On the Local Structure and Lithium Dynamics of $La_{0.5}(Li,Na)_{0.5}TiO_3$ Ionic Conductors. A Raman Study

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We present a Raman study of structural and dynamical properties of the $La_{0.5}(Li,Na)_{0.5}TiO_3$ perovskites, closely related to the $La_{(2-x)/3}Li_xTiO_3$ ionic conductors. Despite intense experimental effort, the structure, lithium location, and diffusion mechanism of these materials are still controversial. The structure of $La_{0.5}(Li,Na)_{0.5}TiO_3$ compounds, in particular, has been refined as rhombohedral by neutron diffraction, with La and Na occupying randomly the A-type site. However, the correlation of their Raman spectra with those of $La_{(2-x)/3}Li_xTiO_3$ compounds indicates that some degree of cationic order is preserved on the nanometric scale and that rhombohedral symmetry may result from an average of ordered domains forming randomly. With regard to dynamical properties, we show that all compounds of the series with [Li] $\neq$ 0 present lithium diffusion, even for compositions below the percolation limit. This result is attributed to lithium diffusion being restricted, in such cases, to finite clusters, not contributing to macroscopic conductivity but being detected by Raman scattering due to the sensitivity of this technique to local environments.

Introduction

The outstanding properties of $La_{(2-x)/3}Li_xTiO_3$ (LLTO) compounds as Li-ion conductors[1] have given rise to research in related compounds, with the aim of improving their electrochemical performance or, at least, in the hope that they might provide some clues on the still controversial structure, lithium location, and mechanism of conductivity in those systems. In this respect, the family of Na-substituted perovskites $La_{(2-x)/3}(Li_{1-y}Na_y)_xTiO_3$ is specially interesting since it has been found that their conductivity does not vary linearly with the lithium content, but falls dramatically for lithium concentration below a certain value. In these compounds Na ions are not mobile; they rather act as barriers for lithium diffusion. This behavior was first studied in $La_{0.5}(Li,Na)_{0.5}TiO_3$ (LLNTO) compounds and explained by a percolation-limited mechanism of Li diffusion,[2] previously proposed for LLTO compounds by Inaguma and Itoh.[3] The authors of ref 2 also apply the percolation mechanism to LLTO compounds[2] and, more recently, to the $La_{0.6}(Li,Na)_{0.2}TiO_3$ series[4] in which the motion has a strong bidimensional character, as in the low-lithium content region of LLTO compounds. A recent work studies the percolation mechanism in low-lithium content LLTO.[5]

To explain spin−lattice relaxation (SLR) times found in NMR experiments, the authors in ref 2 proposed that some lithium mobility is preserved within finite clusters, even for compositions below the percolation limit. In agreement with this interpretation, Katsumata and Inaguma, in their study of the dielectric properties of $La_{0.53}Na_{0.41-x}Li_xTiO_3$ (ref 6) found a peak at 225 K in the dielectric loss of the $x = 0.17$ composition (thus below the percolation limit) that they interpreted as due to lithium jumps between adjacent perovskite unit cells, not yielding lithium conduction but affecting the macroscopic dielectric properties.

With regard to the structural properties of $La_{(2-x)/3}(Li_{1-y}Na_y)_xTiO_3$ perovskites, very different proposals are found in the literature, from monoclinic to pseudocubic symmetry, depending not only on lithium content and thermal history of the samples but also on the experimental technique used for structural characterization. (See refs 1 and 7 for comprehensive information). There is at least a common agreement in that the basic structural feature of these materials is the cation order along an axis, to form alternate La-rich and La-poor planes, accompanied by TiO_6 octahedron tilting. The different structures reported arise from the varying degree of cation order and also from the sense and magnitude of octahedra tilt. The situation is complicated even more by the formation of ordered domains with a distribution of sizes that depend on lithium content and thermal treatments.[7,8]

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In this work we apply Raman scattering to the study of the structure and dynamics of LLNTO compounds. It is known that Raman scattering is sensitive to variations of local structure and thus can give information on aspects such as domain formation, short-range vs long-range structural order, etc., that are at the origin of the wide disparity of structures proposed for $La_{(2-x)/3}(Li_{1-y}Na_y)_xTiO_3$ materials. The sensitivity of this technique to local environments makes it also suitable for questions related to short- or medium-range mobility.

In previous works[8−11] Raman scattering was applied to LLTO compounds. With regard to structural aspects, this technique was particularly useful in the detection of cation-ordered domains in quenched Li-rich samples, despite the almost cubic symmetry found by XRD.[8] Concerning dynamical properties, a correlation was found between the behavior of a high-frequency (HF) band and the concentration and dynamics of lithium ions, from which the activation energy for lithium motion was derived. It is thus expected that some interesting information is obtained concerning the structure and lithium dynamics in Na-doped perovskites.

Experimental Details

$La_{0.5}(Li_{1-x}Na_x)_{0.5}TiO_3$ samples ($0 \le x \le 1$) were produced by solid-state reaction from stoichiometric amounts of Li_2CO_3, Na_2CO_3, La_2O_3, and TiO_2, following the method described in ref 2. The samples used in this study were quenched into liquid nitrogen.

Raman measurements were performed in a DILOR XY spectrometer with a diode array detector, using the 514.5 nm line of an Ar^+ laser. A Linkam TP91 unit and a SMC-TBT cryostat were used for measurements above and below RT, respectively.

Structural Characterization

Our samples are the same as those used in ref 2. According to that work, at the resolution level of XRD they appear as pseudocubic, $Z = 1$ perovskites, with $a_p \approx 3.86$ Å, but are refined as rhombohedral (space group $R\bar{3}c$) in neutron diffraction (ND). In ND refinement, only one type of A site exists, which is randomly occupied by La and Na ions. Ti is located at an inversion symmetry point, and all oxygen atoms are equivalent. Lithium ions are found at the faces of the pseudocubic perovskite, in a squared-oxygen coordination (site 18d in $R\bar{3}c$) with partial occupancy.[2] Rhombohedral symmetry arises from a small tilt of TiO_6 octahedra around the trigonal ⟨111⟩ pseudocubic axis.

Experimental Results and Interpretation

1. In Relation to Crystal Structure. Figure 1shows RT Raman spectra of $La_{0.5}(Li,Na)_{0.5}TiO_3$ compounds as a function of lithium/sodium content. An evident trend toward disorder is observed as Na increasingly substitutes for lithium. To see structural trends, these spectra have been compared with those of LLTO compounds. We present in Figure 2 three spectra of samples with very similar lithium content ([Li] = 0.2−0.25) but with increasing degree of structural disorder. Spectra (a) and (b) correspond to slowly cooled and quenched LLTO samples with [Li] = 0.25, respectively. Spectrum (c) belongs to the $La_{0.5}Li_{0.2}Na_{0.3}TiO_3$ composition. Despite the increasing band broadening and the appearance of some extra peaks, the main features of the spectra can be traced from the most ordered to the most disordered compounds, suggesting that there is a basically common structure in all cases.

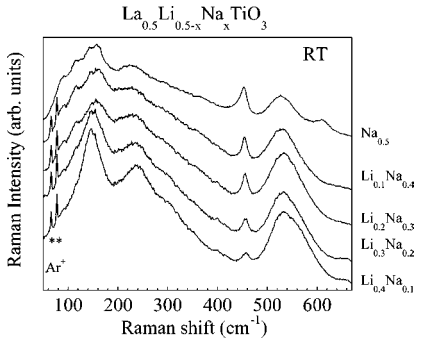

Figure 1. Room-temperature Raman spectra of $La_{0.5}(Li,Na)_{0.5}TiO_3$ compounds.

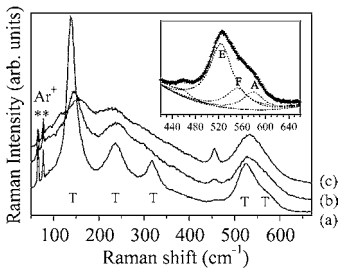

Figure 2. Raman spectra of slowly cooled (a) and quenched (b) LLTO compounds with [Li] = 0.25 are compared with that of $La_{0.5}Li_{0.2}Na_{0.3}TiO_3$ (c). The inset shows the deconvolution of the high-frequency band of spectrum (a) into three Lorentzian bands. Tetragonal-like modes are labeled with a T.

However, it happens that all these samples were given very different structures, depending on the experimental technique used, ranging from orthorhombic *Pmmm* (XRD),[12] or *Cmmm* (ND),[13] and monoclinic *P*2/*m* (high-resolution synchrotron XRD)[7] for compositions similar to that giving spectrum (a), to tetragonal *P*4/*mmm* (XRD) or rhombohedral $R\bar{3}c$ (ND) for sample giving spectrum (b), and pseudocubic (XRD)[2] or rhombohedral $R\bar{3}c$ (ND)[2] for sample giving spectrum (c). The main aspect distinguishing these structures is that cation order occurs in tetragonal, orthorhombic, and monoclinic unit cells, while rhombohedral and cubic structures show fully disordered A-type cations. The Raman activities expected for the different crystal structures proposed in the literature are listed in Table 1.

In previous works we interpreted the Raman spectra of all compositions of the LLTO family within a tetragonal (*P*4/*mmm*, $Z = 2$) double-perovskite cell since both the number of modes and their symmetries were in agreement with the predictions for this group, except for the B_{1g} mode,

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Table 1. Raman Activity Expected for the Different Symmetries Proposed for LLTO Compounds[a]

unit cell	space group	Z	cation order	Raman active atoms	number and symmetry of Raman active modes
cubic	*Pm*3*m*	1	no	none	none
rhombohedral	*R*$\bar{3}$*c*	2	no	La + O	5 : $A_{1g} + 4E_g$
tetragonal	*P*4/*mmm*	2	yes	Ti + O_{eq}	6 : $2A_{1g} + B_{1g} + 3E_g$
orthorhombic	*Pmmm*	2	yes	Ti + O_{eq}	9 : $3A_{1g} + 3B_{2g} + 3B_{3g}$
monoclinic	*Pmma*	4	yes	La + Ti + O	31 : $8A_{1g} + 5B_{1g} + 8B_{2g} + 10B_{3g}$
orthorhombic	*P*2/*m*	4	yes	La + Ti + O	30 : $15A_g + 15B_g$
orthorhombic	*Cmmm*	8	yes	La + Ti + O	29 : $10A_{1g} + 6B_{1g} + 6B_{2g} + 7B_{3g}$

[a] These data correspond to different experimental techniques, as well as to compounds with varying lithium content and thermal treatments. See ref 1 for an extensive description of these lattices and the compounds to which they apply.

which was not identified.[9−11] Tetragonal-like modes are labeled with a T in Figure 2. Mode symmetry was assigned by measurements in large single-crystal grains formed in a LFZ processed sample.[10,14] Splitting of E_g modes or extra peaks attributable to the lower symmetry of slowly cooled samples with low lithium content could not be found, probably due to limited resolution arising from line broadening, in the case of E_g modes, or due to extremely weak activity, for the undetected modes. The situation is reversed at the lithium-rich end: symmetry in Raman scattering appears to be lower than in XRD, since no Raman activity is expected for a cubic perovskite, but a spectrum is clearly detected. This apparent discrepancy is a consequence of domain formation, as discussed in refs 7 and 8.

We now compare the predictions of tetragonal and rhombohedral groups, which are conceptually most different, as explained above. In *P*4/*mmm* symmetry, six Raman active modes are expected; La and apical oxygen ions are inactive, and all modes arise from Ti and equatorial oxygens. Symmetry-adapted coordinates can be found in ref 10. On the other hand, for the *R*$\bar{3}$*c* unit cell five Raman active modes are expected, but Raman activity comes from different atoms: in this lattice Ti is not active but La is. Normal coordinates for this symmetry can be found in ref 15.

The question arises as to whether the spectra of Figure 1 can be explained within a rhombohedral (RH) approach. There are arguments to say that the answer is negative.

A most representative mode of RH perovskites is the A_{1g} mode involving oxygen octahedron tilt around the trigonal axis. This mode is Raman active in RH symmetry but not in tetragonal or OR symmetry and behaves as a soft mode toward a hypothetical phase transition from RH to cubic symmetry upon increasing temperature. We note that such phase transition has indeed been found by neutron diffraction at $T_c \approx 800$ °C in the $La_{0.5}Li_{0.2}Na_{0.3}TiO_3$ member of the series.[16] Though a temperature of 800 °C cannot be reached in our Raman experiments, soft mode behavior should be observed since softening usually occurs at temperatures much lower than T_c, even hundreds of degrees. No such trend has been found, at least up to 600 °C.

Another difficulty arises when we try to explain the similarity between spectra hypothetically coming from a RH lattice and those of well-ordered LLTO compounds, unambiguously involving cation/vacancy ordering. Establishing a link between tetragonal-like and RH-like is specially difficult if we note that there is a change from Ti-active, La-inactive in quasi-tetragonal systems to Ti-inactive, La-active in RH case.

We therefore propose that the spectra of Figure 1 reflect a certain degree of cation order remaining in LLNTO samples, at a scale of a few unit cells. The RH symmetry seen by ND can be the result of ordered nanodomains forming randomly along the three crystallographic axes, together with small octahedron tilts. The broadened appearance of the spectra certainly allows for other distortions, such as small oxygen shifts or octahedra tilts, to coexist with the underlying quasi-tetragonal structure. In fact, this may be the origin of the low-frequency shoulders appearing around 100 cm^{-1} and the remarkable band at 450 cm^{-1}, which clearly increase with Na content. In this respect, it is important to note that the finding of RH symmetry by ND occurs not only for quenched, lithium-rich LLTO samples or in the LLNTO series but also in quenched, Li-poor LLTO compounds,[13] where XRD clearly denotes still remaining quasi-tetragonal ordering.

Thus, the picture of LLNTO and quenched LLTO compounds arises as that of cation-ordered, quasi-tetragonal nanodomains of varying size, embedded in a rhombohedrally arranged matrix.

2. In Relation to Lithium Dynamics. Figure 3 shows the temperature evolution of the spectra of LLNTO samples with Na content of 0.1, 0.2, 0.3, and 0.4. Only the HF region ($\nu > 400$ cm^{-1}) is shown since in our previous work in LLTO we showed that it is in this region that Li dynamics are reflected.[10]

A common behavior is seen for all compounds of the series: upon increasing temperature, the HF band extending from 470 to 650 cm^{-1} loses intensity and becomes more symmetric. To explain that behavior, we recall here the interpretation of the HF band from our previous work in LLTO.[10] As shown in the inset of Figure 2, the HF band is made of three components, E, F, and A, at frequencies close to 525, 560, and 580 cm^{-1}, respectively. All of them are attributed to oxygen vibration. Within the tetragonal approach, the 525 cm^{-1} component is of E_g type (vibration within $x-y$ plane), while the 560 (F) and 580 (A) bands have A_{1g} character (displacements parallel to the *c* axis).[10,14] Since only two A_{1g} modes are expected by symmetry, and one of them, attributed to Ti vibration, is identified at 320 cm^{-1},

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(15) Sanjuán, M. L.; Orera, V. M.; Merino, R. I.; Blasco, J. *J. Phys.: Condens. Matter* **1998**, *10*, 11687.
(16) Várez, A.; Fernández-Diaz, M. T.; Sanz, J. *J. Solid State Chem.* **2004**, *177*, 4665.

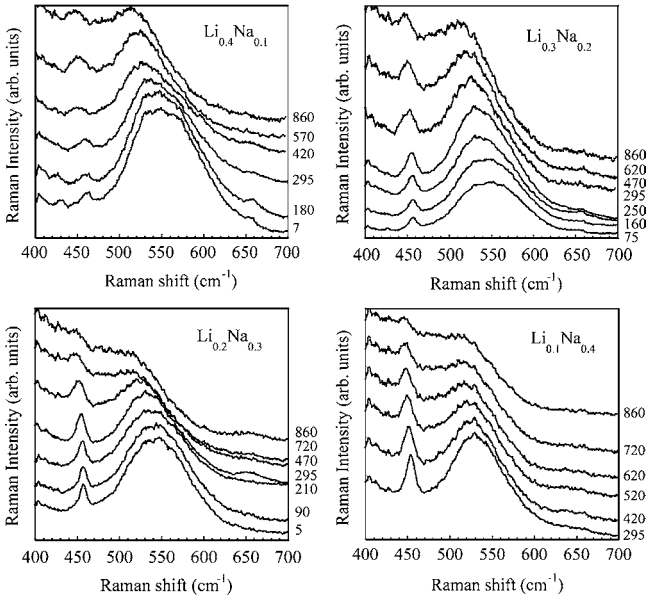

Figure 3. Temperature evolution of the spectra of four compositions of the $La_{0.5}(Li,Na)_{0.5}TiO_3$ series. Only the high-frequency region is shown. Temperatures (in Kelvin) are indicated to the right of each figure.

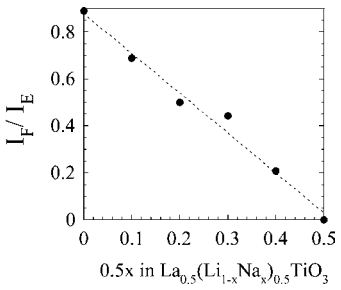

Figure 4. Composition dependence of the F-band intensity, relative to that of the E band at 525 cm^{-1}, along the $La_{0.5}(Li_{1-x}Na_x)_{0.5}TiO_3$ series.

either the F or the A bands must have a forbidden character. In fact, the F component was seen to increase with lithium content[10] and upon quenching from high temperature, both factors resulting in a loss of cationic order, while the A component is observed in well-ordered samples even for very low lithium content. Thus, the 580 (A) component is attributed to the allowed mode of the quasi-tetragonal symmetry, arising from unperturbed regions, while the 560 (F) component would arise from oxygen atoms perturbed by the presence of nearby lithium ions, thus explaining the dependence of the mode on lithium concentration. It is interesting to see in Figures 1 and 2 that the loss of cation order along the *c* axis affects much more the allowed A_{1g} modes (320 and 580 cm^{-1}), involving *c*-axis vibrations, than the in-plane E_g modes. In agreement with the almost complete cation disorder of LLNTO samples, only the F component was needed in profile analysis of these samples.

In ref 10 we showed that the disappearance of F and A oxygen bands on increasing temperature is related to lithium dynamics. We apply here the same ideas to the (Li,Na) mixed compounds. The correlation of the F band with lithium content in these materials is presented in Figure 4. The intensity decrease for increasing Na substitution confirms that, as in LLTO, the mode is activated by the presence of

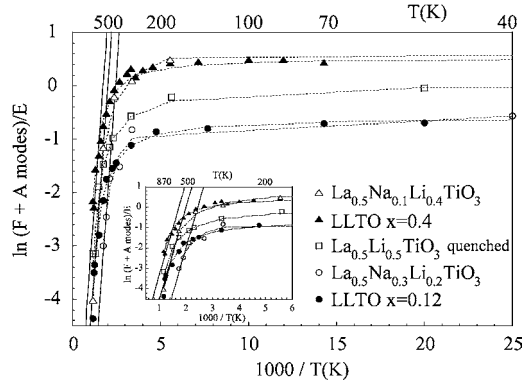

Figure 5. Arrhenius plot of the F (or F + A) band intensities, relative to that of the E band, for several LLTO or LLNTO compounds. The activation energy derived from the fit of the high-temperature region to a straight line is $E_a \approx 0.39$ eV.

lithium ions and suggests that its disappearance on increasing temperature may be related to lithium dynamics. Similarly to cation disorder, lithium dynamics affects more strongly A_{1g} than E_g modes, which suggests that lithium diffusion couples with (or is favored by) preferably *c*-axis oxygen vibration. The participation of lattice vibrations in the conduction mechanism was already proposed in ref 17 to explain the σ_{DC} vs $1/T$ dependence at high temperatures.

Through line shape analysis we derive the temperature evolution of the E and F components of the HF band. We plot in Figure 5 the T dependence of the F (or F + A) intensity relative to that of the E band, for several representative compounds: slowly cooled or quenched members of the LLTO family[10] and two members of the LLNTO series. The first remarkable point is that, independent of the lithium content or thermal treatment, and within experimental error, all samples present the same activation energy for band decrease beyond RT, which means that the local environment *seen* by lithium ions is similar for all these perovskite-type materials, irrespective of the details of long-range structure. The value of the activation energy for lithium diffusion found here ($E_a \approx 0.39$ eV)[18] is in very good agreement with that reported for LLTO compounds from dc conductivity, which is between 0.35 and 0.4 eV.[1]

With regard to lithium dynamics, the most remarkable fact is that the F band decreases gradually with increasing temperature in all compounds, even in cases where the lithium content is below the percolation limit. The simplest explanation of this evolution is that it reflects spatially limited lithium dynamics. In line with ref 2 we consider three stages of lithium dynamics: the local one, at $T < 200$ K, in which motion takes place around symmetrically equivalent sites within the same pseudocubic unit cell. These processes do not have any effect on the Raman spectrum. Above that temperature lithium ions may jump to a contiguous unit cell and from there on. Depending on whether the concentration of ions and vacancies is below or above the percolation threshold, lithium jumps might be restricted within a cluster

(17) Bohnke, O.; Bohnke, C.; Fourquet, J. L. *Solid State Ionics* **1996**, *91*, 21.

(18) The value of $E_a \approx 0.19$ eV given in ref 11 is incorrect. The present work corrects the error.

of several unit cells (medium-range motion) or progress across the whole sample in a long-range motion, thus contributing to macroscopic diffusion. Though having very different consequences for conductivity, the two latter processes are energetically similar and would produce the same effect on the Raman spectrum. Thus, the disappearance of the F band for compositions with Li + vacancy concentration below the percolation limit is attributed to lithium motion being restricted to clusters of several unit cells. This explanation supports the results of dielectric permittivity in ref 6 and of NMR in ref 2.

The final aspect that we have explored is whether our analysis can differentiate between the two- and the three-dimensional character of Li motion, as for instance NMR does.[19] In that case, one would expect the curves of Figure 5 to be different for samples where motion is predominantly 2D (as in slowly cooled LLTO compounds for $T \leq 270$ K) from those where motion is clearly 3D, as in quenched LLTO compounds or in the LLNTO series. Eventually, a transition from 2D to 3D character should also be detected for well-ordered LLTO compounds above ≈270 K, as observed in NMR.[19] A close look at the data in Figure 5 shows that band decrease starts at slightly higher temperatures in slowly cooled LLTO compounds, as compared with LLNTO ones. This fact, together with the observation that the intensity decrease below 250 K is very small for all systems, lead us to conclude that we are only detecting 3D lithium dynamics and that 2D diffusion, as far as it is restricted to the vacancy-rich plane, has no effect on the high-frequency Raman bands involving *c*-axis oxygen vibration.

(19) París, M. A.; Sanz, J.; León, C.; Santamaría, J.; Ibarra, J.; Várez, A. *Chem. Mater.* **2000**, *12*, 1694.

Summary and Conclusions

In summary, Raman scattering proves to be a useful technique in the study of the local structure and dynamics of $La_{(2-x)/3}Li_xTiO_3$ and $La_{0.5}(Li,Na)_{0.5}TiO_3$ systems. The similarity of the spectra of $La_{0.5}(Li,Na)_{0.5}TiO_3$ compounds with those of the LLTO series suggests that some degree of alternating cationic order persists in the Na-containing compounds, despite being refined as pseudocubic by XRD and rhombohedral by ND.[2] This interpretation is in the line already proposed for LLTO in that microstructural characterization is necessary to obtain a thorough knowledge of the structural properties of these materials.[7] No such study has been performed in LLNTO compounds to date.

The temperature evolution of a lithium-dependent mode has been ascribed to the activation of medium- or long-range lithium diffusion above $T \approx 250$ K. In particular, the disappearance of such mode for compositions with lithium + vacancies concentration below the percolation threshold is attributed to lithium motion being restricted within finite clusters, not contributing to long-range conductivity but affecting the spectrum in the same manner as long-range diffusion. The same activation energy is found for LLNTO and LLTO samples, irrespective of lithium content or thermal treatments.

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