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Onset of spontaneous electrostrictive strain below 520 K in Pr-doped $SrTiO_3$

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$Sr_{0.95}Pr_{0.05}TiO_3$ ceramic is shown to exhibit anomalous value of cubic lattice parameter at room temperature. A combination of temperature dependent dielectric and synchrotron x-ray powder-diffraction study has revealed that the anomalous lattice parameter has contribution from spontaneous electrostrictive strain that sets in below 520 K. In analogy with the lead-based classical relaxor ferroelectrics, it is suggested that Pr-doped $SrTiO_3$ is a new class of high-temperature lead-free relaxor ferroelectric system.

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Ever since the discovery of quantum paraelectricity,[1] the polar properties of $SrTiO_3$ (ST) have been investigated extensively in pure and mixed forms.[2–16] At low temperatures bulk ST is an incipient ferroelectric/quantum paraelectric.[1] The onset of a ferroelectric state is suppressed by the ground-state quantum fluctuations of the soft mode.[1] The resulting delicate dielectric state is highly susceptible to dopants and external perturbations. Since the dipolar correlation length of incipient ferroelectric systems grow substantially only well below room temperature,[13] the effect of perturbing fields, more particularly the local electric fields due to chemical substitutions, is expected to be more effective in bringing about a ferroelectric state at cryogenic temperatures. Studies in the past, on the two well-known quantum paraelectric systems, ST (Refs. 2–8, 17, and 18) and $KTaO_3$,[19–23] have shown that ferroelectric correlations develop only at temperatures well below room temperature (300 K). In this scenario, unless something dramatic takes place, a ferroelectric state by chemical substitutions in quantum paraelectric systems is not expected to occur at high temperatures (near 300 K or above). Recently, contrary to this intuitive perception, ferroelectricity at 300 K was reported in Pr-doped ST ceramics.[15] Observation of maxima at ∼500 K in the temperature dependence of permittivity $[\varepsilon'(T)]$, and dielectric hysteresis at 300 K was considered as evidence in support of this claim.[15] However, apart from these macroscopic measurements, so far there has been no report of microscopic (structural) evidence related to the onset of ferroelectricity in Pr-doped ST. In this Brief Report, we present the results of a temperature dependent synchrotron x-ray powder-diffraction (XRPD) study on a representative Pr-doped $SrTiO_3$ composition, $Sr_{0.95}Pr_{0.05}TiO_3$ (SPT-05). It is shown that the system exhibits spontaneous electrostrictive strain below 520 K, a phenomenon which is known for the well-known high-temperature relaxor ferroelectric systems, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and La-substituted $Pb(Zr_{1-x}Ti_x)O_3$ (PLZT).

Ceramic specimen of $Sr_{0.95}Pr_{0.05}TiO_3$ (SPT-05) was prepared by standard solid-state reaction method.[16] Relative permittivity of platinum electroded ceramic pellet of SPT-05 was measured as a function of temperature with a HP 4192 impedance analyzer. Temperature dependent XRPD study up to 400 °C was carried out at HASYLAB (B2 beamline) at the synchrotron source DESY using a wavelength of 0.79 809 Å (calibrated with LaB_6 pattern). Neutron powder diffraction (NPD) was carried out at FRM II, Germany, using a wavelength of 1.548 Å. Raman spectra were recorded on polished pellets in back scattering geometry with Kr^+ laser operated at 531 nm. The spectra were recorded with a Horiba Jobin Yvon T64000 triple spectrometer equipped with a liquid N_2 cooled back-thinned CCD detector.

In conformity with the previous studies,[15,16] XRPD at 300 K of STP-05 revealed a cubic structure. Figure 1 shows XRPD patterns of the calculated, observed, and difference profiles after Rietveld refinement with the cubic perovskite structure. The refined lattice parameter was found to be 3.9052(1) Å, which is nearly the same as the lattice parameter of pure $SrTiO_3$ ($a=3.905$ Å). This, apparently, may suggest that either (i) the Pr ions have not entered the lattice of ST, or (ii) the dual valence states of Praseodymium i.e., Pr^{3+} (radius=1.126 Å) (Ref. 24) and Pr^{4+} (radius=0.96 Å),[24] can occupy both Sr^{2+} (radius=1.44 Å) (Ref. 24) and Ti^{4+} (radius=0.61 Å) (Ref. 24) sites. From the point of view of

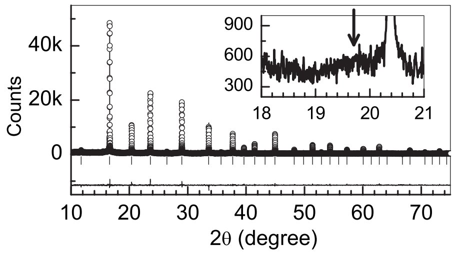

FIG. 1. Rietveld plot of x-ray powder-diffraction patterns of $Sr_{0.95}Pr_{0.05}TiO_3$ after refinement with cubic perovskite structure. The inset shows a magnified view of a limited range of data. The arrow inside the inset indicates the position of the anticipated 3/2 1/2 1/2 superlattice reflection (see text).

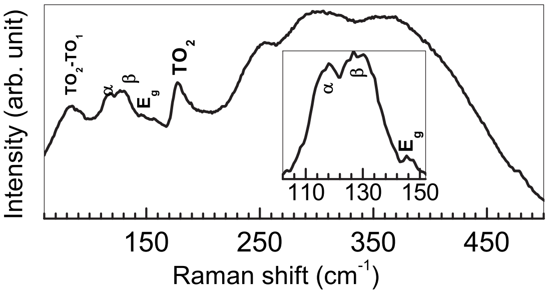

FIG. 2. Raman spectrum of $Sr_{0.95}Pr_{0.05}TiO_3$ at 300 K. The inset shows a magnified plot of a selected region.

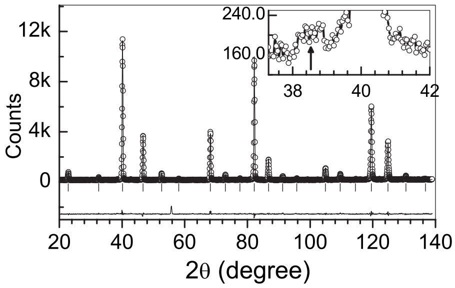

FIG. 3. Observed (open circles), calculated (continuous line through the circles), and difference (continuous line at the bottom of the figure) neutron powder-diffraction pattern of $Sr_{0.95}Pr_{0.05}TiO_3$ at 300 K. The vertical bars indicate the calculated Bragg-peak positions. The inset shows a magnified view of the region where (marked by arrow) the 3/2 1/2 1/2 superlattice reflection is likely to appear (see text).

ionic size consideration, a fraction of the Pr^{3+} and Pr^{4+} replacing the relatively bigger sized Sr^{2+} would tend to shrink the unit cell. This shrinkage can be partially countered if some of the Pr^{4+} ions replace the Ti^{4+} ions. The first possibility of Pr having not entered the ST lattice is ruled out since we did not notice any impurity peaks in the diffraction pattern. The second possibility of mixed site occupancy of the Pr cannot be ruled out, and the issue is discussed later in conjunction with the thermal-expansion behavior of the system.

In order to ascertain the crystal structure of SPT-05 at room temperature more accurately, Raman and neutron powder-diffraction studies were performed. Figure 2 shows the Raman spectra of $Sr_{0.95}Pr_{0.05}TiO_3$. Apart from the broad second-order band centered around 300 cm^{-1}, distinct modes are seen at (a) 80, (b) 117, (c) 127, (d) 145, and (e) 175 cm^{-1}. By comparison with previously published Raman and infrared scattering results on bulk ST (Refs. 3, 6, and 12) and on thin ST films,[10] the modes near 80, 145, and 175 cm^{-1} were identified as TO_2-TO_1 difference mode, structural E_g mode, and polar TO_2 mode, respectively. In our previous report, we have shown that mode near 80 cm^{-1} exhibits decreasing softening tendency with increasing Pr content.[16] The modes at 117 and 127 cm^{-1}, labeled as α and β, respectively, have been assigned as Pr-impurity modes, since they are not part of the modes (Raman/IR active or silent) expected of the host $SrTiO_3$ matrix. The weak E_g mode at $\sim$145 cm^{-1}, revealed more clearly in the inset of Fig. 2, suggests presence of antiferrodistortive (AFD) distortion of tetragonal symmetry.[3] In the present context, the AFD distortion is characterized by out-of-phase tilting of neighboring octahedra along the c axis of the tetragonal cell. Such octahedral tilts lead to doubling of the periodicity of the pseudocubic lattice and appearance of half-integer superlattice reflections in diffraction pattern.[25] The most intense superlattice reflection, 3/2 1/2 1/2, indexed with respect to the pseudocubic cell,[26] is anticipated to appear at $2\theta = 19.75°$ in our XRPD pattern. However, there is no clear evidence of a well defined peak at this angle (inset of Fig. 1). It is known that for very small magnitude of octahedral tilt angle, the characteristic superlattice reflections, which are not visible in a XRPD pattern, becomes easily visible in neutron powder-diffraction (NPD) pattern.[27] In view of this, a NPD pattern with a very good signal-to-noise ratio was recorded for the same powder specimen. A weak correlation in the data is indeed observed at the anticipated 2θ position of the 3/2 1/2 1/2 superlattice reflection (the arrow marked in the inset of Fig. 3). However, in the absence of a well defined peak, the global structure was treated as cubic and structure refinement was carried out accordingly. We argue that the weak E_g mode seen in the Raman spectrum is an indication of short-range order AFD distortion. Presence of short-range-order AFD distortion in the globally cubic phase has been earlier reported for some of the Ca-substituted ST ($Sr_{0.94}Ca_{0.06}TiO_3$ and $Sr_{0.88}Ca_{0.12}TiO_3$).[28] Figure 3 shows Rietveld plot of neutron powder-diffraction pattern of SPT-05 after refinement with the cubic structure. The refined lattice parameter with the neutron data was found to be 3.9048(1) Å. Duran *et al.*[15] have reported a similar value of the lattice parameter 3.9046(1) Å of $x = 0.05$ (Ref. 15) using laboratory x-ray powder-diffraction data. Both the values are very close to the value of 3.9052(1) Å, reported above using the synchrotron XRPD data, thereby confirming independently the anomalous value of the lattice parameter of SPT-05.

Figure 4 shows the variation of the cubic cell volume as a function of temperature of SPT-05, obtained by Rietveld analysis of the XRPD data. A linear fit above 500 K follows the relation $V_{cell} = 58.88(2) + 1.95(3) \times 10^{-3}$ T. The observed volumes depart from the linear fit below $T_B = 520$ K, clearly suggesting onset of spontaneous strain below this temperature. It may be remarked that in the absence of the spontaneous electrostrictive strain, the lattice parameter of SPT-05 at room temperature would have been 3.903 Å, which is

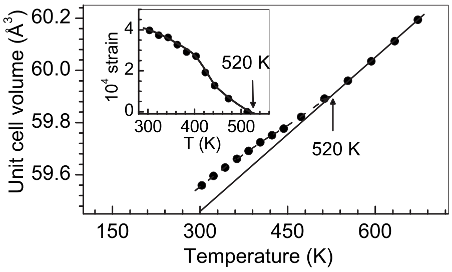

FIG. 4. Temperature variation of unit-cell volume of $Sr_{0.95}Pr_{0.05}TiO_3$. The inset shows temperature evolution of spontaneous electrostrictive strain (see text). The error bars are smaller than the size of the filled circles.

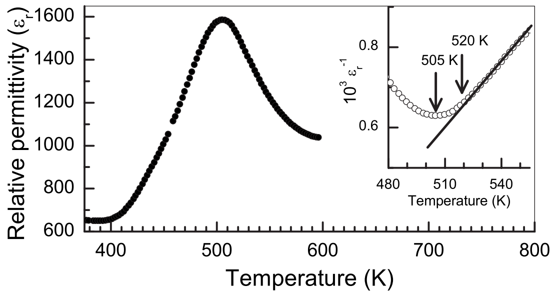

FIG. 5. Temperature variation of relative permittivity of $Sr_{0.95}Pr_{0.05}TiO_3$ at 1 kHz. The inset shows Curie-Weiss fit to the data above T_m.

definitely smaller than the lattice parameter of pure ST (3.905 Å). In this context, it may be noted that the lattice parameter of a 6% Ca^{2+} [which incidentally has the same ionic radii as Pr^{3+} (Ref. 24)] substituted ST is 3.899 Å.[28] Though the Ca concentration is only 1% higher than the Pr concentration in SPT-05, the decrease in the lattice parameter (0.006 Å) is three times more than the corresponding decrease (of 0.002 Å) brought about by 5% Pr substitution in ST. This discrepancy can be explained by assuming that some of the bigger sized Pr^{4+} ions occupy the smaller sized Ti^{4+}, thereby compensating partly for the decrease in the lattice parameter caused by Pr^{3+}/Pr^{4+} occupying the Sr^{2+} site.

The temperature dependence of permittivity of SPT-05 was examined to correlate the spontaneous strain with the dielectric behavior. Figure 5 shows the temperature dependence of the relative permittivity of SPT-05 at 1 kHz. The peak in permittivity occurs at $T_m=505$ K, and the permittivity was found to follow Curie-Weiss law $[\varepsilon_r=C/(T-T_o)]$ above T_m with $C=1.9\times10^5$ and $T_c=390$ K (see inset of Fig. 5). The C value is typical of classical ferroelectrics exhibiting displacive transition such as $BaTiO_3$ and $PbTiO_3$.[29] The departure from Curie-Weiss behavior starts below ~520 K, which is the same temperature (T_B) below which spontaneous strain sets in (Fig. 4). This feature is similar to what is well known for relaxor ferroelectrics such as PMN and La-doped PZT (PLZT).[13] The temperature T_B, known as "Burns temperature," corresponds to the formation of stable nanosized dipolar clusters which grow on cooling, and is responsible for the relaxor ferroelectric behavior.[13,30] The spontaneous strain in SPT-05 therefore owes its origin to the electrostriction effect that sets in due to formation of stable polarized regions in the system. The electrostrictive strain $(\Delta a/a_e)$ at any temperature for a cubic crystal follows the relation $\Delta a/a_e=Q_hP^2$,[30] where Δa at any temperature is the difference between the experimentally observed lattice parameter and the lattice parameter, a_e, expected from the extrapolation of the linearly fitted line above 500 K, Q_h and P are the electrostrictive coefficient, and local polarization, respectively. The temperature variation of the spontaneous electrostrictive strain, which is a measure of the mean-square polarization developing in the system, is shown in the inset of Fig. 4. It may, however, be remarked that while T_B of PMN and PLZT lies ~350 K and ~150 K above their respective T_ms,[13] it is only ~15 K away from T_m for SPT-05. The significantly small difference between T_m and T_B for SPT-05 seems to suggest that, although the dielectric behavior shows signatures of a relaxor ferroelectric system,[16] there is strong tendency in the system to exhibit a ferroelectric phase transition. We propose that the Pr substitution in ST creates giant electric dipoles, the electric field of which tend to freeze/harden the soft ferroelectric mode of the host ST matrix and drive the system toward a displacive type ferroelectric phase transition. In fact, there can be a competition between the relaxor tendency (due to orientational dynamics of the polarization cloud around Pr-defect dipoles) and the tendency for a displacive ferroelectric phase transition.

In conclusion, temperature dependent dielectric and x-ray powder-diffraction studies have revealed that $Sr_{0.95}Pr_{0.05}TiO_3$ exhibits spontaneous electrostriction below 520 K. The apparent similarity of the lattice parameter of the Pr-substituted and pure $SrTiO_3$ is explained in terms of compensating effects of (i) overall small shrinking of the unit cell of ST by mixed site occupancy of the Pr-ions at the Sr and Ti sites, and (ii) tendency to increase the lattice parameter because of electrostrictive strain arising from the development of polarization below 520 K. The comparatively small difference between permittivity maximum temperature (T_m) and the Burn temperature (T_B) suggests that system has the tendency to exhibit a ferroelectric phase transition. We propose that Pr doping creates "giant electric dipoles" around the doped sites which tends to harden/freeze the soft ferroelectric mode of the host ST well above room temperature. The onset of spontaneous electrostriction is similar to what has been known for the strong relaxors such as PMN and PLZT, and hence Pr-doped ST system can be treated as a new lead-free analog of the lead-based high-temperature electrostrictive material.

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