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The ion conducting properties of perovskite solid solutions $(La_{1/2}Li_{1/3+X})TiO_3$

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The structure, microstructure and conductivity parameters of lithium-lanthanum titanates $(La_{1/2}Li_{1/3+X})TiO_3$ (x = 0; 1/10; 1/6; 1/5; 1/4) have been studied. Ionic conductivity has been found to decrease when lithium content increased due to both the cell volume and the A-site vacancy content decreasing. The anomalies on temperature dependences of dielectric permttivity and dielectric losses near 500 and 850K have been observed which may be connected with structural transformation and cation disordering in A-sublattice.

1 Introduction

During the recent years solid lithium ion conductors attract much interest due to their prospects for applications in gas sensors, cathodes in Lithium batteries and as solid electrolytes. Special attention is devoted to perovskite solid solutions $(La_{2/3-X}Li_{3X})TiO_3$ because of their high ionic conductivity which is close to $\sigma \approx 10^{-3}$ S/cm at room temperature [1, 2].

In these compounds the lithium ion conductivity depends on both the lithium ion and vacancy concentration in the A-sublattice and on the so called "bottleneck" dimensions in structural channels which are formed by the oxygen ions and B-site cations.

The ionic conductivity growth with vacant site concentration increasing was reported [2, 3, 5, 6]. The same effect was observed when the smaller B-site ion substituted for titanium due to the interatomic bond lengths changes with the B – O bond strengthening and the Li – O bond weakening [4]. Such changes lead to bottleneck dimension increasing and corresponding decreasing of the ionic conductivity activation energy. A lot of papers has been devoted to the investigation of factors influencing the lithium ionic conductivity in perovskite solid solutions $(La_{2/3-X}Li_{3X})TiO_3$ [1–7]. However, till now some data remain controversial. In particular, different data were reported on crystal structure [1, 3, 5, 6]. Belous reported that the synthesis conditions are the reason of such structure abundance [1]. He explained the variety of results by formation of perovskites with cubic structure at temperatures 1200 – 1250°C in course of firing during 0.5 – 1 h while formation of tetragonal perovskites at higher temperatures 1270 – 1300°C with more prolonged firing during 3 – 5 h due to the ordering effects.

So, the unsolved problems are related mainly to the preparation conditions of Li-containing perovskite solid solutions.

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In this work we studied the phase composition, structure parameters and electroconducting properties of perovskite solid solutions (La$_{1/2}$Li$_{1/3+X}$)TiO$_3$ with x = 0; 1/10; 1/6; 1/5; 1/4 in order to determine the influence of lithium ion concentration on crystal structure parameters and ionic conductivity.

2 Experimental

The perovskite solid solutions (La$_{1/2}$Li$_{1/3+X}$)TiO$_3$ with x = 0; 1/10; 1/6; 1/5; 1/4 were prepared by the conventional solid state reaction method. Oxides La$_2$O$_3$ (99.97%) and TiO$_2$ (99.5%) and carbonate Li$_2$CO$_3$ (99.97%) were used as starting materials. Before synthesis La$_2$O$_3$, TiO$_2$ and Li$_2$CO$_3$ powders were dried for 2 hours at 900°C (oxides) and 600°C (carbonate), respectively.

The stoichiometric quantities of starting reagents were mixed with ethanol and pressed into pellets. Then the compositions were synthesized in air at temperatures from 700 to 1000°C (35 h) with intermediate regrinding and pressing and finally sintered at 1250°C (6 h).

The powder X-ray diffraction method (DRON-3M Cu$_{k\alpha}$-radiation) was used for identification of phase composition and the lattice parameters determination. Microstructure of the samples was studied by the electron microscopy method (JEOL – 35CF). Infrared spectra were collected in the region of 400 – 4000 cm^{-1} using the spectrophotometer SPECORD 75 – IR. The ac-conductivity measurements were carried out by dielectric spectroscopy method over the frequency range from 1 kHz to 1 MHz and the temperature range from 300 to 1000K. Platinum electrodes were fired into smaller surfaces of the bar-like samples.

3 Results and discussion

The X-ray powder diffraction patterns collected indicate the single phase perovskite-related structure formation (Fig. 1). Broad superstructure peaks of weak intensity were observed at $2\theta \approx 25.8$, 34.9, 39.1° (marked with asterisks). Half width of the superstructure peak near $2\theta \approx 25.8°$ is 4-times larger in comparison to the half width of the structural peak 100 situated at $2\theta \approx 21.5°$. Intensity of the peaks grows with increasing the lithium content in the initial mixtures. This may be explained by the cation ordering enhancement when over stoichiometric quantity of the low melting lithium oxide is added to the initial

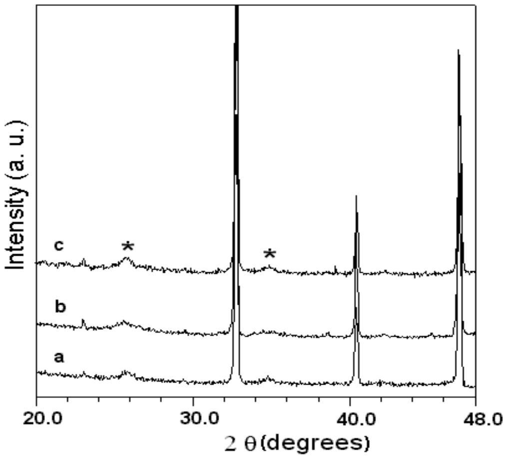

Fig. 1 X-ray diffraction patterns for (La$_{1/2}$Li$_{1/3+}$)TiO$_3$ ceramics with x = 0 (a), 1/6 (b), 1/4 (c).

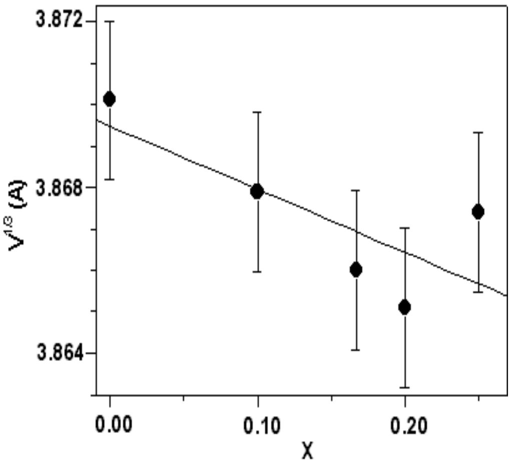

Fig. 2 The average unit cell parameter V$^{1/3}$(x) dependence for (La$_{1/2}$Li$_{1/3+}$)TiO$_3$ ceramics.

mixtures. The convolution of the structural peaks with *hkl* = 002*n* confirmed the tetragonal perovskite unit cell for all the compositions studied.

As Fig. 2 shows, the average unit cell parameter decreases with *x* increasing. This supports the conclusion on possible A-cation ordering and is consistent with decreasing the A-site vacancy concentration with increasing lithium content.

IR spectra of (La$_{1/2}$Li$_{1/3+X}$)TiO$_3$ powders are presented in Fig. 3. They are typical of the perovskite structure and confirm formation of perovskite solid solutions. The wide bands in the ranges of 570 – 600 and 750 – 800 cm^{-1} are known to be connected with the Ti – O bond valence vibrations in octahedron TiO$_6$ [8].

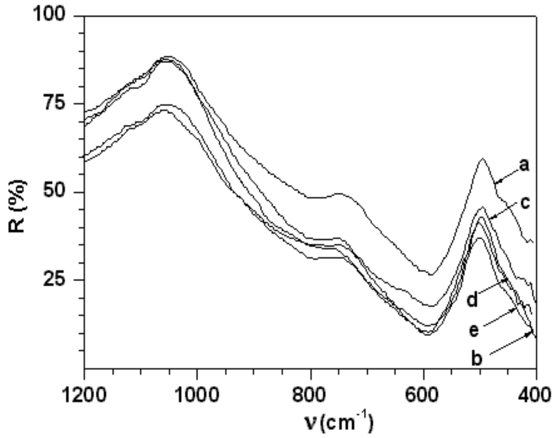

Fig. 3 IR spectra of the (La$_{1/2}$Li$_{1/3+}$)TiO$_3$ powders with x = 0 (a), 1/10 (b), 1/6 (c), 1/5 (d), 1/4 (e).

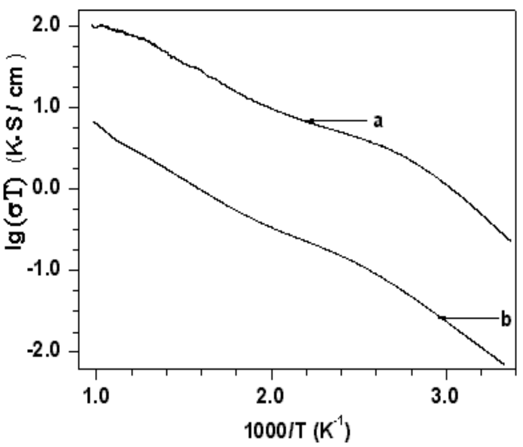

Fig. 4 The lg(σT) versus 1/T dependences (f =1 MHz) for (La$_{1/2}$Li$_{1/3+}$)TiO$_3$ ceramics with x = 0 (a), 1/4 (b).

The micrographs of surface and bulk of the ceramics were obtained by the electron microscopy method. The typical rectangular shape of grains was revealed on surface of ceramics that indicates tetragonal symmetry of the unit cell. This supports our conclusion on the tetragonal symmetry of the unit cell according to the X-ray data and coincides with the literature data on the dependence of the unit cell symmetry on the preparation conditions [1].

The ac-conductivity follows the Arrhenius' law at temperatures higher than 400 K for all the samples obtained (Fig. 4). Decreasing of ionic conductivity was observed for the samples with $x \geq 1/5$ in accordance with the decreasing amount of the A-site vacancies and perovskite lattice contraction with increasing Li ion content. Such changes provide worsening of the ion transport conditions [1–6].

As Fig. 5 shows, anomalies near 500 and 850 K are revealed on temperature dependences of dielectric permettivity. We believe that the low temperature anomaly may be connected with the polymorph crystal structure transformation that was confirmed to be possible for some compositions in the (La,Li)TiO$_3$ series [3]. The corresponding low temperature anomalies on the temperature dependences of dielectric losses are evidently of the same origin (Fig. 6). On the other hand, the high temperature anomalies near ~ 850 K are certainly related to the disordering effects noticed by the X-ray diffraction method [7, 9].

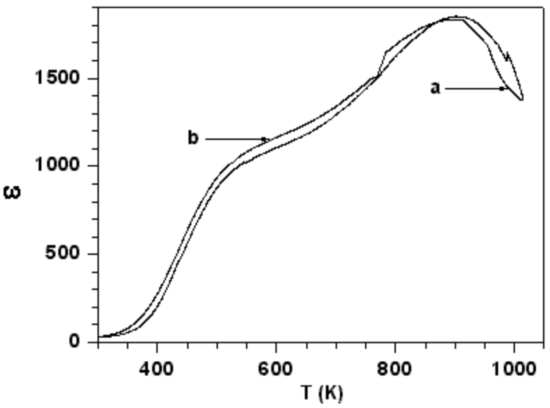

Fig. 5 Temperature dependences of dielectric permettivity ε for $(La_{1/2}Li_{1/3+1/4})TiO_3$ ceramics measured at heating (a) and cooling (b) at f =1 MHz.

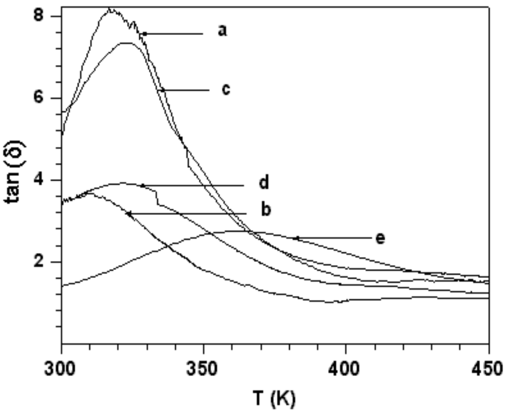

Fig. 6 Temperature dependences of dielectric loss tan δ for $(La_{1/2}Li_{1/3+})TiO_3$ ceramics with $x = 0$ (a), 1/10 (b), 1/6 (c), 1/5 (d) 1/4 (e) measured at f =1 MHz.

4 Conclusion

The tetragonal perovskite solid solutions $(La_{1/2}Li_{1/3+x})TiO_3$ (x = 0; 1/10; 1/6; 1/5; 1/4) have been studied. The lattice volume has been found to decrease along with lithium content increasing. The ionic conductivity follows Ahrrenius' law for all the ceramics studied. It has been shown that ionic conductivity decreases with the cell volume decreasing due to the A-site vacancy content decreasing. Anomalies on temperature dependences of dielectric permettivity and dielectric losses have been revealed. We suppose that dielectric permittivity peaks at ~500K may be related to the structural phase transition while anomalies at ~850K may be connected to the A-site disordering effects.

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References

[1] A.G. Belous, J. Europ. Ceram. Soc. **21**, 1797 (2001).
[2] Y. Inaguma, Ch. Liquan, M. Itoh, and T. Nakamura, Solid State Commun. **86**, 10, 689, (1993).
[3] A.D. Robertson, S. Garcia-Martin, A. Coats, and A.R. West, J. Mater. Chem. **5**, 9, 1405 (1995).
[4] H.-T. Chung, J.-G. Kim, and H.-G. Kim, Solid State Ionics **107**, 153 (1998).
[5] T. Katsumata, Y. Inaguma, M. Itoh, and K. Kawamura, Chem. Mater. **14**, 3930 (2002).
[6] M.A. Paris, J. Sanz, C. Leon, J. Santamaria, J. Ibarra, and A. Varez, Chem. Mater. **12**, 1694 (2000).
[7] O. Bohnke, H. Duroy, J.L. Fourquet, S. Ronchetti, and D. Mazza, Solid Sate Ionics **149**, 217 (2002).
[8] M. Couzi and P. V. Huong, J. Chim. et Phys.-Chim. Biol. **69**, 9, 1339 (1972).
[9] Y. Harada, Y. Hirakoso, H. Kawai, and J. Kuwano, Solid Sate Ionics **121**, 245 (1999).