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Effect of quenching on structure and antiferroelectric instability of $La_{(2-x)/3}Li_xTiO_3$ compounds: a Raman study

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This work is dedicated to Professor Domingo González, from the University of Zaragoza, on the occasion of his retirement.

Abstract

A Raman study of the $La_{(2-x)/3}Li_xTiO_3$ ionic conductors has been performed as a function of temperature, lithium content and synthesis cooling rate. Irrespective of thermal treatment or lithium content, the spectrum can always be explained within a tetragonal symmetry (space group P4/mmm), which suggests that, at a local scale of several unit cells, some cation ordering persists even in samples submitted to quenching conditions. The mode involving mostly in-plane titanium vibration softens on lowering temperature, though a phase transition never occurs. The effect is attributed to the tendency of these double-perovskite systems to antiferroelectric ordering, frustrated by structural disorder. Quenching the samples from high temperature increases cation disorder and suppresses the tendency of these systems toward antiferroelectric instability. A correlation is found between the degree of instability and the parameter $\eta = La1 - La2 - x$, where La1 and La2 stand for the site occupancy factors of lanthanum ions in sites La1 and La2, respectively.

Keywords: Ferroelectric properties; Ionic conductivity; Perovskites; Spectroscopy

1. Introduction

Since the discovery of the excellent behavior of $La_{(2-x)/3}Li_xTiO_3$ compounds (LLTO in the following) as Li-ion conductors,[1,2] intense experimental work has been performed on them with a variety of techniques: structural characterization[3–8] conductivity and dielectric relaxation,[9] NMR,[10,11] etc. During recent years we have undertaken the Raman study of the LLTO family of compounds as a function of lithium content, temperature, thermal treatments and Li isotope substitution.[12,13] To identify the symmetry of the observed modes, polarization measurements were carried out in a fiber processed by the laser floating zone technique, as described elsewhere.[13,14] From these studies, useful information was obtained concerning structure, lithium dynamics and structural stability against Ti antiferroelectric (AFE) ordering. In this work we present a more detailed study of how a rapid cooling rate during synthesis affects the structural and AFE properties.

2. Experimental

Ceramic samples used in this work were produced through a solid-state reaction mechanism.[4] The powders were uniaxially pressed and then heated up to 1350 °C to obtain sintered powders, which were submitted to two different heat treatments: (a) slow cooling rate of 1°/min, and (b) quenching treatment from 1350 °C to liquid-nitrogen temperature (LNT).

Raman experiments were performed in a Dilor XY spectrometer with a diode array detector. Light from an Ar^+ laser at 514.5 nm was focused onto the sample through a 50× microscope objective lens. The power at the sample was $\leqslant 10$ mw and the spectral resolution ≈ 3 cm^{-1}. Raman frequencies were calibrated against Ar^+ plasma lines with an estimated accuracy of ± 0.5 cm^{-1}.

3. Structure

In spite of intense research, there is still some controversy concerning the actual space group (s.g.) of LLTO compounds. However, there is agreement in that the basic unit cell is a double perovskite one, with

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doubling arising from alternation of La-rich and La-poor planes. From this basic unit cell, which has tetragonal symmetry and s.g. P4/mmm, lower symmetries are found depending on the lithium content, cooling rate used in the synthesis and the experimental technique employed in the structural characterization. By means of X-ray diffraction (XRD), in samples cooled at 1 °C/min, an orthorhombic symmetry (s.g. Pmmm) is found for $x<0.3$, and a tetragonal one (s.g. P4/mmm) for $x \geqslant 0.3$.[4] If the samples are quenched from the sintering temperature to LNT, much higher symmetries are found by XRD, yielding in almost every case, except for very low lithium content, a pseudocubic unit cell with $a \approx b \approx c$, but still showing some intensity in the form of broad bands at the angles where superstructure peaks appear.[15] On the other hand, a supercell of dimensions $2a \times 2a \times 2a$ and orthorhombic symmetry is found by neutron diffraction in slowly cooled (SC) samples with low lithium content.[7,8]

4. Experimental results and interpretation

One of the aims of our work was to obtain more insight into the local structure of LLTO compounds, taking advantage of the microscopic character of Raman spectroscopy, as compared with XRD or neutron diffraction. For this purpose we have measured the Raman spectra of polycrystalline samples of both SC and quenched (Q) samples with varying lithium content ($0.12 \leqslant x \leqslant 0.47$). The spectrum of the $x=0.18$ sample before and after the quenching procedure is shown in Fig. 1. Depending on the lithium content and temperature of measurement, the spectrum displays from five to seven bands, whose attribution has been made in previous works[12,13] and is summarized here: bands near 140 and 320 cm^{-1} are ascribed to modes involving mostly in-plane and c-axis titanium vibration, respectively, while all the other modes are assigned to oxygen motion. Coupling of oxygen atoms with lithium cations was proposed to explain the behavior of the highest frequency band as a function of temperature and of lithium content.[13]

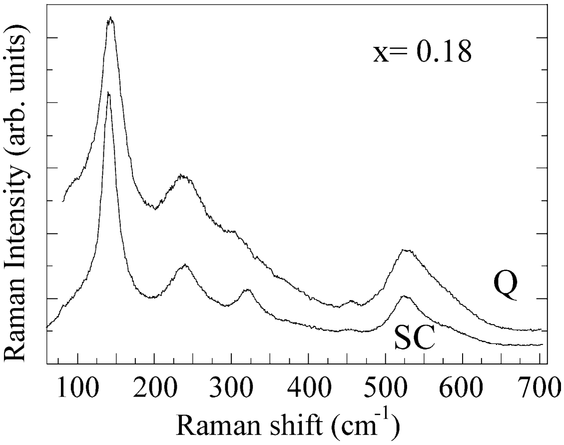

Fig. 1. Room temperature spectrum of the $x=0.18$ sample before and after the quenching procedure.

Irrespective of thermal treatment or lithium content, the spectrum can always be interpreted within a tetragonal approach. In the case of the orthorhombic compounds this can be explained by broadening arising from the disorder inherent to the LLTO system due to the presence of vacancies and lithium ions in La sites. More interesting is the finding of a tetragonal symmetry in Li-rich or in quenched samples, that show a quasicubic XRD pattern, suggesting that some cation ordering persists, at least to a scale of several unit cells.

At this point, the relevant questions are which is the cation distribution at a given temperature, how does quenching alter this distribution, and how are these changes reflected in the XRD diffractogram. In a recent work[15] we have shown that, though La diffusion starts at about 900–1000 °C, this process is slow at these temperatures and some cation ordering may persist at temperatures as high as 1300 °C. Then the simultaneous appearance of a tetragonal spectrum and a quasicubic diffractogram in quenched samples can be explained by the combined effect of two factors: (i) Lanthanum diffusion at high temperatures, that modifies the site occupancy factors (SOF) of La1 and La2 sites with respect to the values present in SC samples, reducing the difference between them. This increased disorder explains the greater broadening of the Raman spectrum of quenched samples, as well as the intensity changes observed for some bands. (Quenching is assumed to preserve the cation distribution given at the temperature of quenching) (ii) The formation of ordered nanoscale domains that yield the tetragonal Raman spectrum but are averaged in XRD to an almost cubic pattern. Atomic disorder at the domain boundary is also assumed to broaden the Raman spectrum.

The preservation of some degree of cation ordering in quenched samples is further supported by the constancy of the activation energy for lithium diffusion in SC and Q samples. In Ref. 13 we showed that the disappearance of the high frequency band with increasing temperature was related to the thermal activation of lithium motion. Only SC samples where included in that analysis. Following the same procedure for Q samples we have now found that the onset temperature and the activation energy for the intensity decrease of the high frequency band are the same as in SC samples. The independence of the activation energy for lithium motion upon thermal treatments is also concluded from conductivity and NMR measurements.[16]

Another important consequence of quenching treatments is the suppression of the tendency of this system toward AFE instability. As shown in a previous work,[12] softening of the mode involving mostly in-plane Ti displacements is observed upon cooling, which was attributed to the tendency of the structure toward AFE ordering by Ti shifts. Fig. 2 shows the temperature dependence of the Raman shift of this mode, ω, for SC and Q samples. It is clearly seen that softening effects decrease with increasing lithium content and upon quenching.

Disorder-induced random fields at the Ti site prevent the occurrence of an actual phase transition. Several factors may determine the degree of disorder, the most important being the imperfect alternation of La-rich/La-poor planes and the presence of Li ions close to a Ti site.

As a measure of the AFE instability we have taken the total frequency shift of the Ti soft mode, Δ, from the highest temperature reached in our experiments (about 870 K) down to 10 K, and tried to find whether there is a unique parameter that permits to explain simultaneously the variations of Δ observed in SC and Q samples.

In Fig. 3a we plot Δ as a function of lithium content (x). Though it is clear that increasing x results in smaller Δs, SC and Q samples yield two separate curves, as one would expect since, for a given Li content, quenching adds disorder at the Ti site. Disorder arising from imperfect La1/La2 alternation may be quantified by the SOF of La cations in La1 and La2 sites, that we will denote just by La1 and La2, respectively. Table 1 shows La1 and La2 values for SC and Q samples of varying lithium content, together with other structural parameters, and Fig. 3b shows Δ as a function of La1−La2. Quite surprisingly, there are still two curves, suggesting that there is more than cation disorder in the origin of the AFE-instability suppression: SC samples with high Li content have a much smaller Δ than Q samples of low lithium content with the same La1−La2 value.

To include the additional contribution of lithium ions, we represent in Fig. 3c the variation of Δ as a function of $\eta = \text{La1} - \text{La2} - x$: The points fit fairly well to a single curve. We conclude that lithium itself is a source of disorder at the Ti site, beyond the structural changes that accompany the increase of lithium content. The goodness of η in describing structural stability, at least concerning AFE properties, can be justified as follows:

We assume that lithium distribution is isotropic so that no preference for La1 or La2 sites occurs. Then, from the x Li ions present in a given composition, equal amounts of $x/2$ ions are assumed to occupy La1 and

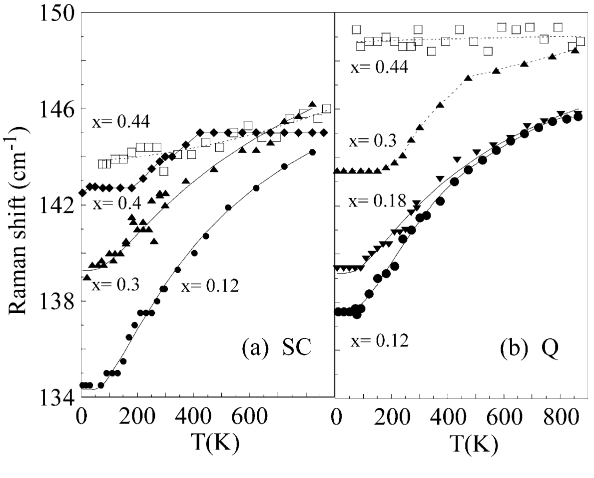

Fig. 2. Temperature dependence of the Raman shift of the mode involving in-plane Ti vibration for some SC (a) and Q (b) samples. Lithium content (x) is specified in each case.

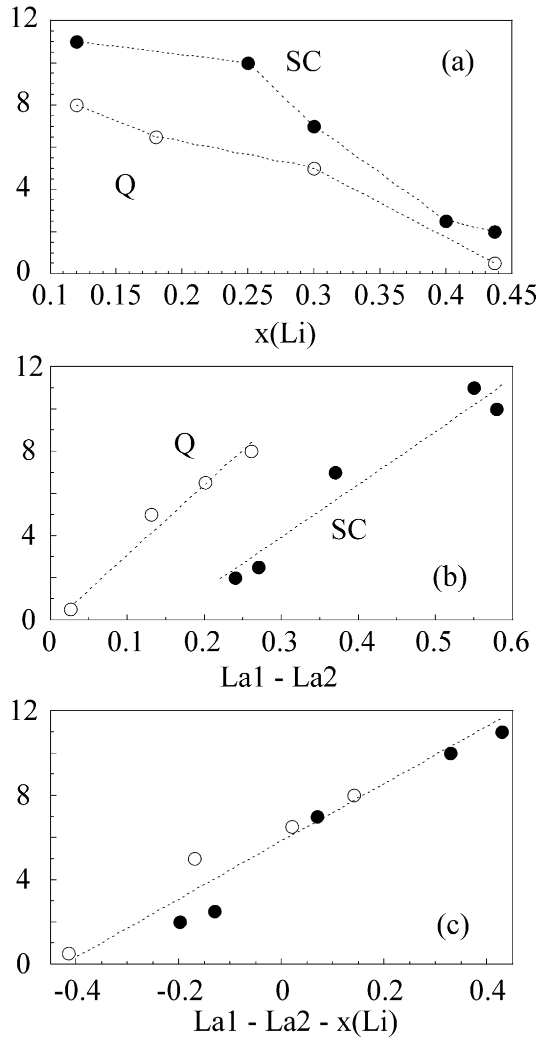

Fig. 3. The total frequency shift of the Ti soft mode, Δ, from 870 K down to 10 K is plotted versus different parameters: (a) Δ as a function of lithium content, (b) Δ as a function of the difference between the site occupancy factors of La1 and La2 sites, La1−La2, (c) Δ as a function of $\eta = \text{La1} - \text{La2} - x$, that we have proposed as a parameter describing the degree of structural instability.

Table 1
Structural data for slowly cooled (a) and quenched (b) LLTO compounds

x (Li)	a (Å)	b (Å)	c (Å)	La1	La2	Δ (cm^{-1})
(a) Slowly cooled						
0.12	3.8747(1)	3.8632(1)	7.7846(1)	0.9	0.35	11
0.25	3.8769(2)	3.8659(2)	7.7855(2)	0.87	0.3	10
0.3	3.8727(3)		7.7510(3)	0.75	0.38	7
0.4	3.8708(3)		7.7491(3)	0.66	0.39	2.5
0.44	3.8700(1)		7.7452(2)	0.62	0.38	2
(b) Quenched						
0.12	3.8780(2)		7.7524(7)	0.737	0.476	8
0.18	3.8788(2)		7.7538(5)	0.707	0.506	6.5
0.3	3.8785(2)		7.7544(7)	0.632	0.501	5
0.44	3.8696(7)		7.7394(1)	0.533	0.507	<1

a, b and c are the lattice parameters in Pmmm or P4/mmm s.g. La1 and La2 stand for the site occupancy factors of La1 and La2 sites. Cell parameters and occupancies for slowly cooled samples are taken from Ref. 4. We also include the soft mode frequency variation between the highest and lowest temperatures, Δ.

La2 sites, respectively. However, it has been found that lithium ions shift toward the center of the squares formed by four oxygen atoms, midway between two La sites.[17] Since La1$\gg$La2 for the most ordered compounds, a Li ion in a La1 site will more likely shift toward a (probably vacant) La2 site, to a location with $z\approx0.25$ (the Ti–O$_{eq}$ plane), than toward another La1 site, which is probably occupied. Similarly, a lithium ion in a La2 site will more likely move within the $z=0.5$ plane toward another (probably vacant) La2 site than toward a (probably occupied) La1 site. From these lithium sites, only those at $z\approx0.25$ are expected to perturb the softening of the in-plane Ti vibration significantly. Since SOF of La1 and La2 sites are normalized to one, the occupancy of lithium ion in the $z\approx0.25$ sites is not $x/2$ but x, thus providing an explanation for the appearance of x in the definition of η.

5. Summary and conclusions

We have presented a Raman study of the LLTO family of compounds, from which information on structural, dynamic and antiferroelectric properties is obtained. Quenching the samples from high temperature increases cation disorder, partially suppressing the La1/La2 alternation along the c-axis. To explain the detection of a tetragonal spectrum in samples with a quasicubic diffractogram we propose that small ordered domains, with dimensions of several unit cells, are formed. Finally, we have found that quenching suppresses the tendency of LLTO systems toward antiferroelectric instability. A parameter is proposed, involving lanthanum site occupancy factors as well as lithium content, to describe the degree of structural stability.

Acknowledgements

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References

1. Belous, A. G. *et al.*, Electroconductivity of perovskites La$_{2/3-x}$M$_{3x}$TiO$_3$ (in Russian). *Ukr. Fiz. Zh.*, 1986, **31**, 576.
2. Inaguma, Y., Liquan, C., Itoh, M., Nakamura, T., Uchida, T., Ikuta, H. and Wakihara, M., High ionic conductivity in lithium lanthanum titanate. *Solid State Commun.*, 1993, **86**, 689.
3. Fourquet, J. L., Duroy, H. and Crossnier-López, M. P., Structural and microstructural studies of the series La$_{2/3-x}$Li$_{3x}\square_{1/3-2x}$TiO$_3$. *J. Solid State Chem.*, 1996, **127**, 283.
4. Ibarra, J., Várez, A., León, C., Santamaría, J., Torres-Martínez, L. M. and Sanz, J., Influence of composition on the structure and conductivity of the fast ionic conductors La$_{2/3-x}$Li$_{3x}$TiO$_3$ ($0.03\leqslant x\leqslant0.167$). *Solid State Ionics*, 2000, **134**, 219.
5. MacEachern, M. J., Dabkowska, H., Garrett, J. D., Amow, G., Gong, W., Liu, G. and Greedan, J. E., Metal–insulator transitions in La$_{1-x}$TiO$_3$, $0.0\leqslant x\leqslant0.33$. Structure–property correlations. *Chem. Mater.*, 1994, **6**, 2092.
6. Várez, A., García-Alvarado, F., Morán, E. and Alario-Franco, M. A., Microstructural study of La$_{0.5}$Li$_{0.5}$TiO$_3$. *J. Sol. State Chem.*, 1995, **118**, 78.
7. Sanz, J., Alonso, J. A., Várez, A. and Fernández, M. T., Octahedral tilting and ordering of vacancies in the fast ion conductor Li$_{0.12}$La$_{0.63}$TiO$_3$ perovskite: a neutron diffraction study. *J. Chem. Soc. Dalton Trans.*, 2002, **7**, 1406.
8. Inaguma, Y., Katsumata, T., Itoh, M. and Morii, Y., Crystal structure of a lithium ion-conducting perovskite La$_{2/3-x}$Li$_{3x}$TiO$_3$ ($x=0.05$). *J. Solid State Chem.*, 2002, **166**, 67.
9. León, C., Santamaría, J., París, M. A., Sanz, J., Ibarra, J. and Torres-Martínez, L. M., Non-Arrhenius conductivity in the fast ionic conductor Li$_{0.5}$La$_{0.5}$TiO$_3$: reconciling spin-lattice and electrical-conductivity relaxations. *Phys. Rev. B*, 1997, **56**, 5302;
   León, C., Rivera, A., Várez, A., Sanz, J., Santamaría, J. and Ngai, K. L., Origin of constant loss in ionic conductors. *Phys. Rev. Lett.*, 2001, **86**, 1279.
10. París, M. A., Sanz, J., León, C., Santamaría, J., Ibarra, J. and Várez, A., Li mobility in the orthorhombic Li$_{0.18}$La$_{0.61}$TiO$_3$ perovskite studied by NMR and impedance spectroscopies. *Chem. Mater.*, 2000, **12**, 1694.
11. Bohnké, O., Emery, J., Veron, A., Fourquet, J. L., Buzaré, J. Y., Florian, P. and Massiot, D., A distribution of activation energies for the local and long-range ionic motion is consistent with the disordered structure of the perovskite Li$_{3x}$La$_{2/3-x}$TiO$_3$. *Solid State Ionics*, 1998, **109**, 25.
12. Sanjuán, M. L. and Laguna, M. A., Raman study of antiferroelectric instability in La$_{(2-x)/3}$Li$_x$TiO$_3$ ($0.1\leqslant x\leqslant0.5$) double perovskites. *Phys. Rev. B*, 2001, **64**, 174305.
13. Laguna, M. A., Sanjuán, M. L., Várez, A. and Sanz, J., Lithium dynamics and disorder effects in the Raman spectrum of La$_{(2-x)/3}$Li$_x$TiO$_3$. *Phys. Rev. B*, 2002, **66**, 54301.
14. Várez, A., Sanjuán, M. L., Laguna, M. A., Peña, J. I., Sanz, J. and de la Fuente, G. F., Microstructural development of the

$La_{0.5}Li_{0.5}TiO_3$ lithium ionic conductor processed by the laser floating zone (LFZ) method. *J. Mater. Chem.*, 2001, **11**, 125.

15. Várez, A., Ibarra, J., Rivera, A., León, C., Santamaría, J., Laguna, M. A., Sanjuán, M. L. and Sanz, J., Influence of quenching treatment on structure and conductivity of the $Li_{3x}La_{2/3-x}TiO_3$ series. *Chem. Mater.*, 2003, **15**, 225.
16. Rivera, A., León, C., Santamaría, J., Várez, A. and Sanz, J., unpublished results.
17. Alonso, J. A., Sanz, J., Santamaría, J., León, C., Várez, A. and Fernández-Díaz, M. T., On the location of Li^+ cations in the fast Li-cation conductor $La_{0.5}Li_{0.5}TiO_3$ perovskite. *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 619.