Journal of the European Ceramic Society 21 (2001) 1797–1800

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Lithium ion conductors based on the perovskite $La_{2/3-x}Li_{3x}TiO_3$

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Received 4 September 2000; received in revised form 7 November 2000; accepted 15 November 2000

Abstract

Reflection spectra and the parameters of dispersion oscillators of the perovskites $La_{2/3-x}M_{3x}TiO_3$, where M is Li, Na, K are presented in the paper. In the case when M is Li the above perovskites exhibit high lithium ion conductivity. The origins of the lithium ion conductivity in the materials of the system $La_{2/3-x}Li_{3x}TiO_3$ are discussed on the grounds is of both the research data obtained and the reference data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ionic conductivity; Perovskites; Sensors; Sintering; Spectroscopy

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1. Introduction

Recently, much attention has been paid to lithium ion conductors with high conductivity which have potential applications in solid battery electrolytes and gas sensors. The perovskite structure seems to be the most attractive for the development of lithium conducting materials. This is due to the structural channels and the formation of structural vacancies in the crystalline sublattice. However, when only lithium ions occupy A sites in perovskite ABO_3, the small-size lithium ion does not meet the steric requirements of the perovskite sublattice, and as a consequence, the perovskite structure is not formed. Our approach was to the following effect: the perovskite sublattice placed in structural channels should contain a large lanthanum ion, which meets all geometric requirements, and a small lithium ion, which can move down the structural channels. This idea was first utilized by us in the materials $La_{2/3-x}Li_{3x}TiO_3$,[1,2] $La_{2/3-x}Li_{3x}Nb_2O_6$.[3,4] At the present time, there are extensive experimental data related to lithium conducting perovskites $La_{2/3-x}Li_{3x}TiO_3$. In this study some crystal-chemical peculiarities of the system $La_{2/3-x}Li_{3x}TiO_3$, which are responsible for the high lithium ion conductivity, were analyzed.

2. Experimental procedure

The samples were produced by a conventional ceramic technique. The investigation was carried out using chemical and XRD phase analysis (DRON-3M device using CuK_α radiation). Oscillation spectra in the far infrared region were examined using a double-beam spectrometer FIS-3 (4–400 cm^{-1}) and a single-beam device FIS-21 (30–5000 cm^{-1}) and a spectrophotometer Specord 75-IR was used for the middle infrared region (400–4000 cm^{-1}).

Electrical conductivity was measured with direct current and by means of an R-5021 AC Bridge. To measure the temperature dependencies of these conductivity, a measuring cell was designed, which makes it possible to carry out investigations in the temperature range of 20–600°C in air and in an inert atmosphere.

3. Results and discussion

Temperature processing of starting reagents, taken in an appropriate ratio corresponding to the composition $La_{1/2}Li_{1/2}TiO_3$, have shown that a short-time firing at 1200–1250°C (for 0.5–1 h) results in the formation of a perovskite structure with a cubic unit cell (a_p). The rise in both the temperature (up to 1270–1300°C) and the processing time (up to 3–5 h) results in tetragonal deformation of the unit cell as well as in doubling of the cell parameter along the c axis (a_p, a_p, $2a_p$). It should be

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PII: S0955-2219(01)00118-2

noted that the literature contains different data on lattice parameters of materials with the composition $La_{2/3-x}Li_{3x}TiO_3$.[5–14] The first communication about the synthesis of cubic perovskite with the formula $La_{1/2}M_{1/2}TiO_3$, where M is alkaline metal from lithium to rubidium, refers to 1953.[5] In the later studies [6,7] the other members of the series $Li_{1/2}Ln_{1/2}TiO_3$ (Ln = Nd, Sm, Gd, Y, Dy) have been synthesized and have been determined to have rhombic perovskite structure. In Refs. 8 and 9 these materials have been reported to have the structure of tetragonal tungsten bronze. Furthermore, Refs. 10 and 11 denote the presence of the ordering of La^{3+} and Li^{3+} ions along the c axis (a_p, a_p, $2a_p$) or along all three axes.[11,13] Our experimental data as well as contradictory reference data, relative to the processing of the compounds $La_{1/2}Li_{1/2}TiO_3$, may be understood by taking into account that the ordering of lanthanum and lithium ions strongly depends on the processing temperature. At lower temperatures La^{3+} and Li^{3+} ions are randomly distributed over the cubic unit cell, while, when increasing the temperature and heating time, they are ordered along the *c* axis. In the latter case tetragonal lattice deformation (a_p, a_p, $2a_p$) occurs. The further increase in heating time results in the additional ordering of La^{3+} and Li^{3+} ions on the plane X0Y forming a tetragonal cell with the parameters $\sqrt{2}a_p$, $\sqrt{2}a_p$, $\sqrt{2}a_p$,.[13] However, it should be noted that questions related to the structure of the materials of the system $La_{2/3-x}Li_{3x}TiO_3$ are not yet completely clarified.

In order to examine oscillation spectra of the perovskites $La_{2/3-x}M_{3x}TiO_3$ (M–Li, Na, K) the materials used differed by site occupancy. In some materials the lanthanum sublattice included only partially filled vacancies ($La_{7/12}Li_{1/3}\square_{1/6}TiO_3$, $La_{7/12}Na_{1/4}\square_{1/6}TiO_3$, $La_{7/12}K_{1/4}\square_{1/6}TiO_3$) whereas in the other materials the vacancies were completely filled up ($La_{1/2}Li_{1/2}TiO_3$, $La_{1/2}Li_{1/2}TiO_3$, $La_{1/2}Li_{1/2}TiO_3$). According to the data previously obtained by us [11,12] in the case of partially filled vacancies ($La_{7/12}M_{1/4}\square_{1/6}TiO_3$, M–Li, Na, K) the rhombic unit cell was discovered, while in the latter case, when all vacancies were filled up ($La_{1/2}M_{1/2}TiO_3$, M–Li, Na, K), the tetragonal unit cell was indicated.

In accordance with the group-theoretic analysis of normal oscillations of crystal lattice the presence of eight optical oscillations in the tetragonal perovskite has been presumed.[15] The number of experimentally recorded reflection bands in the spectra of $La_{1/2}Li_{1/2}TiO_3$, $La_{1/2}Na_{1/2}TiO_3$, $La_{1/2}Na_{1/4}K_{1/4}TiO_3$, satisfactorily agrees with the results of group-theoretic analysis (Fig. 1). Oscillation spectra of rhombic-distorted perovskites $La_{7/12}Na_{1/4}TiO_3$ and $La_{7/12}Li_{1/4}TiO_3$, according to the data of group-theoretic analysis, should comprise 25 IR active oscillations,[16] which is much greater then the number of reflection bands that were recorded (Fig. 1). The difference observed might originate from the fact that some deviations from ideal structure in rhombic-distorted perovskites are faint so part of the oscillation bands does not represent noticeable splitting.

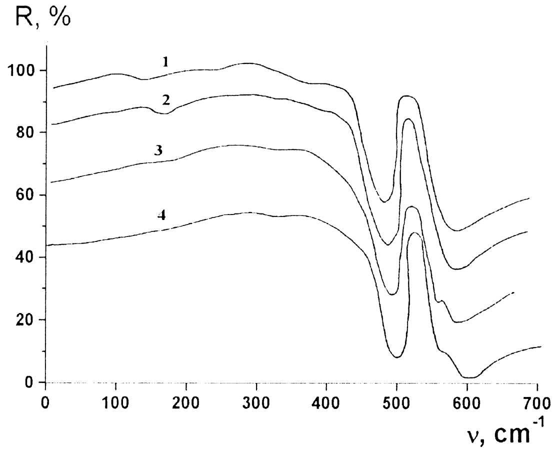

Fig. 1. Reflection spectra of polycrystalline lanthanum titanate; (1) $La_{1/2}Na_{1/4}K_{1/4}TiO_3$; (2) $La_{1/2}Na_{1/2}TiO_3$; (3) $La_{7/12}Na_{1/4}TiO_3$; (4) $La_{7/12}Li_{1/4}TiO_3$.

According to Ref. 17 the oscillations which occur within the region of 450–900 cm^{-1} are related to the valence oscillations while those within the region of 250–400 cm^{-1}are related to the deformation oscillations of oxygen octahedron TiO_6. In the far IR region ($\nu <$ 200 cm^{-1}) the complex oscillation, true to perovskite type, is observed.[16] Apparently, it should also comprise atom movement in La-sublattice because, when changing 1/4 Na in $La_{1/2}Na_{1/2}TiO_3$ to heavier K, the shift of this band towards low frequencies is observed together with slight increase in the permittivity.[18] The same behavior is observed also in the case of the compounds $La_{7/12}M_{1/4}TiO_3$ when changing from M = Li to M = Na.

Because of slight deviations from ideal structure, the spectra of both rhombic-distorted and tetragonal perovskites are very similar. The difference is only related to the valence oscillations of oxygen octahedron TiO_6. They have almost regular shape in $La_{1/2}Na_{1/2}TiO_3$ and $La_{1/2}Na_{1/4}K_{1/4}TiO_3$ while in $La_{7/12}Na_{1/4}TiO_3$ and $La_{7/12}Li_{1/4}TiO_3$ another oscillation with low intensity is also observed above 750 cm^{-1} (Fig. 1). Similar splitting of the high-frequency band was first observed by Last in $BaTiO_3$ with a reduction from cubic lattice symmetry to orthorhombic, and was ascribed to the partial re-degeneration of the oscillations.[19]

The distinctive feature of the compounds $La_{7/12}M_{1/4}TiO_3$ is that 1/6 sites in the La-sublattice are vacant. In the case when the atoms of both rare-earth elements and alkali metals were statistically distributed, two octahedrons TiO_6 would have different local symmetry [15] which would result in doublet bands in the region of 250–900 cm^{-1}. Whereas doublet bands were not experimentally observed the vacancy distribution in

Table 1
Parameters of the dispersion oscillators $(La_{2/3-x}M_{3X}\square_{1/3-2x})TiO_3$

$La_{1/3}Na_{1/2}TiO_3$				$La_{7/12}Na_{1/4}\square_{1/6}TiO_3$				$La_{7/12}Li_{1/4}\square_{1/6}TiO_3$			
$\varepsilon = 105$				$\varepsilon = 87$				$\varepsilon = 77$			
ω_{TO} cm^{-1}	ω_{LO} cm^{-1}	$\Delta\varepsilon$	g	ω_{TO} cm^{-1}	ω_{LO} cm^{-1}	$\Delta\varepsilon$	g	ω_{TO} cm^{-1}	ω_{LO} cm^{-1}	$\Delta\varepsilon$	g
127	184	83.0	0.68	133	178	55	0,64	138	153	33,0	0,68
199	224	7.6	0.18	201	224	19,5	0,31	182	231	30,0	0,53
240	335	7.7	0.32	230	265	4,1	0,3	246	319	6,8	0,34
337	374	0.2	0.15	270	343	1,8	0,26	326	493	1,0	0,30
375	482	0.1	0.03	345	490	0,2	0,1	–	–	–	–
555	752	0.4	0.08	563	694	1	0,11	557	720	1,0	0,08
805	844	0.1	0.15	789	860	0,3	0,3	791	848	0,1	0,20
$\varepsilon_\infty = 5, 1$				$\varepsilon_\infty = 5, 1$				$\varepsilon_\infty = 5, 1$			

these compounds presumably represents the trend to ordering.

When examining reflection spectra obtained by means of variance analysis [20] the parameters of dispersion oscillators have been determined to form the basis for the description of experimental reflection spectrum (see Table 1). It should be noted that, regardless of alkaline ion, contribution of optical polarization is always the same ($\varepsilon_\infty = 5.1$). This indicates that the matrix of lanthanum titanate mainly determines the contribution of optical polarization into the permittivity. Alkaline ions influence the properties of the perovskites $La2/3-xM_{3x}$ TiO_3 (M–Li, Na, K) only at low frequencies. This is because of the fact that alkaline ions, in particular lithium ions, are not tied with the rigid framework in the perovskite $La_{2/3-x}Li_{3x}TiO_3$ unlike, for example, electrolytes with the structure γ-Li_3PO_4, which allows them to contribute to the conductivity.

The examination of temperature dependencies of the ESR linewidth ^7Li and ^{23}Na in the perovskites $La_{2/3-x}M_{3x}TiO_3$ (M–Li, Na) as well as the time of lattice-spin relaxation (T_i) of the above nuclei shows that lithium and sodium ions are movable inside the lattice cavity formed by oxygen octahedra TiO_6. The distinctive feature of lithium ions consists in the fact that they shift from the center for a greater distance than sodium ions towards positions with far higher electric field gradients (EFG). The latter results in a lower activation energy of sodium ions in comparison with that of lithium ions, when they are moving within the structural cavities formed by oxygen octahedra. The results obtained show that the extending bottleneck size in the perovskites — when introducing large lanthanum or titanium ions — does not result in the decrease of activation energy of the conduction ions.[21,22] This could be explained by simultaneous extension of bottleneck size and the size of structural cavity formed by oxygen octahedra TiO_6. At the same time an increase in the cavity size initiates noticeable bias of small lithium ions from the center towards the positions with high electric field gradients, which increases activation energy of lithium ions during their movement along the structural channel.

The investigations carried out have shown that lithium ion conductivity is essentially affected on the one hand by the ratio of lithium ions and the vacancies in lanthanum sublattice which contains shared lithium and lanthanum ions, and the vacancies, and on the other hand by the size of conducting channels formed by oxygen octahedra. The latter is to a great extent determined by the ionic radii of the rare-earth ion (Fig. 2).

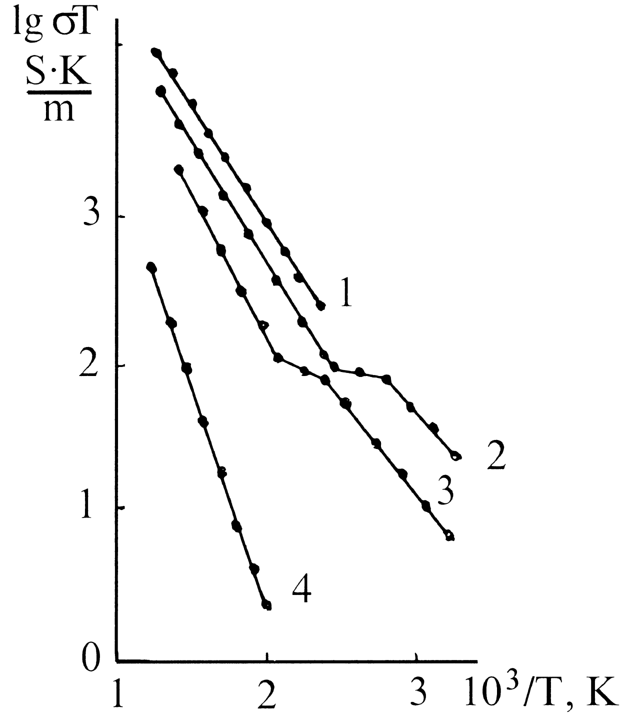

Fig. 2. lg (σT) of the perovskites as a function of temperature: (1) $La_{13/24}Ti_{3/8}\square_{1/12}O_3$; (2) $La_{1/2}Li_{1/2}TiO_3$; (3) $La_{3/5}Li_{1/5}\square_{1/5}TiO_3$; (4) $Nd_{1/2}Li_{1/2}TiO_3$.

4. Conclusion

High lithium ion conductivity in the materials of the system $La_{2/3-x}Li_{3x}TiO_3$ is due to a number of factors, which are, in particular, as follows: (a) lithium ions are not tied with the rigid lattice framework, and are, therefore, able to contribute to the conductivity; (b) the bottleneck size of structural channels as well as the size of the cavities, formed by oxygen octahedra, on the one hand are not large enough to allow the shift of lithium ions towards high electric field gradients, and on the other hand are large enough to provide the movement of lithium ions down the structural channels; (c) there is the chance in a wide-ranging ratio control of lithium ions and the vacancies in the lanthanum sublattice of the perovskites $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$.

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