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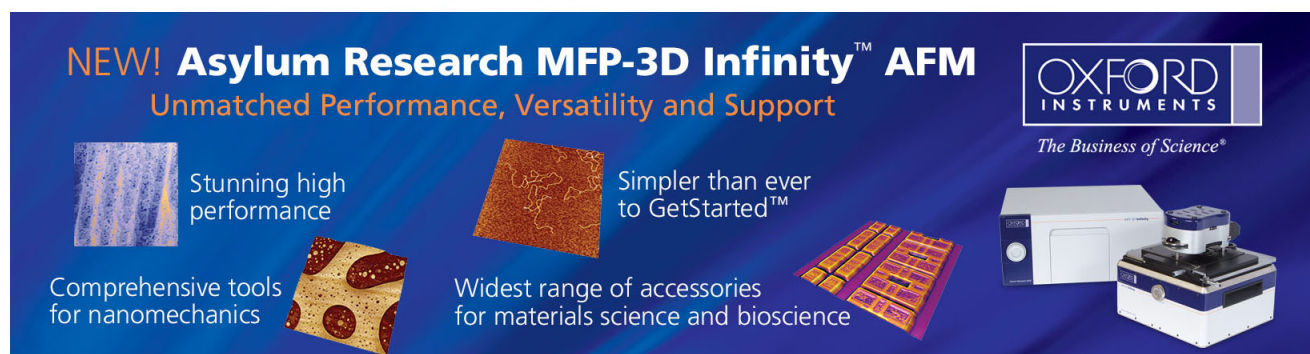
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Decreasing giant splitting of longitudinal and transverse optical phonons in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ due to Pb covalency

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In contrast to the increase of giant splitting of longitudinal optical (LO) and transverse optical (TO) phonons in polycrystalline $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ [Phys. Rev. B. **64**, 224103-1 (2001)], a decreasing splitting of the softest $A_1(1\text{TO})$ and the hardest $A_1(3\text{LO})$ was observed in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$. A similar structure but anomalous discrepancies in lattice dynamics of ABO_3 perovskite are related to the diverse electronic states of Pb^{2+} and Ba^{2+} ions. In this article, Pb–O interaction is proposed to be more hybridized than Ba–O, and thus the change of effective charge to the LO–TO splitting may be the dominant mechanism in $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$, while unit-cell volume change is in the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ systems. © 2002 American Institute of Physics. [DOI: 10.1063/1.1513660]

Perovskites are important in materials science because of their technological applications that follow from their ferroelectricity, piezoelectricity, nonlinear optical behavior, and others.^{1–4} With a chemical formula of ABO_3 , these compounds are generally composed of a three-dimensional framework of corner sharing BO_6 octahedra. They are also well known for their phase transitions, possibly affecting their physical and chemical properties significantly. The ternary systems formed by the compounds such as barium titanate, lead titanate, and strontium titanate, are of particular interest in the field of dielectrics.^{5–7}

The ferroelectric characteristics of perovskites can be controlled by replacing the *A* and *B* cations. The $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ (PST) system classically illustrates ferroelectric solid solutions with a perovskite structure.⁸ Although Raman experiments have, since 1950, been performed to elucidate such properties of PbTiO_3 and PST systems as functions of temperature and grain size,^{9–12} the reason why similar, but chemically different, perovskites, display very different ferroelectric behavior remains unknown.

Ferroelectric transition occurs as a result of a balance between the long-range Coulomb interaction and short-range forces.¹³ The Coulomb interaction can make the ferroelectric sensitive in response to details of domain structure, defect, and boundary conditions. Such interaction also leads to the splitting of longitudinal optical (LO) and transverse optical (TO) phonons. The Born dynamical effective charges are critical to the studying of these Coulomb effects. Recently, Zhong *et al.*¹⁴ performed giant LO–TO splitting, caused by Coulomb interactions, in ABO_3 cubic perovskite compounds, using the local density approximation. The calculated Born dynamical effective charges are 3.9 for Pb, 2.7 for Ba, 2.5 for Sr, and 7.1 for Ti, respectively.

However, Cohen¹³ theoretically calculated that Pb–O covalent bonding in tetragonal PbTiO_3 differs from Ba–O ionic bonding in BaTiO_3 . Most recently, charge-density distributions of PbTiO_3 obtained by the maximum entropy

method/Rietveld analysis from synchrotron-radiation x-ray powder data, have shown that tetragonal PbTiO_3 forms a two-dimensional network of covalent bonding,¹⁵ consisting of the Ti–O₅ pyramid combined with Pb–O bonding. The ionic states, which are estimated by subtracting the atomic number from the number of electrons around atoms obtained from Ref. 15, are 1.1 for Pb, 1.9 for Ba, and 2.4 for Ti. These experimental results are consistent with the theoretical prediction of Cohen.¹³

Our recent study of the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) system,

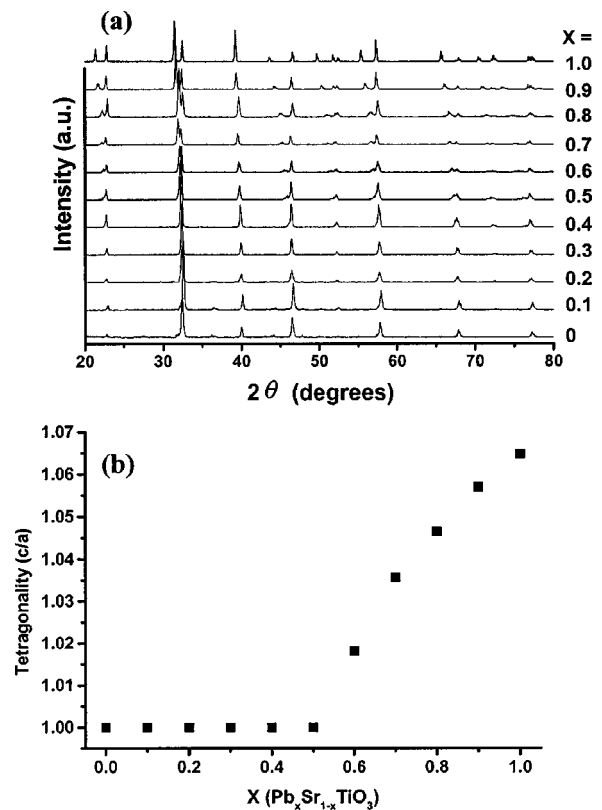


FIG. 1. (a) Powder XRD patterns of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ samples with various x values and (b) c/a (a and c are lattice constants) ratio after Rietveld refinement.

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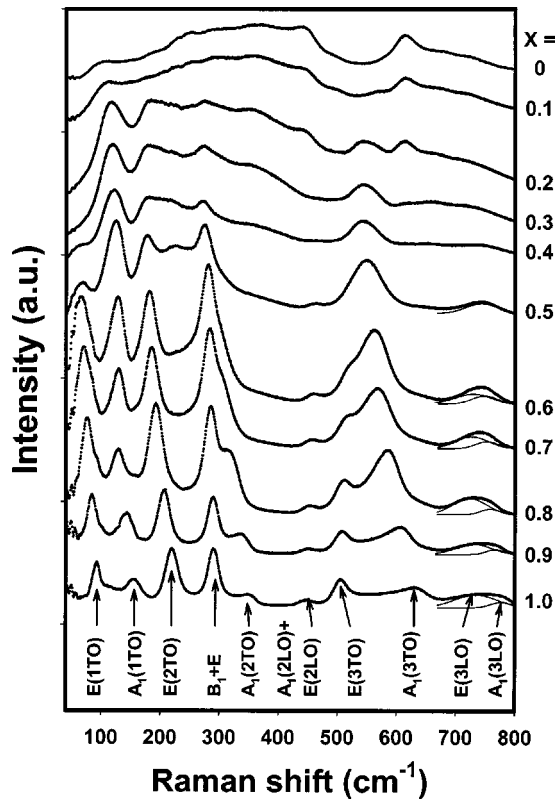


FIG. 2. Raman spectra of polycrystalline $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ at room temperature. The dotted symbols and solid lines represent experimental and fitting results of $E(3\text{LO})$ and $A_1(3\text{LO})$, respectively.

elucidated the repulsion of giant LO–TO splitting when the tetragonal phase changed toward the cubic phase, explained by a decrease in the dimensions of the cell and a strengthening of electron–phonon coupling,¹⁶ which represented the first experimental evidence of lattice dynamics governed by the Coulomb interaction. This letter reports the attractive LO–TO splitting behavior, in contrast to that in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, as the PST polycrystalline in the tetragonal phase changes toward a highly symmetrical cubic structure. The abnormal lattice dynamics follow from the fact that the hybridization between lead and oxygen states is stronger than that between barium and oxygen, as reported by Cohen¹³ and Kuroiwa *et al.*¹⁵

The sol–gel technique was adopted to prepare $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ polycrystalline powders, to yield homogeneous samples with a highly accurate composition. Then, 1–2 mm thick ceramic pellets with diameters of around 10 mm were obtained by sintering at 1300 °C for 3 h. The atoms in microcrystals are well arranged during gelation at a low temperature. The sintering temperature is far below the melting point of PST, and so provides insufficient free energy to rearrange atoms and thus avoid lattice relaxation by high-temperature synthesis, such as in the solid-state reaction method. X-ray powder diffraction patterns were obtained using a SHIMADZU XD-5 diffractometer with the monochromated high intensity Cu– $K\alpha$ line of wavelength 1.5405 Å over the range $20^\circ < 2\theta < 80^\circ$. The resulting x-ray diffraction (XRD) patterns were then analyzed by the Rietveld refinement procedure. Raman-scattering data were obtained using a SPEX 1877C triple spectrograph equipped with charge-coupled device (PHOTOMETRICS CC220) cooled to 140 K.

All spectra reported here are unpolarized because no orientation of the polycrystalline $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ samples was preferred.

Figure 1(a) shows XRD patterns of samples with various x values, obtained by the aforementioned sol–gel processes. Figure 1(b) plots the x dependence of the tetragonality, c/a , and lattice constants following Rietveld refinement. Figure 1(b) shows that the tetragonality declines from 1.064 to 1 as x changes from 1 to 0.5, corresponding to the well-known tetragonal–cubic phase transition. A c/a of 1.064 for PbTiO_3 is equivalent to the result calculated from the synchrotron-radiation data.¹⁵

Figure 2 displays the Raman spectra of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ polycrystalline powders taken at room temperature for various x values. Lorentzian line fitting was adopted to resolve the highly overlapping $E(3\text{LO})$ and $A_1(3\text{LO})$ modes.¹⁷ The fitting results are in good agreement with experimental spectra as shown in Fig. 2. Figure 2 also shows the phonon modes assigned following Foster *et al.*¹⁸ to clarify the structural variation of the PST system. Among the A_1 -symmetry modes, the $A_1(\text{TO})$ mode is especially interesting, since the $A_1(1\text{TO})$ mode consists of displacements of the Ti and oxygen ions relative to lead ions and is, with the $E(1\text{TO})$ mode, a soft mode. According to Fig. 2, these lowest TO phonon modes are found to be “softened” and the linewidth increases with decreasing Pb content. The “softening” can be observed down to $x=0.5$. The significant changes of Raman spectra and vanishing soft mode indicated that the $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ system undergoes a ferroelectric-to-paraelectric phase transition around $x=0.5$. The transition point at $x=0.5$ is consistent with XRD measurements. Moreover, the spectra observed in the paraelectric phase indicated that the Raman selection rule is relaxed ascribed to the disordered positions of the Ti atoms in the unit cell of the polycrystalline samples. Besides, as shown in Fig. 2, the $A_1(1\text{TO})$ mode exhibits an anomalous line shape that consists of several subpeaks as for a high Pb content (tetragonal phase). The anharmonicity of this mode was first reported by Foster *et al.*¹⁸ and was attributed to the anharmonic nature of the effective interatomic potential. However, determining the parameters of the peaks was practically difficult because of the extensive overlapping as described in Ref. 19.

Following the calculation of Born effective charges of ABO_3 perovskites determined by Zhong *et al.*¹⁴ and Waghmare and Rabe,²⁰ the calculated mode effective charge for the softest TO mode is the largest, as listed in Tables III and IV of Refs. 14 and 20, respectively. Therefore, the softest mode will couple most strongly with the electric field. The strong mode mixing via Coulomb interaction is such that the softest TO [$A_1(1\text{TO})$] mode is the most closely associated with the hardest LO [$A_1(3\text{LO})$] mode that gives rise to giant LO–TO splitting¹⁴ in ABO_3 compounds, especially for the ferroelectric phonon modes. The splitting behavior is dominated by

$$D_{mn}^{\text{LO}} = D_{mn}^{\text{TO}} + \frac{4\pi e^2}{\Omega} \frac{Z_m^* Z_n^*}{\epsilon_\infty(0)}, \quad (1)$$

where D represents the dynamical matrix and is proportional to the square of the vibration frequency, Ω is the volume of the unit cell, and Z^* is the Born effective charge. Figure 3

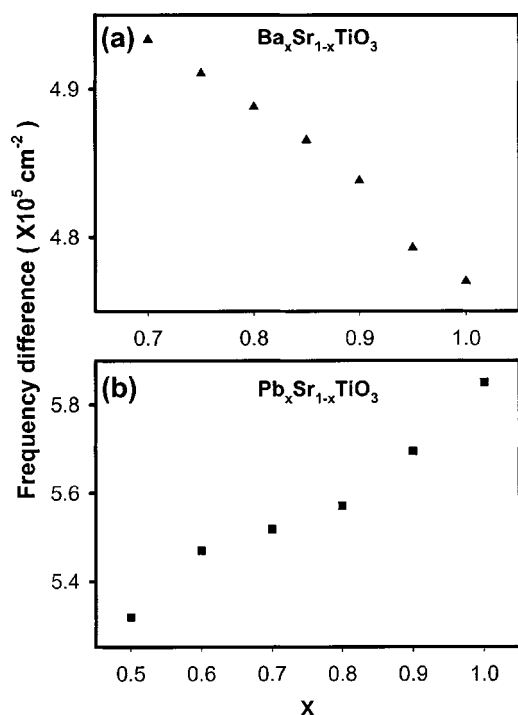


FIG. 3. Difference between square of $A_1(3LO)$ and $A_1(1TO)$ phonon frequencies for (a) $Ba_xSr_{1-x}TiO_3$ and (b) $Pb_xSr_{1-x}TiO_3$ system in tetragonal phase.

shows the difference between the square of $A_1(3LO)$ and $A_1(1TO)$ phonon frequencies for BST and PST, and the experimental results of BST, as shown in Fig. 3(a), are replotted from Fig. 6 of Ref. 16. The LO–TO splitting clearly exhibits increasing behavior in BST, but decreasing behavior in PST [see Fig. 3(b)] by reducing tetragonality toward the cubic phase. It can also be clearly seen that the degree of the LO–TO splitting of pure $PbTiO_3$ ($\sim 5.83 \times 10^5 \text{ cm}^{-2}$) is higher than that of pure $BaTiO_3$ ($\sim 4.78 \times 10^5 \text{ cm}^{-2}$), and both materials have similar unit-cell volume (63.2 and 64.2 \AA^3 , respectively). The difference indicates that the Pb–O hybridization^{13,15} might be the origin of the larger LO–TO splitting (Coulomb interaction).

According to Fig. 1(b), the cell dimensions of $Pb_xSr_{1-x}TiO_3$ clearly decline as x changes from 1 to 0.5. In the BST system, substituting Ba for substitute Sr causes the unit-cell volume to dominate Eq. (1), even with the limited volume variation. Therefore, the BST system in the tetragonal phase exhibits increased giant LO–TO splitting as the cell dimensions decrease.¹⁶ One would expect that the shrinkage of the lattice in the PST system could lead to further LO–TO splitting while lowering the Pb content of the PST system such as in the BST system. However, the electronic densities of states, calculated by Cohen¹³ and Kuroiwa *et al.*,¹⁵ reveal that the Pb $6s$ state is strongly hybridized with the O $2p$ state, whereas Ba is fully ionic in the tetragonal phase. The diverse types of chemical bonding may influence the Born effective charge, Z^* , accordingly. Indeed, Zhong

*et al.*¹⁴ have shown that most $Z^*(A)$ s are close to their nominal ionic valence, except for $Z^*(Pb) = 3.9$, and almost constant regardless of the B ion. Figure 3(b) reveals that the LO–TO splitting or Coulomb interaction is lowered by substituting Sr for Pb, but not dominated by the shrinkage of the cell dimension as in the BST system.¹⁶ Because of the higher Born effective charge of Pb than those of other A-site divalent cations (Ba, Sr), the role of Pb ions added into PST might exhibit anomalous contrast to Ba ions added into BST accordingly. More Pb–O covalent bonding as Sr ions are replaced with Pb ions would enhance the LO–TO splitting in PST system.

In conclusion, this investigation described the lattice dynamics of $Pb_xSr_{1-x}TiO_3$ polycrystalline powder prepared by the sol–gel method. In addition to identifying the phase transition by a variation of the lattice and phonon modes, the decreasing behavior of giant LO–TO splitting has been directly observed. The presence of substitution Pb^{2+} and Ba^{2+} ions on $SrTiO_3$ yields anomalous discrepancies in lattice dynamics, by altering electronic states. The decreasing LO–TO splitting phenomenon observed in PST rather than the increasing in the BST system is ascribed to the fact that Pb–O interaction is more hybridized than Ba–O and, thus, the change of effective charge to the LO–TO splitting may be the dominant mechanism in $Pb_xSr_{1-x}TiO_3$, while unit-cell volume change is in the $Ba_xSr_{1-x}TiO_3$ systems. These results provide useful information to support further theoretical studies on lattice dynamics for ABO_3 perovskites.

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