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Effect of *A*- and *B*-cation substitutions on the phase stability of $PbTiO_3$ ceramics

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Raman scattering studies of Nd-modified lead titanate $Pb_{1-3y/2}Nd_yTiO_3$ (PNT), $y=0.02$, 0.10, and $Pb(Zr_xTi_{1-x})O_3$ (PZT), $x=0.10$, 0.20, bulk ceramics were made at ambient temperatures between 4.2 and 297 K. Our measurements reveal splitting of the $E\oplus B_1$ symmetry peak at low temperatures in both the PNT and PZT samples. Some splitting of three $E(\mathrm{TO})$ peaks in the PZT samples [except for the $E(2\mathrm{TO})$ peak in the sample with $x=0.10$] and of the $E(3\mathrm{TO})$ peak in the PNT samples was also found. We discuss the phase stability of lead titanate based perovskites from the point of view of our experimental results and recent theoretical calculations. Raman results reveal that all $A_1(\mathrm{TO})$ symmetry modes in all samples are anharmonic down to the lowest measurement temperature. [S0163-1829(99)05701-X]

Lead titanate has a tetragonal space group symmetry C_{4v}^1 with one ABO_3 formula unit per unit cell. Thus, it has 12 optical modes, which can be categorized to three A_1-symmetry modes, eight E-symmetry modes (four degenerate pairs), and a B_1-symmetry mode. Foster *et al.*[1] found from single crystal experiments that the $A_1(1\mathrm{TO})$ mode of lead titanate consists of four subpeaks. They proposed a model in which they attribute the anomalous line shape of the $A_1(1\mathrm{TO})$ mode to the anharmonic nature of the effective interatomic potential associated with this phonon.[1] Calculations made in Ref. 2 show that the tetragonal symmetry of lead titanate is stabilized relative to the trigonal phase down to lowest temperatures by the unit-cell relaxation (large c/a-axis ratio). The first-principles study of stability and vibrational properties of tetragonal $PbTiO_3$ by Garcia and Vanderbilt[3] was motivated in part by a previously reported transition to an orthorhombic phase at low temperatures on the basis of x-ray and optical measurements.[4] The analysis in Ref. 3 of the energetics of B_1 distortions shows that a low-temperature transition of this kind is possible, in principle, but not likely in ferroelectric $PbTiO_3$. The calculations also gave positive elastic constants for all unit-cell-preserving distortions, thus ruling out transitions to a monoclinic structure (E distortions) or to a 45°-rotated orthorhombic structure (B_2 strain). Furthermore, the results in Ref. 3 show that there are no mechanical instabilities (soft modes) associated with normal modes at the Brillouin-zone boundary that could cause a phase transition with cell doubling. Recently, Waghmare and Rabe showed that the coupling of local polar distortions to strain is responsible for both the stability of the tetragonal phase relative to the trigonal one and the first-order transition observed in $PbTiO_3$.[5] We discuss the role of the *A*- and *B*-cation substitutions to the local symmetry of lead titanate ceramics reflected by Raman spectra. We made low-temperature Raman measurements to Nd-modified lead titanate (PNT) and lead zirconate titanate (PZT) samples and paid special attention to the determination of the local temperature. At low temperatures, the laser beam may cause noticable local heating, and thus we estimated the local temperature from the ratio between Stokes and anti-Stokes intensities of the $E(1\mathrm{TO})$ mode. We also determined the instrumental response function using white light. This instrumental function takes into consideration the sensitivity of the Raman system as a function of wave length, which is not constant due to the different slit values used for the measurement of anti-Stokes and Stokes spectra, variations in the sensitivities between different pixels of the CCD detector, and variations in the grating efficiency. The power of the laser beam on the samples was adjusted to be ≈ 50 μW (PZT samples) and ≈ 125 μW (PNT samples) during the measurements. We tried to find a compromise between the small local heating and high signal to noise ratio. Low laser beam intensity does not necessarily mean that the local heating is small. This is because low power necessitates longer integration times and this leads to local heating, since the thermal conductivity of the samples is low. In addition, the amount of local heating not only depends on heat capacity and thermal conductivity, but also on the sample geometry and conductivity between the sample holder and sample.

Ceramic PZT samples were prepared from high-purity oxides through a usual ceramic route. First, oxides were weighted in desired Zr/Ti ratios, ball-milled, annealed at 850 °C and ground and ball milled again and pressed into a pellet form and sintered at 1100 °C. According to the x-ray diffraction measurements at room temperature, samples were homogeneous and contained only tetragonal perovskite phase. PNT ceramic samples were prepared by Siemens in Germany.

The $A_1(1\mathrm{TO})$ mode consists of displacements of the Ti and oxygen ions relative to lead ions.[6] The anharmonicity for this mode was first reported in the paper by Foster *et al.*[1] and for the Nd-modified lead titanate and lead zirconate titanate ceramics together with numerical calculations in Refs. 7 and 8. In lead titanate single crystals, the subpeaks were at 148.5, 137.5, 126.5, and 110.5 cm^{-1} at 400 K.[1] Among the A_1-symmetry modes, the $A_1(1\mathrm{TO})$ mode is of special interest, since it is the soft mode together with the $E(1\mathrm{TO})$ mode (both originate from the T_{1u} mode of the cubic phase). Fig-

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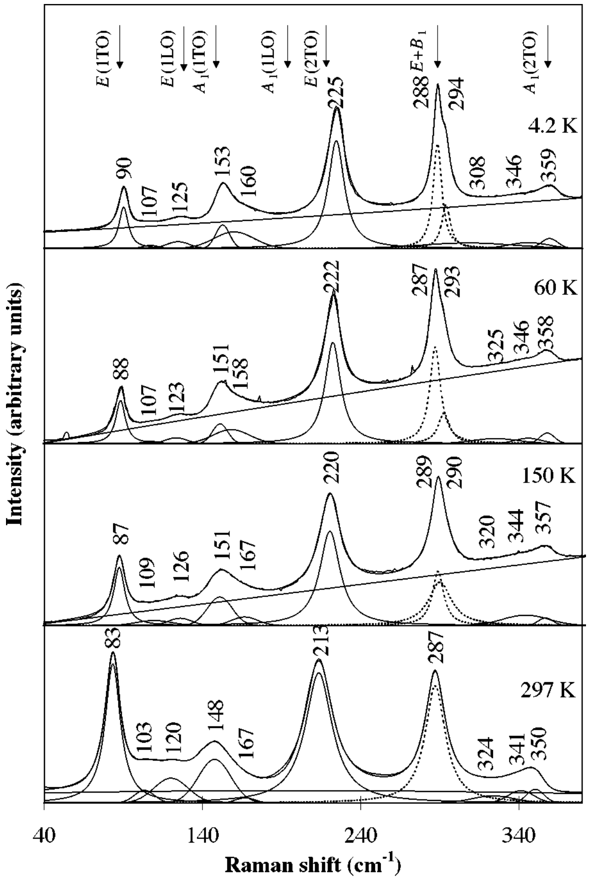

FIG. 1. Low-frequency Raman spectra of the $Pb_{0.97}Nd_{0.02}TiO_3$ sample measured at ambient temperatures of 4.2, 60, 150, and 297 K together with a curve fit. (B_1 and E symmetry modes are plotted by dotted line). The positions of different Raman peaks at room temperature in $PbTiO_3$ (Ref. 10) are also shown at the top.

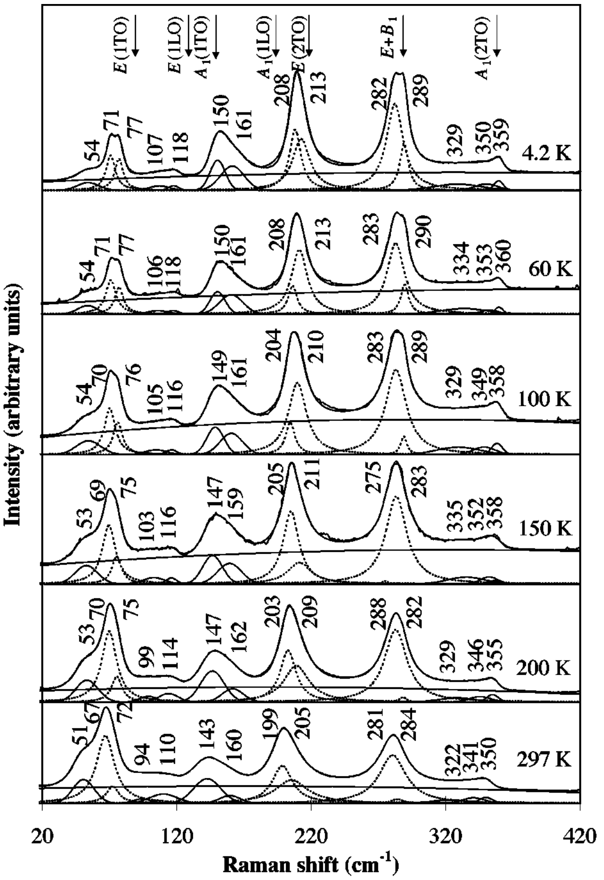

FIG. 2. Low-frequency Raman spectra of the $Pb(Zr_{0.20}Ti_{0.80})O_3$ sample measured at ambient temperatures of 4.2, 60, 100, 150, 200, and 297 K together with a curve fit. The splitting of the $E(1TO)$, $E(2TO)$, and $E \oplus B_1$ modes is shown by the dotted line. The positions of different Raman peaks at room temperature in $PbTiO_3$ (Ref. 10) are also shown at the top.

ure 1 shows the low-frequency Raman spectra measured at ambient temperatures of 4.2, 60, 150, and 297 K of the $Pb_{0.97}Nd_{0.02}TiO_3$ sample together with the curve fit.

The $A_1(2TO)$ mode consist of displacements of the Ti ion relative to oxygen ions and lead ions.[6] The anomalous line shape of this mode was earlier described to be due to the oblique phonons, but our low-temperature measurements suggest that at low temperatures the $A_1(2TO)$-mode vibration consists of subpeaks, as can be seen from the shoulders in the Raman spectra of the $Pb_{0.97}Nd_{0.02}TiO_3$ and $Pb(Zr_{0.20}Ti_{0.80})O_3$ samples measured at 4.2 K (local temperature was estimated to be 20 K) in Figs. 1 and 2.

In the $A_1(3TO)$ mode Ti ions move in the c-axis direction together with the oxygen ions lying between Ti ions.[6] Figure 3 shows the high-frequency spectra of the $Pb_{0.85}Nd_{0.10}TiO_3$ sample measured at ambient temperatures of 4.2, 60, 150, and 297 K. Figure 4 shows the high-frequency Raman spectra of the $Pb(Zr_{0.20}Ti_{0.80})O_3$ sample measured at various temperatures between 4.2 and 297 K, together with the curve fit. The frequency range between 500 and 700 cm^{-1} is especially interesting. Earlier we observed that PNT ceramics have a very strong peak at around 560 cm^{-1} (Ref. 7) and now it can be seen, that the peak around 660 cm^{-1} has several shoulders (see Figs. 3 and 4). These shoulders were more clearly seen in the case of $Pb_{0.97}Nd_{0.02}TiO_3$ sample, and were at positions 573, 602, and 627 cm^{-1} in addition to the strongest peak at 653 cm^{-1} at 4.2 K. We connect these shoulders to the anharmonic nature of the $A_1(3TO)$ mode. The strongest peak at around 560 cm^{-1} may correspond to the trigonal nanodomains. It was found that the intensity of the peak at around 560 cm^{-1} increases with increasing Nd concentration and decreasing temperature in PNT samples.[7] This peak probably corresponds to the local symmetry change and may not be seen by measurement techniques revealing long-range order (such as neutron or x-ray diffraction). The evolution of the peak at around 560 cm^{-1} can be clearly seen as a function of temperature from Fig. 3 (see also Figs. 3 and 4 in Ref. 7). It should be noted that the anharmonicity is most clearly seen at low temperatures, where the anharmonicity due to the temperature has its smallest value.

Our experimental study shows that the calculation of the A_1-symmetry modes cannot be realistically done from the basis of a harmonic approximation but necessitates an anharmonic potential well approach. One way to estimate this anharmonicity is to use the mean field approximation, which can also qualitatively explain the temperature and Nd-concentration dependence of the subpeaks of the A_1-symmetry mode vibrations. We found from our simple double-well potential calculations based on the *ab initio* electronic-structure calculations in Ref. 2, that the subpeak

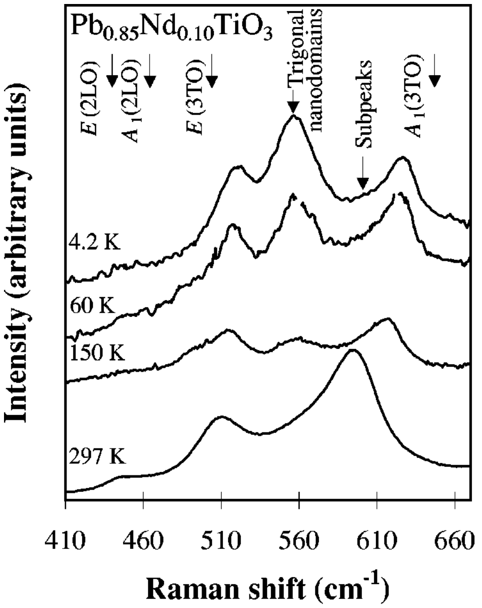

FIG. 3. High-frequency Raman spectra of the $Pb_{0.85}Nd_{0.10}TiO_3$ sample measured at ambient temperatures of 4.2, 60, 150, and 297 K. The peak at 560 cm^{-1} is tentatively assigned to the trigonal nanodomains. The asymmetry of the $A_1(3TO)$ mode originating from the subpeaks is also indicated by an arrow. The positions of different Raman peaks at room temperature in $PbTiO_3$ (Ref. 10) are also shown at the top.

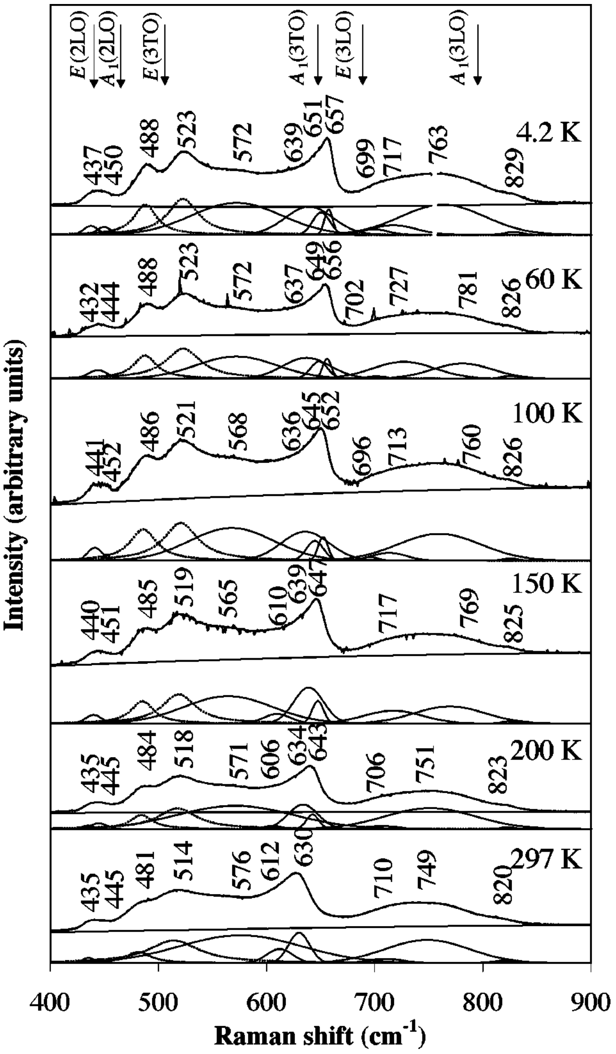

FIG. 4. High-frequency Raman spectra of the $Pb(Zr_{0.20}Ti_{0.80})O_3$ sample measured at ambient temperatures of 4.2, 60, 100, 150, 200, and 297 K together with a curve fit. The splitting of the $E(3TO)$ mode is shown by the dotted line. The positions of different Raman peaks at room temperature in $PbTiO_3$ (Ref. 10) are also shown at the top.

structure of the $A_1(1TO)$ mode of lead titanate and lead zirconate titanate can be realistically described with this method. As discussed in Ref. 9, the effect of the Nd addition on the properties of $PbTiO_3$ ceramics is very similar to the effect of an increase in temperature. For example, the intensity of the low-energy $A_1(1TO)$ mode subpeaks increases with increasing temperature (due to the change in the occupation of energy levels as described by the Bolztmann factor) and with increasing Nd concentration. This can be partly explained by the decrease in the polarization with increasing temperature and increasing Nd concentration. The Raman spectra measured from the $Pb(Zr_{0.20}Ti_{0.80})O_3$ sample also shows the temperature evolution of the mode around 53 cm^{-1}. It is seen that the relative intensity of this mode decreases with decreasing temperature. We measured the corresponding spectra from $Pb(Zr_{0.10}Ti_{0.90})O_3$ sample, and this mode nearly vanished at an ambient temperature of 4.2 K. This mode probably corresponds to the nonlocalized vibrations between the two minima in the double-well potential picture (see more detailed discussion in Refs. 8 and 9).

Figures 1 and 2 show that the degeneracy of the E- and B_1-symmetry modes at around 290 cm^{-1}, which was reported to be degenerate in lead titanate,[10] seems to be broken. In the B_1-symmetry mode only oxygen ions, nearly coplanar with titanium ions, move in opposite directions. In the E-symmetry mode all ions are moving in the tetragonal ab-basal plane. However, since the samples were ceramic, it was not possible to check the symmetry of the modes and thus it cannot be said for sure that the modes at around 290 cm^{-1} in Figs. 1 and 2 are due to the splitting of the degeneracy of the E- and B_1-symmetry modes. The first-principles calculations in Ref. 3 show the splitting and give a little higher frequency to the B_1-symmetry mode in tetragonal $PbTiO_3$. Raman spectra from both the PZT and PNT ceramic samples show that in many cases E-symmetry peaks are split (see Figs. 2, 3, and 4). The frequency splitting from the fits (not all shown) at 4.2 and 297 K are shown in Tables I and II. The splitting of the $E(3TO)$ mode of PNT samples as a function of Nd concentration at ambient temperatures of 11 and 300 K are also shown in Ref. 7 (Figs. 3 and 4; Tables I and II). A possibility for this splitting of E-symmetry modes may be in the break-up of the tetragonal symmetry

TABLE I. Frequency splitting of the E-symmetry modes in PZT and PNT ceramic at an ambient temperature of 4.2 K.

	$E(1TO)$	$E(2TO)$	$E+B_1$	$E(3TO)$
$Pb(Zr_{0.10}Ti_{0.90})O_3$	78, 85	218	287, 291	500, 524
$Pb(Zr_{0.20}Ti_{0.80})O_3$	71, 77	208, 213	282, 289	488, 523
$Pb_{0.97}Nd_{0.02}TiO_3$	90	225	288, 294	506, 514
$Pb_{0.85}Nd_{0.10}TiO_3$	79	213	283, 289	

TABLE II. Frequency splitting of the E-symmetry modes in PZT and PNT ceramic at an ambient temperature of 297 K.

	$E(1\mathrm{TO})$	$E(2\mathrm{TO})$	$E+B_1$	$E(3\mathrm{TO})$
$\mathrm{Pb(Zr_{0.10}Ti_{0.90})O_3}$	74, 78	207	284	492, 513
$\mathrm{Pb(Zr_{0.20}Ti_{0.80})O_3}$	67, 72	199, 205	281, 284	481, 514
$\mathrm{Pb_{0.97}Nd_{0.02}TiO_3}$	83	213	287	
$\mathrm{Pb_{0.85}Nd_{0.10}TiO_3}$	69	199	281	

due to the A- and B-cation substitutions. However, it is not possible to say from our Raman data, if the possible symmetry change is only local or also reflects a long-range symmetry change. Both peaks in the split modes are of comparable intensity at low temperatures in Figs. 2 and 4, which means the majority of the sample is nontetragonal. Therefore, low-temperature diffraction experiments (also with neutrons) would be very valuable for the interpretation of the Raman results. On the other hand, our Raman data cannot rule out the possibility that inhomogeneous distribution of dopant atoms (Zr or Nd) is the reason for the observed splitting. Actually, it is likely that if there is a local symmetry change in the crystal, it occurs together with the composition fluctuation. The anharmonicity, which occurs quite naturally in the motion involved in the c-axis direction, would not probably play so important a role in the case of motion in the basal plane. This is because the strong polarization is in the c-axis direction. It seems to be that both the nature of the bonding between lead and oxygen and the change in the strain are essential in the determination of the stable phase, such as theoretical calculations predict.[2,5] Nd substitution for lead replaces part of the covalent bonding between A cations and oxygens by weaker ionic bonding. The Zr substitution for Ti decreases the tetragonal strain and finally turns the tetragonal PZT to the trigonal phase. Waghmare and Rabe[5] studied the energy of the tetragonal, trigonal, and orthorhombic phases in the case of an unstrained cubic unit cell and in the case where the unit cell was allowed to relax with respect to homogeneous strain. They found that in the former case the trigonal phase has the lowest energy and tetragonal the highest energy and in the latter case the trigonal phase has the highest energy and tetragonal the lowest energy. The difference between the energies of trigonal and tetragonal phases was ≈ 8 meV/cell and between the trigonal and orthorhombic phases ≈ 3 meV/cell.[5] The differences are small, indicating that the phase stability of lead titanate is sensitive to A- and B-cation substitutions. It should be noted, that the frequency difference in the splitting of the E-symmetry modes is nearly constant as a function of temperature (a small increase with decreasing temperature occurs), as can be seen from our curve-fit results. This difference was found to increase with increasing Zr content. It is also interesting to note that the higher frequency peak originating from the $E(3\mathrm{TO})$ mode has nearly the same frequency in the case of $\mathrm{Pb(Zr_{0.10}Ti_{0.90})O_3}$ and $\mathrm{Pb(Zr_{0.20}Ti_{0.80})O_3}$ samples (524 and 523 $\mathrm{cm^{-1}}$ at 4.2 K).

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