

# Phonon mode and phase transition behaviors of $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$ relaxor ferroelectric ceramics determined by temperature-dependent Raman spectra

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The composition dependence of phase transition temperature in  $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$  (PSTH) ceramics ( $0 \leq x \leq 0.2$ ) has been investigated by Raman spectra. From the typical phonon mode variations, the PSTH ceramics unambiguously undergoes three structural transformations with increasing the temperature from 82 to 673 K. It was found that the  $F_{2g}$  phonon mode disappears above the Curie temperature. Moreover, the PSTH ceramics exhibited the paraelectric to ferroelectric phase transitions at 287, 293, 313, 320, and 330 K with the composition. The phenomena can be ascribed to the enhanced length of Pb-O-Ta bonds induced by the incorporation of  $\text{Hf}^{4+}$  ions. © 2011 American Institute of Physics. [doi:10.1063/1.3614431]

For several decades, much effort has been made on the relaxor ferroelectric oxides with perovskite structure because of the high dielectric permittivity, strong electrostrictive, excellent pyroelectric, and electro-optic coefficients.<sup>1-7</sup> In particular, lead-based relaxor ferroelectrics with complex perovskite structure of  $\text{PbB}'\text{B}''\text{O}_3$ , have been widely studied as a potential generation materials.<sup>3-6</sup> Among these materials, lead scandium tantalate ( $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  or PST) is of high interest due to different structural order of the  $B$ -site cations. It is well known that the  $B$ -site order plays an important role in physical properties of complex perovskites, such as dielectric response, the peak permittivity, and phase transition temperature.<sup>8-11</sup> Moreover, PST exhibits a spontaneous ferroelectric (FE) phase transition and long range ferroelectric ordering on cooling as compared to canonical relaxors.<sup>1,12</sup> On the other hand, PST-based solid solutions, such as  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3\text{-PbTiO}_3$  (PSTT),  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3\text{-PbZrO}_3$  (PSTZ), have attracted much attention because their dielectric and pyroelectric properties can be improved.<sup>13,14</sup> One can expect that  $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$  (PSTH) ceramics will present the better properties since  $\text{PbHfO}_3$  has the similar structure and physical properties to  $\text{PbZrO}_3$ . It was reported that enhanced dielectric and pyroelectric properties of PSTH ceramics can be realized at low composition of  $x$ .<sup>15</sup> However, few reports about phase transition and lattice vibration of PSTH have been presented up to now. Fortunately, Raman spectra which can provide some invaluable information on the order-disorder phenomena and phase transitions.<sup>2,16,17</sup>

The PSTH ceramics with the  $\text{PbHfO}_3$  composition from 0 to 0.2 were prepared by hot-pressing sintering method.<sup>15</sup> The PSTH powders were first synthesized by the "two-stage calcination route." Then the ceramics were prepared by the oxygen

hot-pressing method. The samples with 5 wt. % excess  $\text{PbO}$  were heated to 1320 °C under the oxygen pressure of 25 MPa for 2 h, then cooled to 900 °C with the cooling rate of 3 °C/min. There is the perovskite structure with no impurity phases observed from the XRD pattern (not shown). The degree of structural ordering can be described by the  $B$ -site order  $S$  parameter, where  $S = 1$  for full order,  $S = 0$  for completely disordered material.<sup>10</sup> For  $x = 0.00, 0.05, 0.10, 0.15, 0.20$ , the value of  $S$  is evaluated to 0.72, 0.42, 0, 0, 0, respectively.<sup>15</sup> Temperature-dependent Raman scattering experiments were carried out by a Jobin-Yvon LabRAM HR 800 UV micro-Raman spectrometer and a Linkam THMSE 600 heating stage from 82 to 673 K.

For comparison, Raman spectra of the PSTH ceramics with  $x = 0$  and 0.15 at different temperatures were presented in Fig. 1 and Fig. 2, respectively. According to group theory, the ferroelectric phase Raman active modes are  $3A_1(\text{R,IR})+A_2(\text{inactive})+4E(\text{R,IR})$ .<sup>1,18,19</sup> It is well known that IR spectroscopy can provide some information on phonon modes and dielectric functions of the materials. However, both Raman scattering and IR spectra are sensitive to the local symmetry due to different selection rules. In order to give comprehensive study on the atomistic vibration and temperature-induced phase transformation, Raman scattering is necessary and complementary, as compared to the IR spectra. The Raman spectra are similar to those from other  $(A'A'')(B'B'')\text{O}_3$  relaxor ferroelectrics, such as  $\text{PbMn}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ ,  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3\text{-PbTiO}_3$ .<sup>3,12,20</sup> The highest vibration bands at 830 and 794  $\text{cm}^{-1}$  are assigned to the  $A_{1g}$  and  $E_g$  phonon modes. The scattering peaks at 550 and 58  $\text{cm}^{-1}$  are generated from the cubic  $F_{2g}$  phonon modes. The phonon modes located at 81 and 530  $\text{cm}^{-1}$  are derived from the splitting of the cubic  $F_{2g}$  modes. The lattice vibrations at 358 and 313  $\text{cm}^{-1}$  are derived from the  $F_{2u}$  mode. The intensity ratio between the higher-wavenumber and lower-wavenumber for the  $F_{2u}$  mode is sensitive to the correlation length of coherent Pb shifts with respect to the oxygen atoms and the

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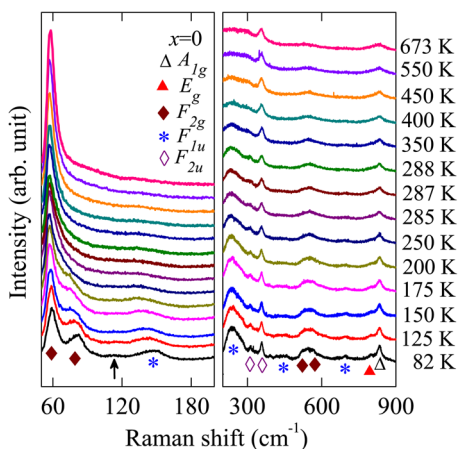


FIG. 1. (Color online) Raman scattering of the  $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$  ceramics at different temperatures from 82 to 673 K. The arrow indicates an additional vibration at  $109\text{ cm}^{-1}$ , which may arise from Brillouin zone-boundary modes activated.

degree of orientational ordering of lone pairs.<sup>18</sup> The Raman signals at  $698$ ,  $420$ ,  $240$ , and  $146\text{ cm}^{-1}$  are from the rhombohedral modes, corresponding to IR-active  $F_{1u}$  modes.<sup>18,19</sup>

Note that the number of Raman active modes in Fig. 2 becomes less and the lineshape is slightly different from that in Fig. 1. Four main bands located at  $830$ ,  $794$ ,  $550$ , and  $58\text{ cm}^{-1}$  are observed in the high temperature phase of ordered PSTH, which is in agreement with the group theory analysis. Moreover, the weak IR-active mode at  $240\text{ cm}^{-1}$  can be observed even at  $673\text{ K}$ , which is due to “dirty” modes arising from the rhombohedral structural distortions. The weak peaks at  $698$ ,  $550$ , and  $146\text{ cm}^{-1}$  become more pronounced with decreasing the temperature, which is apparently owing to an increment of the ferroelectric structural distortion. It should be noteworthy that the peak at  $81\text{ cm}^{-1}$  is harden and enhanced with decreasing the temperature. Mihailova *et al.* stated that non-coplanarity of the Pb and O atoms in the plane perpendicular to the body diagonal can be stabilized on cooling.<sup>18</sup>

Fig. 3 shows the composition dependence of Raman spectra for the PSTH ceramics recorded at 82 and 673 K. For ordered samples, the number of the phonon modes observed at 82 K is less than that predicted theoretically. This may be

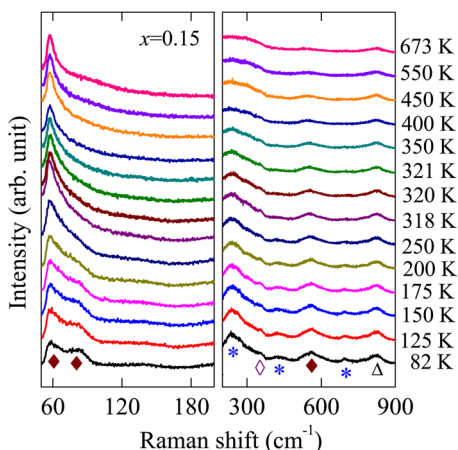


FIG. 2. (Color online) Raman scattering of the  $0.85\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-0.15\text{PbHfO}_3$  ceramics at different temperatures from 82 to 673 K.

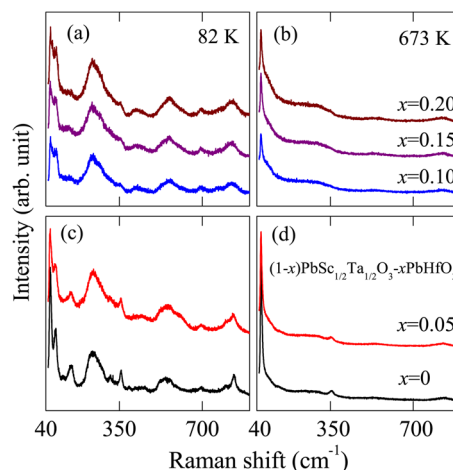


FIG. 3. (Color online) Raman spectra of the  $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3-x\text{PbHfO}_3$  ceramics with different composition presented at 82 K and 673 K.

attributed to the broadening and overlapping of the Raman lines.<sup>2,3</sup> A slight decrease in the intensity of the two bands near  $830$  and  $358\text{ cm}^{-1}$  can be observed with the addition of  $\text{PbHfO}_3$ . This may be ascribed to the variation of the B-site order and structural effects, which influence the Sc-O-Ta stretching vibrations. The intensity reduction of the Raman mode at  $358\text{ cm}^{-1}$  reflects the shorten coherence length of Pb-O bond. The splitting of the  $F_{2u}$  mode occurs for the PSTH ( $x=0, 0.05$ ) ceramics, which indicates that the correlation of the lone pairs within Pb-O plane and the Pb atoms shift towards the same direction. The phonon mode at about  $313\text{ cm}^{-1}$ , which corresponds to antiphase Sc-Ta vibrations, is forbidden for the disordered samples. It can be observed that the intensity ratio for the  $F_{2u}$  mode decreases with the composition for the PSTH ( $x=0, 0.05$ ) ceramics, which further confirms that the Sc/Ta order is lowered. For partially ordered PSTH ( $x=0, 0.05$ ) ceramics with the  $Fm\bar{3}m$  symmetry, three main modes located near  $58$ ,  $550$ ,  $830\text{ cm}^{-1}$  are observed at 673 K. Nevertheless, the origin of the high temperature phonon modes may be owing to the existence of the 1:1 chemical order in the Sc/Ta sublattice and breaking the translational symmetry.<sup>1</sup>

Figs. 4(a)-4(e) show the frequency variation of the  $A_{1g}$ ,  $F_{2g}$ ,  $F_{1u}$  phonon modes as a function of temperature for the PSTH ceramics. Three phase transition regions can be easily recognized based on the abrupt variations with increasing the temperature. **At the temperature region between 175 and 200 K, a rhombohedral to monoclinic or a rhombohedral to triclinic phase transition occurs, which depends on whether the rhombohedral phase is considered to be of  $R3m$  or  $R3$  symmetry.**<sup>12</sup> The **paraelectric (cubic) to ferroelectric (rhombohedral) phase transition takes place at 287, 293, 313, 320, and 330 K for the PSTH ceramics with  $x=0, 0.05, 0.10, 0.15,$  and  $0.20$ , respectively.** **The third structural transformation occurs at the character temperature ( $T^*$ ), which increases with the addition of  $\text{PbHfO}_3$ .** This can be ascribed to the stabilization by the tetragonal strain and the enhanced correlations between the polar nanoregions. It was known that the vibration bands between  $150$  and  $900\text{ cm}^{-1}$  are related to  $\text{BO}_6$  bending and stretching phonon modes.<sup>3,11,20</sup> The temperature dependence of the bands arising from the Sc/Ta cation localized ( $240\text{ cm}^{-1}$ ), symmetry O-Sc/Ta-O bending ( $550\text{ cm}^{-1}$ ),

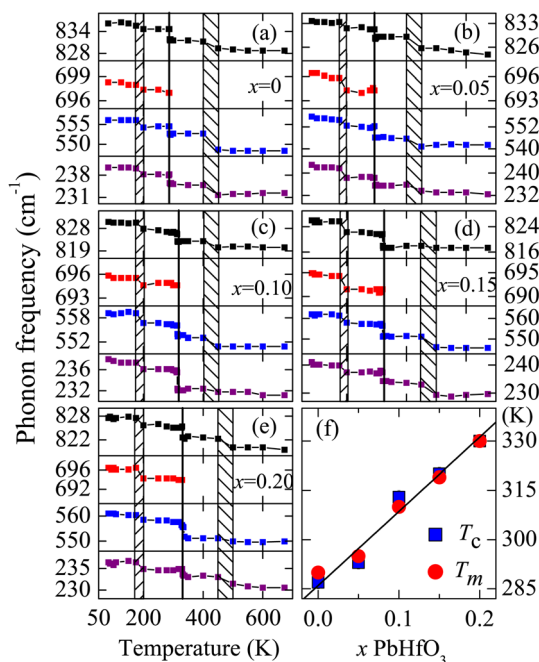


FIG. 4. (Color online) The frequency variations of the  $A_{1g}$ ,  $F_{2g}$ ,  $F_{1u}$  phonon modes as a function of temperature for the  $(1-x)\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_{3-x}\text{PbHfO}_3$  ceramics. (f) Composition dependence of the phase transition temperature and the solid line is the linearly fitting result to guide the eyes. Note the peak temperature of dielectric maximum ( $T_m$ ) is presented for comparison.

asymmetry Sc/Ta-O stretching ( $698\text{ cm}^{-1}$ ), and symmetry Sc/Ta-O stretching ( $830\text{ cm}^{-1}$ ) modes indicates different structural changes on cooling in the PSTH ceramics. Mitoseriu *et al.* found that the anomalous behavior of the peak position, bandwidth, or intensity is directly related to the phase transition mechanism.<sup>2</sup> The appearance of the phonon mode at  $109\text{ cm}^{-1}$  demonstrates a reduction of local symmetry and phase transition as justified by the further splitting of the low wavenumber cubic  $F_{2g}$  mode at  $45\text{ cm}^{-1}$ , which cannot be detected by our Raman spectra due to the limitation in the experimental condition.<sup>12</sup> It was reported that hybridization between the titanium  $3d$  states and the oxygen  $2p$  states is important for ferroelectricity in  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  perovskite-type materials.<sup>21</sup> Therefore, off-centered  $B$  cation shifts are crucial for the structural modifications. The phonon mode at  $240\text{ cm}^{-1}$  drops in intensity near  $T_c$  for all the samples, which indicates that the rhombohedral distortion takes place. Furthermore, the mode near  $240\text{ cm}^{-1}$  becomes broadening and obviously remains a very broad asymmetric feature above the  $T_c$ . On the other hand, with the addition of  $\text{PbHfO}_3$ , the enhancement of the peak near  $698\text{ cm}^{-1}$  can be observed in Fig. 3. The phenomenon indicates that the presence of  $\text{Hf}^{4+}$  in the  $B$ -site induces additional local structural distortion. In other words, the  $\text{BO}_6$  octahedral distortion changes the Sc/Ta-O bond lengths in the same octahedron.

Let us shed light on the paraelectric to ferroelectric phase transition temperature. A relation between the  $T_c$  and  $\text{PbHfO}_3$  compositions is displayed in Fig. 4(f). The  $T_c$  continuously increases from  $287\text{ K}$  for the PSTH ( $x = 0$ ) ceramic

to  $330\text{ K}$  for the PSTH ( $x = 0.20$ ) ceramic, which can be linearly expressed by  $286 + 226x$ . This may be ascribed to the fact that internal structure of the polar regions is still rhombohedral with small doping of  $\text{PbHfO}_3$ . Note that the peak position of the phonon modes shows the anomalous pattern around the phase transition temperature. Similar phenomenon were observed in the Raman spectra from other perovskite-type materials.<sup>2,16,17</sup> The variations indicate that the fluctuation of the local order and the change of force constants induce the crystal structure transformation during the phase transition, which further affect the optical and dielectric properties. It is known that the  $\text{PbHfO}_3$  ceramic has a higher Curie temperature (about  $488\text{ K}$ ) for cubic to tetragonal phase transition than that of PST.<sup>22</sup> Thus, the ferroelectrically active  $\text{Hf}^{4+}$  ions can contribute to the overall polarization. Moreover, it has been reported that the shifts of Pb and ferroelectrically active  $B''$  cations can influence the phase transition temperature in the relaxor ferroelectric materials.<sup>11,23</sup> The incorporation of  $\text{PbHfO}_3$  can stretch the average length of the Pb-O-Ta bonds, reduce the  $B$ -site ordering, form the Ta-O-Hf or Hf-O-Hf chains, and thus result in an increase of  $T_c$ . Finally, it should be noted that the linear increment of  $T_c$  with  $x$  obtained by Raman spectra agrees well with the temperature dependence of the peak temperature from dielectric maximum ( $T_m$ ) determined by dielectric measurements.<sup>15</sup>

In conclusion, the composition dependence of the phase transition temperature in the PSTH ceramics has been investigated by the Raman spectra.

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