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Raman study of antiferroelectric instability in $La_{(2-x)/3}Li_xTiO_3$ $(0.1\leqslant x\leqslant 0.5)$ double perovskites

M. L. Sanjuán and M. A. Laguna
Instituto de Ciencia de Materiales de Aragón (Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas), Facultad de Ciencias, 50009 Zaragoza, Spain

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A Raman study of the double-perovskite system $La_{(2-x)/3}Li_xTiO_3$ is presented. The in-plane vibration of Ti cations shows a soft-mode behavior on lowering the temperature, though the softening ceases below 60 K. The freezing-in of the atomic displacements involved would result in an antiferroelectric order, but the tendency to instability is suppressed by structural disorder arising from lithium doping and incomplete cation ordering in the *A* site of the perovskite.

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I. INTRODUCTION

Ferroelectricity (FE) is a common property of ABO_3 perovskites.[1] In the simplest case, FE behavior occurs as a consequence of a displacive phase transition driven by a zone-center TO mode involving the displacement of *A* or *B* cations along high-symmetry axes of the perovskite. Antiferroelectric (AFE) phase transitions have been less studied and have focused in $PbZrO_3$ and its solid solutions $(Pb, La)(Zr, Ti)O_3$.

In some cases FE is not fully achieved on lowering temperature and the paraelectric phase is stabilized by the zero-point fluctuations of the atoms involved in the soft-mode displacements. Examples of these *incipient* FE are $SrTiO_3$, $KTaO_3$, $CaTiO_3$ (Refs. 2–4), and rutile TiO_2.[5] In such cases, the TO soft-mode frequency ω_s never collapses to zero, but stabilizes below a certain temperature T_1, which determines the onset of quantum effects. Conversely, the static dielectric constant of an incipient FE does not diverge at a critical temperature, but reaches a plateau below approximately T_1.

In this work we report on similar effects appearing in the double-perovskite system $La_{(2-x)/3}Li_xTiO_3$ $(0.1\leqslant x\leqslant 0.5)$, whose basic unit cell is formed by stacking of two pseudocubic unit cells of parameter a_0. The doubling of the cell is a consequence of the ordering along the *c* axis of lanthanum-rich and lanthanum-poor planes (see Fig. 1).[6–8] In spite of intense experimental work, the precise location of Li atoms is not known yet.[9]

These compounds are excellent ionic conductors[6,10] with possible use as solid-state electrolytes in lithium secondary batteries and have been studied in the past few years by a variety of techniques: structural characterization[7,8,11] conductivity and dielectric relaxation,[12] NMR,[13,14] etc. In this work we shall not be concerned with their conducting properties, but will report on the unusual behavior of their Raman spectra as a function of temperature and lithium doping. In particular, we shall focus on the anomalous softening of the Raman mode associated with Ti in-plane vibration, which suggests a tendency of the double-perovskite structure toward AFE instability. We note that incipient FE has been found in $La_{0.5}Na_{0.5}TiO_3$,[15] but there is an essential difference between sodium and lithium systems: the Na compounds do not show the alternating plane ordering along the *c* axis.

The symmetry of $La_{(2-x)/3}Li_xTiO_3$ can be described as roughly tetragonal [space group (SG) $P4/mmm$] though small orthorhombic (OR) or rhombohedral distortions have been reported, depending on the lithium content, synthesis procedure, thermal treatments, and structural characterization technique. The OR distortions yield either a double-perovskite cell with parameters $a\approx a_0$, $b\approx a_0$, $c\approx 2a_0$, and SG *Pmmm*, or the *diagonal cell* of dimensions $a\approx\sqrt{2}a_0$, $b\approx\sqrt{2}a_0$, $c\approx 2a_0$.[8,16,17,11] We note that inversion point symmetry is preserved in these distortions; according to recent neutron diffraction data, no phase transitions occur below room temperature (RT).[18]

II. EXPERIMENTAL DETAILS

Ceramic samples used in this work were produced through a solid-state reaction mechanism and are the same studied in Ref. 8, where structural details can be found. Care was taken to use samples that had been synthesized following the same route, in order to avoid additional disorder effects. A cooling rate of 1 °C/min was held from the sintering temperature down to RT. This resulted in an OR *Pmmm* structure for $x<0.3$ and tetragonal $P4/mmm$ for $x\geqslant 0.3$ at RT. If faster cooling rates are used, the lithium-poor compounds present also a tetragonal structure. A small amount of lithium is required to stabilize the perovskite phase; undoped $La_{2/3}TiO_3$ can only be grown under reducing conditions.[16,17]

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 typically 3 cm^{-1}. Raman frequencies were calibrated against Ar^+ plasma lines with an estimated accuracy of ± 0.5 cm^{-1}. Possible sample heating during spectra recording was controlled by means of Stokes–anti-Stokes ratio measurements. Within the errors usually associated with this method we found that temperature increase is $\leqslant 10°$, which is attributed to the excellent transparency of these materials.

III. EXPERIMENTAL RESULTS

In the tetragonal unit cell of space group $P4/mmm$ (Fig. 1) the site symmetries and expected zone-center modes are

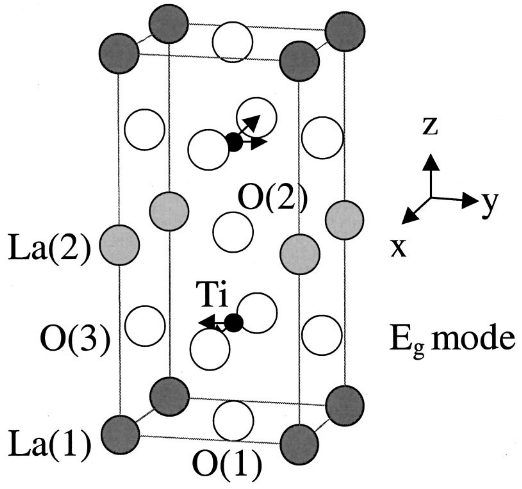

FIG. 1. Unit cell of the tetragonal double-perovskite structure of $La_{(2-x)/3}Li_xTiO_3$ $(0.1\leqslant x\leqslant 0.5)$ and symmetry-adapted displacements for the Ti E_g mode.

the following: La(1), $4/mmm$: $A_{2u}+E_u$; La(2), $4/mmm$: $A_{2u}+E_u$; *Ti*, $4mm$: $A_{1g}+E_g+A_{2u}+E_u$; O(1), $4/mmm$: $A_{2u}+E_u$; O(2), $4/mmm$: $A_{2u}+E_u$; O(3), $2mm$: $A_{1g}+B_{1g}+2E_g+A_{2u}+B_{2u}+2E_u$. We therefore expect within this symmetry six Raman-active modes $(2A_{1g},B_{1g},3E_g)$ involving Ti and O(3) atoms. For the present work we shall not be concerned by the actual site of Li ions and assume that they occupy vacant lanthanum sites.

Properly, for the low-lithium-content region one should consider the more accurate OR space group *Pmmm*, in which nine Raman-active modes are expected. However, several arguments have inclined ourselves to use the tetragonal SG for our analysis: (i) the number of modes observed is lower than predicted by the OR SG and agrees with the tetragonal prediction. (ii) In the lithium-rich region, where symmetry is indeed tetragonal, the spectra show essentially the same features as in lithium-poor compounds. (iii) Also the spectra of fast-cooled, lithium-poor samples, with tetragonal symmetry, present basically the same features as slowly cooled compounds, except for some frequency shifts and disorder-induced broadening. (iv) A transition from OR to tetragonal symmetry is found at about 500 °C in an OR, $x=0.18$ sample,[13] but no significant change is observed in the Raman spectrum at that temperature. Thus we conclude that, at our level of resolution, data can be interpreted within the tetragonal $P4/mmm$ group. OR splittings, if present, remain unresolved under the disorder-induced linewidth.

The RT Raman spectra of $La_{(2-x)/3}Li_xTiO_3$ $(x=0.12,0.25,0.3,0.4,0.5)$ ceramic samples are shown in Fig. 2(a). The corresponding spectra at low temperature are given in Fig. 2(b). We can see at least five bands in each spectrum, which we have labeled from *A* to *E*. In this work we shall focus in the lowest-frequency mode, feature *B*. A more complete description of the Raman spectra will be given elsewhere.

Several arguments support our attribution of this band to a mode involving the motion of the Ti cations: (i) Its low frequency points to a vibration of a heavy atom. (ii) On partial substitution of Ti by Al, it shifts to higher frequencies much more than the other modes.[19] (iii) Its frequency is very similar to that of the TO soft mode of $SrTiO_3$ at high temperature, far from any critical behavior.[20] (iv) In the double-perovskites $La_{1/3}NbO_3$ and $La_{1/3}TaO_3$, the mode appears at lower frequencies along the sequence of increasing masses (Ti, Nb, Ta).[21]

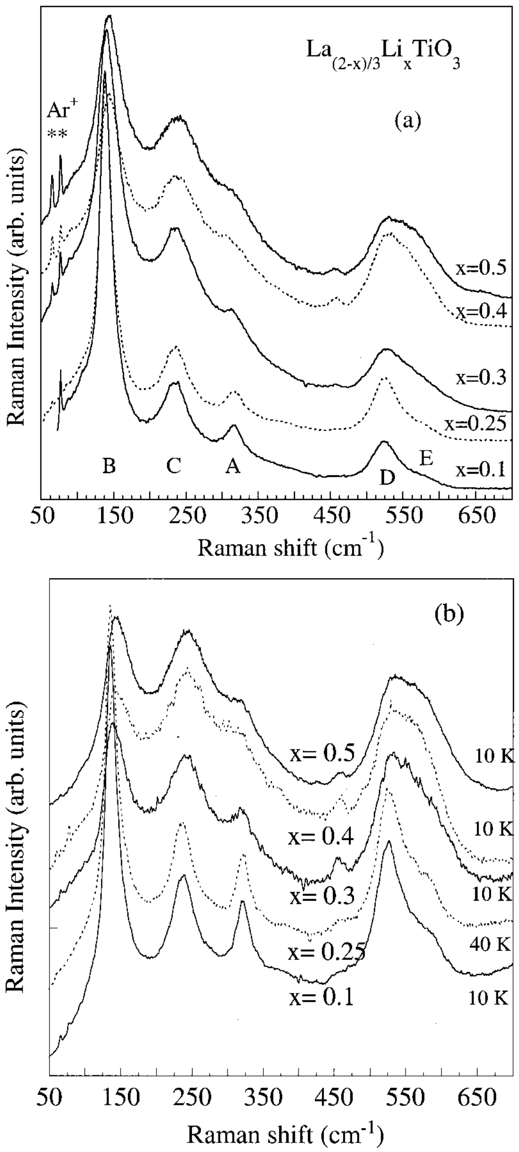

FIG. 2. Raman spectra of $La_{(2-x)/3}Li_xTiO_3$ at RT (a) and at low temperature (b).

Due to the depolarization of light in polycrystalline samples, we cannot assign a symmetry to the modes observed in these spectra. For this purpose, we have measured the Raman spectrum of a $La_{(2-x)/3}Li_xTiO_3$ fiber $(x=0.5)$ processed by the laser floating-zone method, in order to get single-crystalline samples. Longitudinal and transverse sections were studied by x-ray diffraction (XRD), electron microscopy, and Raman scattering. Details can be found in Ref. 22.

The transverse section of the fiber presented single-crystal grains of the $La_{(2-x)/3}Li_xTiO_3$ phase of about 50–100 μm diameter with $0.1<x<0.3$. According to XRD data, this

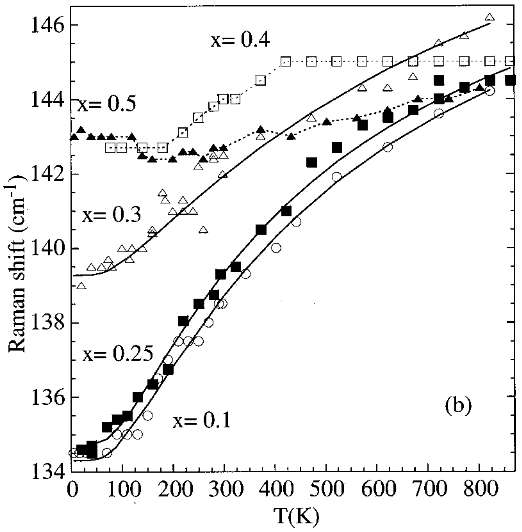

FIG. 3. Temperature dependence of the Raman shift of the Ti E_g mode. Solid lines are fits to the Barrett expression; dashed lines are guides for the eye.

phase had tetragonal $P4/mmm$ symmetry, which is attributed to the fast cooling rates involved in the method. For the present work the important result is that these grains were oriented in a (111) pseudocubic plane so that the growth direction was parallel to a $\langle 111 \rangle$ axis of the perovskite. We performed Raman measurements within one of such grains as a function of the angle of sample rotation around the $\langle 111 \rangle$ axis. The evolution of the peak intensities was compared with that calculated from the Raman tensors pertaining to $4/mmm$ symmetry in the configuration of incident and scattered electric fields held within the pseudocubic (111) plane. These measurements allow us to assign peaks *B*, *C*, and *D* to E_g symmetry species, while *A* and *E* peaks behave like A_{1g} modes. The B_{1g} mode has not been identified yet. The similarity between spectra collected in the fiber and those of ceramic samples allows us to assume that polarization properties are also extrapolable to the spectra presented in this work.

Therefore, band *B* corresponds to the E_g mode involving mainly the vibration of Ti cations within the tetragonal *a-b* plane, with perhaps some admixture of oxygen motion with the same symmetry (see Fig. 1).

Figure 3 shows the temperature evolution of the *B* mode frequency in $La_{(2-x)/3}Li_xTiO_3$. An increase is found in all compounds upon heating except perhaps for $La_{0.5}Li_{0.5}TiO_3$. In parallel to this hardening, the linewidth decreases by 2–5 cm^{-1}, depending on the compound. The temperature dependence of the Raman shift becomes weaker as the lithium content is increased and almost disappears, within experimental accuracy, for $La_{0.5}Li_{0.5}TiO_3$. All other modes show softening of a few cm^{-1} upon heating from 10 to 800 K.

IV. DISCUSSION

The presence of a mode with softening properties suggests that the lattice may be unstable against the atomic displacements involved in that mode. Alternatively, softening might be due to a strong fourth-order anharmonicity of the potential that would shift the average resonance frequency upward as temperature is increased.[23] However, we note that this effect would be accompanied by a parallel line broadening, contrary to the narrowing observed. Moreover, the almost universally found FE or AFE instabilities in Ti, Nb, and Ta perovskites leads in a natural way to our present interpretation of experimental results in terms of lattice stability.

In this sense, it is important to see that the condensation of the in-plane *B* cation mode would result in an AFE phase with parallel ordering in tetragonal *a-b* planes and antiparallel ordering along the *c* axis. AFE ordering is forced by the presence of inversion symmetry at (1/2,1/2,1/2). Within the theory of phase transitions this would be an AFE transition driven by a zone-center mode, a possibility that was already suggested in Ref. 1. As regards to the actual Ti displacements involved, we note that a shift along $\langle 110 \rangle$ directions, with equal *x* and *y* displacements, has the same E_g symmetry and seems more likely to occur. This displacement pattern is similar to that found in the AFE phase of $Sr_{1-x}Ca_xTiO_3$ $(0.18 \leqslant x \leqslant 0.4)$ (Ref. 24) or $NaNbO_3$.[25]

The experimental evolution of the Ti-mode Raman shift resembles that of the TO mode in incipient FE. This is not surprising, since the E_g soft mode of the double-cell system can be viewed as a superposition of two single-cell TO modes with alternating phase in each subcell. In incipient FE the temperature dependence of the static dielectric constant ε can be described by the Barrett model[26] and fitted to $\varepsilon = A + B/[(T_1/2)\coth(T_1/2T) - T_0]$, T_0 representing an effective Curie temperature and T_1 the temperature below which quantum effects can be expected. *A* and *B* are constants. The validity of this expression and the origin of the classical to quantum crossover are discussed in Refs. 2 and 27. Through the Lyddane-Sachs-Teller relation $\varepsilon(T)\omega_s^2 = \mathrm{const}$, the soft-mode frequency ω_s of incipient FE can be fitted to $\omega_s = \{C + D/[(T_1/2)\coth(T_1/2T) - T_0]\}^{-1/2}$ with *C* and *D* constant. Values of the fitting parameters for several systems are given in Table I.

To exploit the similarity with incipient FE, we have fitted our experimental data to the Barrett expression with parameters given in Table I. The crossover temperature T_1 is much higher in our systems than in incipient FE. We also find a negative and high value of T_0, as occurs in $La_{0.5}Na_{0.5}TiO_3$ and rutile. Since the Barrett expression is derived through a first-order approximation in the treatment of fluctuations, which are crucial in understanding the temperature evolution of the soft-mode frequency, doubt arises as to whether these parameters have a reliable physical meaning or should rather be taken as phenomenological ones for comparison purposes only. Barrett parameters can be related to those derived from the model of linearly coupled anharmonic oscillators, as given, for instance, in Refs. 2 and 27. We then find that T_1 is, in temperature units, the harmonic frequency ω_1 and that T_0 is proportional to $m\omega_1^2(V - m\omega_1^2)/\lambda$, where *V* measures the strength of intercell coupling, which tends to destabilize the lattice, and λ is the coefficient of the on-site quartic anharmonic potential term. The highly negative value of T_0 is associated to both a small *V* and to the high value of ω_1.[28]

TABLE I. Relevant data for La$_{(2-x)/3}$Li$_x$TiO$_3$ and incipient FE compounds. $\omega_{\mathrm{max}}-\omega_{\mathrm{min}}$ is the difference between the maximum and minimum values of the soft-mode frequencies as a function of temperature, either from Raman experiments or from other techniques. $T_1/2$ and T_0 are parameters of fitting to the Barrett expression. Fitting parameters for $x=0.4$ are only temptative. The two values of T_1 and T_0 given for TiO$_2$ correspond to measurements of the dielectric constant along the c and a axes, respectively.

	$\omega_{\mathrm{max}}-\omega_{\mathrm{min}}$ (cm^{-1})	$T_1/2$ (K)	T_0 (K)
LaLiTiO $x=0.12$	11	145	-300
LaLiTiO $x=0.25$	10	145	-240
LaLiTiO $x=0.3$	7	130	-620
LaLiTiO $x=0.4$	2.5	(160)	(-760)
LaLiTiO $x=0.5$	$\leqslant 2$		
LaLiTiO $x=0.12$[a]	8		
LaLiTiO $x=0.18$[a]	6.5	145	-370
La$_{1/3}$NbO$_3$ (Ref. 21)	15	130	-720
La$_{1/3}$TaO$_3$ (Ref. 21)	4	140	-730
La$_{0.25}$Li$_{0.25}$TaO$_3$ (Ref. 21)	3.5		
SrTiO$_3$ (Ref. 2)	>130	42	38
KTaO$_3$ (Ref. 3)	>80	28.5	13.1
CaTiO$_3$ (Ref. 4)		52	-159
La$_{0.5}$Na$_{0.5}$TiO$_3$ (Ref. 15)		90	-770
TiO$_2$ (Ref. 5)	>30	68,78	$-166,-179$

[a] Samples quenched from 1350 °C to LNT.

The finding that $m\omega_1^2-V>0$ means in fact that the mode is not unstable at any temperature. This represents a strong difference with SrTiO$_3$ and KTaO$_3$, where the soft-mode stabilization at low temperatures has been attributed to quantum fluctuation effects. A more rigorous calculation of the fluctuation term[27] allows one to reduce the number of parameters to 3, giving more realistic values for λ, but little affecting T_1 and T_0.

We now seek a physical explanation for the higher stability of our compounds as compared with incipient FE perovskites: A plausible one may be the lattice disorder, which contributes in two ways: (i) Static disorder. The random distribution of La and Li cations creates a random dipolar field at the Ti sites. (ii) Dynamic contribution. The fluctuating dipoles created by the lithium impurities can couple with the Ti vibration, resulting in some sort of low-frequency relaxation that prevents further softening, in a mechanism similar to that occurring in diffuse phase transitions (see Ref. 1, p. 287 ff.). Both mechanisms would yield the decrease of AFE interactions upon increasing x, as observed. The degree of structural order can be quantified by the site occupancy factor of La in La(1) and La(2) sites. In the undoped or slightly doped compounds La almost fully occupies site La(1), while La(2) site accommodates the remaining La atoms and vacancies.[7,8] As lithium is introduced, the occupancies of sites 1 and 2 by La atoms tend to become equal and the symmetry approaches the cubic limit. A drastic change occurs at $x\approx 0.3$,[7,8] where the symmetry evolves from an elongated pseudotetragonal one $(c/2>a\cong b)$ to an almost cubic cell $(c/2\cong a)$. A drastic change is also observed in our results at the same composition, as shown in the first column of Table I, indicating that AFE properties and structural order are closely related. A further support is given by the results in quenched samples with $x=0.12$ and $x=0.18$, which present a smaller degree of softening as compared with slowly cooled samples of similar Li content.

Another important point is the relevance of the actual OR symmetry in the appearance of the hypothetical AFE ordering. Since, at our level of resolution, no splitting of the E_g modes has been observed, we have no indicator of the lower symmetry that might be followed in parallel to the Ti mode shift. At this respect, we note that in AFE perovskites, such as Sr$_{1-x}$Ca$_x$TiO$_3$,[24] PbZrO$_3$, and NaNbO$_3$,[29,25] AFE order derived from antiparallel cation shifts is accompanied by the simultaneous condensation of antiferrodistortive (AFD) modes involving BO$_6$ octahedra tilts. Thus AFE seems to be favored by the presence of octahedra tilts, in agreement with first-principles calculations[30] according to which FE and AFD instabilities suppress each other. Interestingly, in our systems tilts are observed in undoped[16] or slightly doped compounds[18] and disappear as lithium content increases, in parallel with the magnitude of the AFE effect.

Since the mode under discussion is not a polar one, the behavior of the dielectric constant cannot be predicted *a priori*. According to Kittel[31] and Okada,[32] the static permitivity in AFE systems is not necessarily discontinuous at the phase transition and may have a small value even at T_c. Moreover, dielectric measurements at low frequency in these systems are dominated by the lithium dynamics contribution, which obscures any possible intrinsic temperature dependence. A high but almost constant ϵ was found for La$_{2/3}$TiO$_{3-\delta}$ below RT.[33] More experimental work is clearly needed in this field.

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