedral crystal structure with R-3c space group. No peaks related to the alternative phases had been detected in the spectra. Thus we concluded that high-phase purity series of LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ ($x = 0, 0.05, 0.075, 0.1$ and $0.15$) solid electrolyte synthesized. In general NASICON-type structure, Ti, P and O atoms are in the (12c), (18e) and (36f) Wyckoff positions, respectively. Li is assumed to occupy in the (6b) position. We assume that the niobium element is completely occupying the (12c) site evidence that there is no impurity peak in XRD pattern. So all the diffraction peaks are sharp and distinguishable that there is no impurity peak in XRD pattern. So all the peaks related to the alternative phases have been detected. These results agree reasonably well with previous crystallographic data for this type of compounds.

The lattice parameters and unit cell volume of LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ ($x = 0.05, 0.075, 0.1$ and $0.15$) are calculated by using UnitCell software (1995). In general, the lattice parameter increases because the substituted element (Nb) ionic radius (62 Å) is larger than titanium (56 Å). In this study, the variation in the lattice parameters is in good agreement with the previous studies. Although there are some other factors affecting the increase in the lattice parameters such as the disposition of Li$^+$ ions, it has been reported that the ionic radii of substituted are the fundamental limitation, which proves that in fact substitution of Ti$^{4+}$ takes place. It can be deduced that the Li$^+$ ions are displaced from $M_1$ site to $M_2$ site with the increase in $x$ value, which result in a higher delocalization of lithium within the structure, since the $M_2$ sites are bigger size. In fact, in the case of Nb system when $x > 0.1$, the fraction of ions in $M_2$ is higher than in $M_1$, giving rise to an intermediate situation between LiTi$_2$(PO$_4$)$_3$ and Li$_3$M$_2$(PO$_4$)$_3$, but with a higher degree of disorder. Figures 3 and 4 show the variation of lattice parameters, unit cell volume and experimental density with $x$-value.

### 3. Fourier-transform infrared spectroscopy (FT-IR)

Figure 5 shows FT-IR spectra of pure and Nb-doped LTP electrolyte materials prepared at 1100°C for 4 h by solid-state reaction method. In this spectrum, mainly four series of bands are present at 270–300, 300–550, 550–700 and 800–1200 cm$^{-1}$. In LiTi$_2$(PO$_4$)$_3$, the spectra dominated by intense intramolecular PO$_4^{3-}$ stretching modes ($v_1$ and $v_3$) that range from 1300 to 700 cm$^{-1}$. $v_4$ is expected to yield five IR active vibrational modes (2A$_{2u}$+3E$_{u}$) and two IR active modes are expected for $v_2$ (2E$_{u}$). Four bands detected at 537, 606, 679 and 708 cm$^{-1}$ of LiTi$_2$(PO$_4$)$_3$ are assigned to $v_4$. The far-IR spectrum LiTi$_2$(PO$_4$)$_3$ contains at least three intense bands at 351, 435 cm$^{-1}$. The main contribution to the spectra intensity belongs to the stretching and deformation bands of PO$_4^{3-}$ groups (320–550 cm$^{-1}$), as well as to the stretching vibrations of TiO$_6$-groups (550–650 cm$^{-1}$). The frequency of sharp band and the broad features between 700 and 750 cm$^{-1}$ in the spectrum of LiTi$_2$(PO$_4$)$_3$.

#### Table 1. X-ray diffraction patterns of LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ ($x = 0, 0.05, 0.075, 0.1$ and $0.15$).

| S. No. | Sample                  | $a$ (Å) | Unit cell volume (Å$^3$) | Crystallite size (nm) |
|-------|-------------------------|---------|-------------------------|-----------------------|
| 1     | LiTi$_2$(PO$_4$)$_3$    | 8.4959  | 1295.622                | 7.5543                |
| 2     | Li$_{1.97}$Ti$_{0.03}$Nb$_{0.05}$(PO$_4$)$_3$ | 8.5249  | 1309.759                | 12.533                |
| 3     | Li$_{1.9}$Ti$_{0.1}$Nb$_{0.05}$(PO$_4$)$_3$ | 8.5137  | 1307.652                | 14.099                |
| 4     | Li$_{1.85}$Ti$_{0.15}$Nb$_{0.05}$(PO$_4$)$_3$ | 8.5764  | 1333.835                | 11.417                |
| 5     | Li$_{1.8}$Ti$_{0.2}$Nb$_{0.15}$(PO$_4$)$_3$ | 8.5234  | 1314.665                | 13.133                |
Figure 3. Variation of lattice parameters with $x$-value for LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ ($x = 0, 0.05, 0.075, 0.1$ and $0.15$).

Figure 4. Variation of density with concentration for LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ ($x = 0, 0.05, 0.075, 0.1$ and $0.15$).

Figure 5. FTIR spectra for LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ ($x = 0, 0.05, 0.075, 0.1$ and $0.15$).
(PO₄)₃ are somewhat lower than expected for PO₄³⁻ stretching modes. These modes are identified as P-O-P stretching vibrational modes. The substitution of Ti⁴⁺ for Nb⁵⁺ does not noticeably influence the spectra. The form of high frequency bands becomes more complicated, evidencing a slight distortion or nonequivalence of PO₄³⁻ groups as result of introduction of Nb⁵⁺ ions in the structure. When doping concentration increases, the intensity of the bands also increases. This shows usually correlates with the diminishing of particle size of material and decreases of electronic conductivity [13–15].

3.1. Microstructural analysis

In order to determine whether the difference in conductivity could be related to a change in microstructure or not, scanning electron microscope (SEM) micrographs of the cross-sectional area of the sintered pellets have been performed. The microstructure of the pellets strongly depends on the sintering temperature. The pellets sintered at 1100°C present a uniform microstructure with large grains obtained. A homogeneous microstructure appears, as presented in Figure 6. The grain sizes of the sintered pellets are in the range of 6 μm which is in good agreement with previous results. As concentration increases, the surface area covered by large grains becomes predominant. The same structure with large and small grains is uniformly distributed for sintered pellets for all concentration. For LTP materials (x = 0.05–0.15), conductivity is reported to be of similar values with the earlier reports. The presence of larger grains is then expected to be beneficial to conductivity. The chemical composition of the sintered compounds has been observed by Energy Dispersive Spectroscopy (EDS) analysis. All the elements except lithium are observed in the spectrum with appropriate concentration [16,19].
4. Impedance spectroscopy

In impedance technique, the real and imaginary parts of impedance of the sample are measured simultaneously as a function of frequency. The measured impedance data can be represented in the other three forms, using the interrelations as follows:

- **Complex impedance**
  \[ Z^* = Z' - jZ'' \]

- **Complex Admittance**
  \[ Y^* = Y' + jY'' = \frac{1}{Z^*} \]

- **Complex permittivity**
  \[ \varepsilon^* = \varepsilon' - j\varepsilon'' = \frac{1}{j\omega C_0 Z^*} \]

We have investigated the impedance and dielectric studies by electrochemical impedance spectroscopy technique, measurements of pellets of composition LiTi\(_{2-x}\)Nb\(_x\)(PO\(_4\))\(_3\) with \((x = 0.05, 0.075, 0.1\) and \(0.15\)) after sintered at 1100°C for 4 h. The impedance plots \((Z' \text{ vs. } Z'')\) at different temperatures have been presented in Figure 7. The logarithmic frequency increases in an anticlockwise manner on the Z' axis. Two semicircular arcs are observed in the temperature range 303–573 K with the arcs becoming smaller with increase in temperature and shrinking from right to left of the Z' axis. This implies a reduction in the diameter of the arcs which result in an increase in electrical conduction due to reduction in resistance of the sample. It is observed that the peak intensity \((Z')\) of one of the arcs is dominant, while the other with a smaller diameter has smaller peak intensities which lie outside the frequency range of investigation as the temperature increases.

![Figure 7. Nyquist plots for LiTi\(_{2-x}\)Nb\(_x\)(PO\(_4\))\(_3\) \((x = 0, 0.05, 0.075, 0.1\) and \(0.15\)).](image)
increases. When the dopant concentration is increasing, the arc of the semicircle is increasing. This shows the decreasing of the conductivity then concentration increasing [20,21].

### 4.1. Dielectric constant ($\varepsilon_r$)

The dielectric constant $\varepsilon_r$ is calculated from the capacitance measured in parallel plate geometry by

$$\varepsilon_r = \frac{C L}{\varepsilon_0 A}$$

where $C$ – capacitance in F, $L$ – thickness of the pellet, $\varepsilon_0$ – permittivity of free space and $A$ – area of cross section of pellet.

From Figure 8, it is observed that the dielectric constant $\varepsilon_r$ is decreasing with increasing temperature. The decrement of dielectric constant $\varepsilon_r$ is rapid at lower temperatures and showed almost frequency-independent behavior at higher temperature.

The temperature dependence of $\varepsilon_r$ was also investigated in the temperature range 300–573 K and frequency range 50 Hz–5 MHz as shown in Figure 8. It is observed that at high frequency, the material shows an almost temperature-independent behavior. Thus, the capacitance of the bulk is almost independent of temperature and slight increment observed is due to ion migration. There are no peaks observable either, resulting in non-Debye behavior which is in contrast to earlier

![Figure 8. Variation of dielectric constant with frequency for composition LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ with ($x = 0, 0.05, 0.075, 0.1$ and $0.15$).]
results. It is possible that the ratios of the ions in this composition may be responsible for absence of relaxation behavior. Additionally, the peaks may not have been observed as a result of the frequency which may be outside the frequency range in which the coupling of the ions is supposed to lead to a relaxation. At lower temperatures, all the plots show a slow rise in ε, with increase in the temperature, increases the dielectric constant and attaining a maximum value of ε = 576 at 393 K. In the case of LiTi2−xNb x(P04)3 with (x = 0.05, 0.075, 0.1 and 0.15) showing that the dielectric response is high compared to what has been reported for NASICON [9,22]

4.2. AC conductivity

The AC conductivity of the synthesized compounds is determined by using this equation:

\[ \sigma_{ac} = \epsilon_r \epsilon_0 \omega \tan \delta \]

where εr is the dielectric constant, \( \epsilon_0 \) is the permittivity of the free space, \( \omega \) is the angular frequency and tanδ is the dissipation factor.

As it is noticeable in Table 2 and Figure 9, the electrical conductivity generally decreases with niobium substitution. Especially important is the similar value observed with the lowest level of substitution, x = 0.05, compared with the sample x = 0. The conductivity values are decreasing up to x = 0.3. In systems where the inter- and intra-grain activation energy is similar, differences in conductivity are normally related to the connectivity between grains, which have a higher concentration of imperfections near the grain boundary. In this work, the maximum conductivity is found in the sample LiTi2−xNb x(P04)3 at x = 0 at room temperature, which is in fact the most studied composition of the LiTi2(P04)3 derivatives. The decrease in the conductivity is due to the influence of porosity of the synthesized samples [23,24]. The niobium doping compounds lower the conductivity then the mother compound. The reason is that the Nb substitution occurs on the 6b lithium site as Nb5+, it is really immobile ion, the conductivity decreases where a higher amount of Nb5+ is found on the lithium site. Other aspect to be taken into account concerning the lower conductivity of the Nb-doped samples is the lithium amount on the 6b site, too: the lithium content in the synthesis stoichiometry is lower than 1, which is instead the value used in the undoped samples by taking into account all the factors affecting our conductivity data our results put into evidence that the Nb substitution on the lithium site plays a more relevant role than the porosity and lithium content of the samples [26]. The ac conductivity values at room temperature and at 300°C are listed in Table 3.

Table 2. Grain sizes of LiTi2−xNb x(P04)3 (x = 0, 0.05, 0.075, 0.1 and 0.15).

| S. No. | Sample | Grain size (μm) |
|-------|--------|----------------|
| 1     | LiTiPO4 | 1.333          |
| 2     | Li0.95Ti1.05Nb0.05(P04)3 | 2.636 |
| 3     | Li1.025Ti1.075Nb0.025(P04)3 | 2.396 |
| 4     | Li1.03Ti1.07Nb0.03(P04)3 | 3.385 |
| 5     | Li1.05Ti1.05Nb0.05(P04)3 | 1.395 |

Table 3. AC conductivity values of LiTi2−xNb x(P04)3 (x = 0.05, 0.75, 0.1 and 0.15) at 100 Hz.

| Compound | Conductivity at RT (S/cm) | Conductivity at 300°C (S/cm) |
|----------|---------------------------|-----------------------------|
| x = 0    | 2.0715 × 10^{-5}         | 5.0287 × 10^{-5}            |
| x = 0.05 | 4.2570 × 10^{-6}         | 1.4799 × 10^{-5}            |
| x = 0.075| 7.0457 × 10^{-6}         | 4.1433 × 10^{-5}            |
| x = 0.1  | 1.8671 × 10^{-8}         | 9.9074 × 10^{-7}            |
| x = 0.15 | 8.2476 × 10^{-9}         | 6.5247 × 10^{-7}            |

Table 4. Activation energy values of LiTi2−xNb x(P04)3 (x = 0.05, 0.75, 0.1 and 0.15).

| S. No. | Compound | Activation energy (eV) |
|--------|----------|------------------------|
| 1      | LiTiPO4 | 0.2614                 |
| 2      | B-1     | 0.2468                 |
| 3      | B-2     | 0.2474                 |
| 4      | B-3     | 0.2478                 |
| 5      | B-4     | 0.2485                 |

5. Activation energy

The variation of activation energy with composition in the bulk is smaller than in the grain boundaries as shown in Figure 10.

This small variation may be due to changes in the size of the electrochemical window in the conduction path. Li+ ions placed in M1 sites are surrounded by six oxygen atoms inside an antiprism and the jump to M2 sites implies passing through the lateral face of this site which constitutes the bottleneck because the activation energy of bulk conduction decreases with the substitution content in the three systems independently of the ionic radii of substituent. Thus, the variation of the activation energy is due to different location of Li+ ions, changing from M1 to M2 sites as demonstrated by XRD. When M1 sites are empty, repulsion forces between oxygen atoms are increased, extending the M1 site and increasing the size of [27].

The result conformed that the conduction pathways in LTP is similar to the original NASICON compound LiTi2(P04)3. Let us next look to the concrete pathways and barrier height of lithium migration that can be determined with nm energy minimization. One unit cell is using periodic boundary conditions proved to be best suitable as simulation box. The activation energies
are obtained from the Arrhenius representation with AC conductivity and are listed in table. Activation energies for all compounds obtained from the Arrhenius plots are 0.2614, 0.2468, 0.2474, 0.2478 and 0.2485 eV which are shown in table 4. All the values are good agree within ±0.04 eV for niobium-doped compound. The value activation energy for undoped compound is higher than the doped compound. This is due to that the lithium ions may refuse across the metal, metal bottlenecks but the values of conductivity and activation energy cannot be directly compared [26].

5.1. Cyclic voltammetry (CV)

It is an electrochemical method that can be used to understand the reaction of basic electrochemistry and also used to understand redox behavior, redox stability of a given molecule, organic reactions, organometallic chemistry, polymer chemistry and quantification of ionizable drugs. In order to understand the electrochemical window of the solid-state electrolyte LTP, a simple method of CV has been carried out. The active material coated on steel foil (cell) is placed in Swagelok setup containing 1 M LiPF$_6$ dissolved in ethylene carbonate and dimethyl carbonate (1:1, volumetric ratio). Lithium metal was
used as both counter and reference electrodes. The entire cell setup was assembled in an argon-filled glove box and tested with Biologic potentiostat/galvanostat model VMP3 at a scan rate of 0.1 mV/s for 20 cycles between 0.5 and 3.5 V.

The CV curves of LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ for 20 cycles are shown in Figure 11. A pair of oxidation and reduction peaks for LiTi$_{2}$ (PO$_4$)$_3$ is observed between $-1.0$ and $1.75$, indicating only one step of lithium intercalation/de-intercalation into NASICON structure in good agreement with previous literature. By applying the empirical formula, this rhombohedral NASICON-type crystal structure can accommodate up to 2 mol lithium atoms to form Li$_3$Ti$_2$(PO$_4$)$_3$ upon discharge. This reduction is reversible and upon charging the material is oxidized back to LiTi$_{2}$ (PO$_4$)$_3$.

Equations 1 and 2 illustrate the reduction and oxidation (redox) reactions. At the time of discharging process, occur reduction reaction at the LiTi$_2$(PO$_4$)$_3$, namely

$$\text{LiTi}^{+4}(\text{PO}_4)_3 + 2\text{Li}^+ + 2e^- \leftrightarrow \text{Li}_3\text{Ti}^{+3}(\text{PO}_4)_3.$$  \hspace{1cm} (1)

while charging, occurs the oxidation reaction at the LiTi$_2$(PO$_4$)$_3$ is

$$\text{Li}_3\text{Ti}^{+3}(\text{PO}_4)_3 \leftrightarrow \text{LiTi}^{+4}(\text{PO}_4)_3 + 2\text{Li}^+ + 2e^-.$$  \hspace{1cm} (2)

From the CV results of Nb-doped LTP shows two pairs of redox peaks at potential of B-1, B-2, B-3 and B-4 are $-0.8063$ to $1.7081$, $-1.1990$ to $1.7852$, $-0.7349$ to $1.7028$ and $-0.7957$ to $1.7028$, respectively. This indicates that the increase of niobium content increases the potential separation between anodic and cathodic peak and it will improve the ionic conductivity of the material and the rate stability of LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ with ($x = 0.05, 0.075, 0.1$ and $0.15$) [26–29].
6. Conclusion

LiTi$_{2-x}$Nb$_x$(PO$_4$)$_3$ with ($x = 0, 0.05, 0.075, 0.1$ and $0.15$) has been synthesized by solid-state reaction method at 1100°C to obtain single phase. XRD pattern conform the formation of NASICON structure and there is no impurity phase. Both crystallite sizes and lattice parameters increase with increasing niobium concentration. The vibrational properties of NASICON-type Nb-doped LiTi$_2$(PO$_4$)$_3$ are studied by FT-IR and it conforms the dopant exactly occupies Ti site of the corresponding host lattice. The frequency dependent AC conductivity is calculated at different temperatures and it shows the behavior of ionic material. Modulus formalism ensures that the non-Debye-type relaxation presents in the all prepared compounds.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Aono H, Idris MA, Sadaoka Y. Ionic conductivity and crystal structure for the Li$_{3-2x}$Cr$_{2-x}$Ta$_x$(PO$_4$)$_3$. Solid State Ionics. 2004;166:53–59.
[2] Good Enough JB, Hong HYP, Kafalas JA. Fast Na$^+$-ion transport in skeleton structures. Mater Res Bull. 1976;11:203.
[3] Wang GX, Bradhurst DH, Dou SX, et al. LiTi$_2$(PO$_4$)$_3$ with NASICON-type structure as lithium storage materials. J Power Sources. 2003;124:231–236.
[4] Kosavo NV, Osintsev DI, Uvarov NF, et al. Lithium titanium phosphate as cathode, anode and electrolyte...
for lithium rechargeable batteries. Chem Sustainable Dev. 2005;13:253–260.

5. Thangadurai V, Ashok K, Gopalakrishnan J. New lithium – ion conductors based on the NASICON structure. J Mater Chem. 1999;9:739–741.

6. Orbiuakas A, Dindune A, Kanepe Z, et al. Synthesis, structure and peculiarities of ionic transport of Li1.6Mg0.3Ti1.7(P04)3 ceramics. Solid State Ionics. 2003;157:177–181.

7. Arbi K, Mandal S, Rojo JM, et al. Dependence of ionic conductivity on composition of fast ionic conductors Li1.4-xTix2.4Alx(P04)3. 0 ≤ x ≤ 0.7. A parallel NMR and electric impedance study. Chem Mater. 2002;14:1091–1097.

8. Maldonado-Manso P, Losilla ER, Lara MM, et al. High lithium ionic conductivity in the Li1.6AlxGe2Ti2-x-y (PO4)3 NASICON series. Chem Mater. 2003;15:1879–1885.

9. Mariappan CR, Galven C, Crosnier-Lopez M-P, et al. Synthesis of nanostructured Li1+xTi3-xP3O12 powders by a Pechini-type polymerizable complex method. J Solid State Chem. 2006;179:450–456.

10. Savitha T, Selvasekarapandian S, Ramya CS, et al. Electrical conduction and relaxation mechanism in Li2.15AlZr[PO4]3. J Mater Sci. 2007;42(2):5470–5475.

11. Kobayashi YO, Tabuchi M, Nakamura O. Ionic conductivity enhancment in Li1+xTi3-xP3O12 based composite electrolyte by the addition of lithium nitrate. J Power Sources. 1997;68:407–411.

12. Ramaraghavulu R, Buddhudu S. Analysis of structural, thermal and dielectric properties of Li1.2Ti4.8P3O12 ceramic powders. Ceramics Int. 2011;37:3651–3656.

13. Eddahaoui K, Mele G, Benmokhtar S, et al. Photodegradation of - nitrophenol in aqueous suspension by using new titanium phosphates Li0.50M0.22Ti2 (PO4)3 (M= Ni, Mn and Co) catalyzed processes. Int J Advanced Res Chem Sci (IJARCS). 2015;21:32–33.

14. Bushiri MJ, Antony CJ, Aatiq A. Raman and FTIR studies of the structural aspects of Nasicon-type crystals: AFETi (PO4)3 [A= Ca, Cd]. J Phys Chemistry Solids. 2008;69:1985–1989.

15. Julien CM, Jozwiak P, Garbarczyk J. Vibrational spectroscopy of electrode materials for rechargeable lithium batteries. IV. Lithium metal phosphates. Proceedings of the international Workshop Advanced techniques for Energy Sources Investigation and Testing; 2004 Sept 4–9; Sofia, Bulgaria. L1-4-L4-12.

16. Capsoni D, Bini M, Ferrari S, et al. Role of lithium excess and doping in Li1.14Ti2.3Mn4 (PO4)3, (0.00 ≤ x ≤ 0.10). J Phys Chem. C2012;116:1244–1250.

17. Pinus Y, Stenina IA, Rebrov AI, et al. Cation mobility in modified Li1.4(Ti2.4Nb4 (PO4)3 lithium titanium NASICON phosphates. Russian J Inorg Chem. 2009;54:1177–1180.

18. Shaikhislamova AR, Zhuravlev NA, Stenina IA, et al. Ion transport in complex phosphate Li3.2xNb4 xIn2.8 (PO4)3. Doklady Phys Chem. 2008;118–120.

19. Ortiz GF, Lopez MC, Lavela P, et al. Improved lithium – ion transport in NASICON –type lithium titanium phosphate by calcium and iron doping, SoSi- 1303. Solid State Ionics. 2014;262:573–577.

20. Anantharamulu N, Prasad G, Vithal M. Preparation, characterization and conductivity studies of Li0.25Al2-x Sb(P04)3. Bull Mater Sci. 2008;31(2):133–138.

21. Ortiz GF, Lopez MC, Lavela P, et al. Improved lithium–ion transport in NASICON –type lithium titanium phosphate by calcium and iron doping. Solid State Ionics. 2013.

22. Ahmadu U, Tomas S, Jonah SA, et al. Equivalent circuit models and analysis of impedance spectra of solid electrolyte, Na0.25Li0.75Zr2 (PO4)3. Adv Mat Lett. 2013;4(3):185–195.

23. Kobayashi Y, Takeuchi T, Tabuchi M, et al. Densification of Li1+xTi3-xP3O12 based solid electrolytes by spark- plasma- sintering. J Power Sources. 1999;81:82–853.

24. Xiaoxiong X, Wen Z, Jianguo W, et al. Preparation and electrical properties of NASICON- type structured Li1.4Al0.4 Ti1.6 (PO4)3 glass- ceramics by the citric acid– assisted sol-gel method. Solid State Ionics. 2007;178:29–34.

25. Yu I, Pinus IA, Stenina A, et al. Cation mobility in modified Li1.4Ti2.4Nb4 (PO4)3 lithium titanium NASICON phosphates. Russian J Inorg Chem. 2009;54(8):1177–1180.

26. Mouahid FE, Zahir M, Maldonado-Manso P, et al. Na–Li exchange of Na1.3Ti2.2Al4 (PO4)3 (0.6<x<0.9) NASICON series: a Rietveld and impedence study. J Mater Chem. 2001;11:3258–3263.

27. Perez- Estebanez M, Isasi- Marin J, Tobbens DM, et al. A systematic study of Nasicon-type Li1+xM3Ti2-x (PO4)3 M: (Cr, Al, Fe). Solid State Ionics. 2014;266:1–8.

28. Wu XM, Li XH, Wang SW, et al. Preparation and characterisation of lithium-ion conductive Li1.3Al0.7Ti1.7 (PO4)3. Thin Solid Films. 2003;25:103–107.

29. Wang H, Huang K, Zeng Y, et al. Electrochemical properties of TiP2O7 and LiTi3 (PO4)4 as anode material for lithium ion battery with aqueous solution electrolyte. Electrochimica Acta. 2007;52:3280–3285.