JOURNAL OF ADVANCED DIELECTRICS
Vol. 7, No. 1 (2017) 1750003 (5 pages)

DOI: 10.1142/S2010135X17500035

World Scientific
www.worldscientific.com

Low temperature Raman scattering study of barium doped lead ytterbium tantalate ceramics

Dibyaranjan Rout*,§, Swetapadma Praharaj*, V. Subramanian† and V. Sivasubramanian‡
*Department of Physics, School of Applied Sciences, KIIT University
Bhubaneswar-751 024, Odisha, India
†Department of Physics, Indian Institute of Technology, Madras Chennai-600036, India
‡Materials Science Division, IGCAR, Kalpakkam-603102, India
§droutfpy@kiit.ac.in, dibyaranjanr@gmail.com

Received 13 September 2016; Revised 29 December 2016; Accepted 29 December 2016; Published 2 February 2017

Raman spectra of a complex perovskite system $(Pb_{1-x}Ba_x)(Yb_{0.5}Ta_{0.5})O_3$, $x = 0.0, 0.1$ and 0.2 have been studied at low temperature in the range of 10–250 K. The fascination of the system is that it undergoes a crossover from a highly ordered antiferroelectric ($x = 0.0$) to ferroelectric ($x = 0.1$) to disordered relaxor ferroelectric ($x = 0.2$). The nature of splitting that prevails in F_{2g} ($\approx 60\,cm^{-1}$), F_{1g} ($\approx 538\,cm^{-1}$) modes and their gradual merging and disappearance with x indicates an orthorhombic symmetry for $x = 0.0$ and a pseudo-cubic structure for $x = 0.2$. The mode at $420\,cm^{-1}$ suggests the existence of rhombohedral distortion in all the compositions. The soft mode behavior of the F_{2g} modes has been analyzed by fitting the data with the power law $\omega_s = A(T_C - T)^{\beta}$.

Keywords: Perovskite oxides; B-site ordering; Raman scattering; soft mode.

1. Introduction

Since last four decades, relaxor ferroelectrics (RFEs) with complex perovskite structure $A(B'B'')O_3$ have been extensively studied owing to their potential applications and fascinating basic Physics.[1–9] The characteristic properties of RFEs include (i) high dielectric constant, (ii) strong dielectric dispersion around T_m, the temperature corresponding to the dielectric constant maximum, (iii) diffused phase transition around T_m and (iv) absence of macroscopic polarization far below T_m. The polar nanoregions (PNRs) exhibited in RFEs are believed to be responsible for the multi-scale dynamics and spatial in-homogeneity that leads to the above peculiar properties. Generally, RFEs are nonpolar paraelectrics at high temperature, upon cooling PNRs start appearing at T_B; the so-called Burn temperature and then grow with further decreasing temperature. Nevertheless, when the temperature lowers down to a temperature named freezing temperature (T_f), PNRs become large enough resulting their dynamics to slow down to an extreme point and get frozen into a glassy phase i.e., nonergodic relaxor phase. In some earlier reports, the existence of PNRs in RFEs has already been verified experimentally[9–14] and also explained the mechanism behind their formation employing different models.[14–18] However, a conclusive understanding of the physics defining RFEs is still lacking and needs further attention.

In viewpoint of lattice dynamics in displacive ferroelectrics, it has been inferred that the phase transitions are caused by softening and condensation of transverse optic (TO) phonon modes at zone center. The previous studies demonstrate that in RFE, the dispersion of the transverse acoustic (TA) and low-energy TO phonons at temperatures above T_B were noticed to be identical to that observed in the PE phase of normal displacive ferroelectrics. Moreover, the optic mode exhibited in RFEs softens in a similar manner mostly seen in displacive type ferroelectrics when the temperature approaches T_B and follows the Cochran law $\omega_s = A(Tc - T)^{\beta}$. Further, the TO modes in RFEs at $T < T_f$ behave consistently with the distinctive behavior of a ferroelectric soft mode. However, in the temperature range between T_B and T_f, the lattice dynamics of RFEs are different from normal ferroelectrics.[19–22]

Using Raman scattering, many groups have studied the soft mode behavior of a displacive or a RFE separately and distinctively. In this present work, an interesting solid solution $(Pb_{1-x}Ba_x)(Yb_{0.5}Ta_{0.5})O_3$ (PBYT) is considered for investigation which undergoes a crossover in phase transition from antiferroelectric ($x = 0.0$) to ferroelectric with diffuse transition ($x = 0.1$) and then to RFE ($x = 0.2$). In the literature, it is also mentioned that the composition $x = 0.0$ exhibited weak relaxor behavior around the antiferroelectric to ferroelectric transition.[9] In fact, the virgin composition $x = 0.0$ is highly ordered but the degree of ordering decreases with increasing x.[23,24] Although the degree of ordering is verified by room temperature XRD and Raman spectra, till date, the low temperature Raman study has not been done. As the T_m values shifted to lower temperature, it may be

interesting to study the Raman spectroscopy at lower temperature to acquire useful information. This study focuses on the Raman spectra of the above mentioned three compositions exhibiting different degree of ordering and phase transition behavior. Emphasis has been given to the phonon dynamics involved in those samples below the freezing temperature T_f and hence the Raman spectra were recorded at a very low temperature range (250–10 K).

2. Experimental

The $(Pb_{1-x}Ba_x)(Yb_{0.5}Ta_{0.5})O_3$, $x = 0.0, 0.1$ and 0.2 ceramics were prepared by solid-state reaction with optimized calcination and sintering temperatures of 900°C and 1325°C for 4 h respectively.[9] The Raman spectra were taken in the frequency range 1000–40 cm^{-1} in the low temperature range 250–10 K and recorded in back scattering geometry using 200 mW output power of 488 nm line of an Ar-ion laser. The scattered light was analyzed using a double monochromator (SPEX 14018) and detected with a photo-multiplier tube (Hamamatsu R120) operating in a photon counting mode. For recording Raman spectra at low temperature, a Linkam stage was used along with a 20× objective. The position and full width at half maximum (FWHM) of the Raman peaks were obtained by fitting the spectra with Lorentzian line shape (Jandel peak fit program).[24] For each spectra, the number of lines were chosen to obtain a best fit.

3. Results and Discussion

Figure 1 shows the Raman spectra of PBYT ceramics at 10 K in the range 40–1000 cm^{-1}. The number of modes are deconvoluted as 44, 23 and 15 (approximately) for $x = 0.0, 0.1$ and 0.2, respectively, and it clearly suggests a structural change with increasing x. As per the earlier report,[23] the

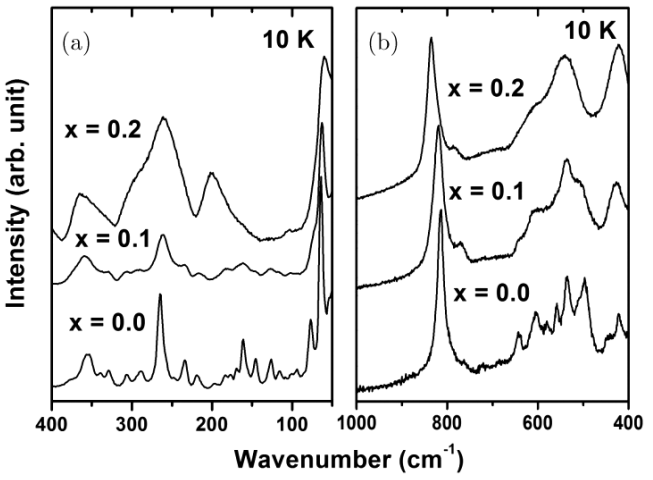

Fig. 1. Raman spectra of $(Pb_{1-x}Ba_x)(Yb_{0.5}Ta_{0.5})O_3$ ceramics at 10 K.

structure of PBYT changes from orthorhombically distorted pseudo-monoclinic cell (space group *Pbnm*) at $x = 0.0$ to a pseudo-cubic (space group $Fm\bar{3}m$) for $x = 0.2$. Again, there is possibility of decrease of B-site ordering leading to the disappearance of splitting and subsequently merging and broadening of modes. Further, the number of modes observed for $x = 0.2$ is more than the number (4: $A_{1g}+E_g+2F_{2g}$) predicted theoretically for $Fm\bar{3}m$.[25] This indicates a deviation of the local structure from the average structure due to the presence of PNRs as the system exhibited relaxor behavior. Nevertheless, the contribution of phase coexistence and distortion cannot be brushed aside because the composition $x = 0.2$ is suggested as the morphotropic phase boundary for the present solid solution.[24] Figure 2 plots the temperature dependence of Raman spectra for all the ceramics in the frequency range 40–100 cm^{-1}. In this frequency range, three strong peaks are observed for $x = 0.0$ and one broad peak for $x = 0.2$. The mode observed around 60 cm^{-1} is assigned to the F_{2g} Pb-localized mode. Generally, in complex perovskites, F_{2g} mode arises due to the movement of A-site cations along with the oxygen atoms and the position of the mode expected to be influenced by the mass of A cation and A–O bond parameters.[26]

As per theoretical calculation, in cubic symmetry, the F_{2g} modes are triply degenerate but when the symmetry reduces to orthorhombic, these modes split into three lines. Our results show excellent matching to the theoretical prediction as the composition, $x = 0.2$ with pseudo-cubic symmetry display a single broad peak and subsequently split into three peaks around the peak at 60 cm^{-1} for the composition $x = 0.0$ exhibiting orthorhombic symmetry. Again, it appears that there is a small shift observed for F_{2g} towards lower frequency with Ba concentration as anticipated because the mass of Pb is more.

Nevertheless, a careful study of this mode as a function of temperature reveals a reasonable softening of the mode and can be assigned to the soft mode in this system. Temperature dependence of the soft mode wave number is plotted in Fig. 3 for all the three compositions. Figure 3(a) is reproduced to carry out a comparative study.

The soft modes show a nonlinear variation and fit into the power relation $\omega_s = A(T_C - T)^{\beta}$, where ω_s is the mode frequency, A is a constant, T_C is the expected ferroelectric phase transition temperature and β is a critical exponent related to order parameter.[27] Actually, this PBYT system is a very interesting system. As per the temperature-dependent dielectric data, PYT exhibits weak relaxor behavior at lower temperature, marked by transition from antiferroelectric to ferroelectric state.[24] With increasing Ba, the relaxor behavior becomes stronger. Generally, it is considered that the relaxor phase transition is not a first-order phase transition rather it is likely to be a second-order phase transition.[28] Moreover, the optic mode exhibited in RFEs softens in a similar manner mostly seen in displacive type ferroelectrics when the temperature approaches T_B and follows the Cochran law.[27]

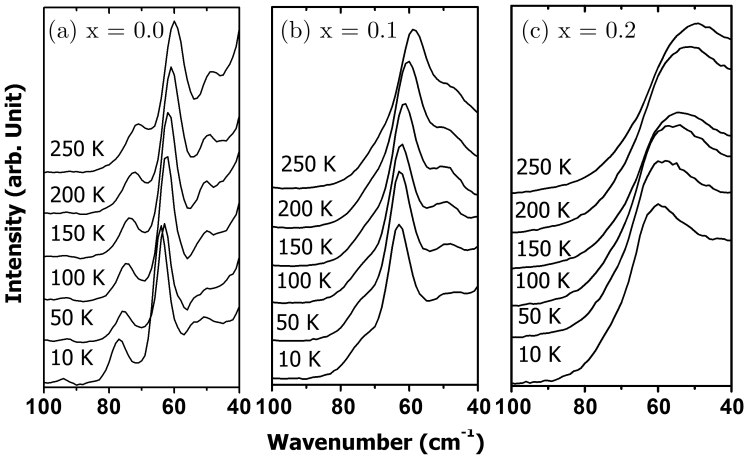

Fig. 2. Temperature-dependent Raman spectra in the frequency range 100–30 cm^{-1}.

Further, the TO modes in RFEs at $T < T_f$ behave consistently with the distinctive behavior of a ferroelectric soft mode.[22] In analogy to the above facts, we have used Cochran law $\omega_s = A(Tc - T)^{\beta}$ to analyze the soft mode for the system.

In Fig. 3, the experimental data are shown by scattered points and the solid lines are the fitted curves to the above mentioned power law. The fitting parameters are given in the figure. The fitting parameters indicate a gradual increase of constant A and a gradual decrease of the critical exponent β as Ba concentration increases. This decrease of β may be related to the gradual crossover from first-order phase transition to diffuse transition then to weak relaxor behavior. It can be inferred that the degree of interaction between the PNRs and their freezing temperatures are different in those compositions, which may directly or indirectly influence the phonon dynamics. Moreover, the T_c values 426 K ($x = 0.0$), 390 K ($x = 0.1$) and 283 K (0.2) obtained from the fitting are in close accordance with the ferroelectric phase transition temperatures reported earlier in dielectric constant versus temperature data for the compositions respectively.[9,24] Hence, the possibility of a significant contribution of the soft mode in the ferroelectric phase transition in all the compositions cannot be avoided.

Figure 4 shows the Raman spectra in the range 400–100 cm^{-1} recorded at different temperatures. In this frequency range, three major peaks at $\approx 200, 259$ and 360 cm^{-1} are observed at $x = 0.2$, but with reduction of symmetry at lower compositions, each one of the peak clearly split into three peaks and several new peaks appeared. The broad peak around 200 cm^{-1} with a hump around 177 cm^{-1} emerges due to the relative rotation of octahedron due to size mismatch in B′–O–B″ bond and attributed to F_{1g} mode. The other two strong peaks at ≈ 259 and 360 cm^{-1} attributed to F_{1u} mode due to asymmetric O–B–O bending vibration arising from rhombohedral structural distortion and F_{2u} mode due to electron-phonon coupling of Pb^{2+} lone pair electrons respectively. The changes noticed in those modes further evidence the orthorhombic symmetry along with rhombohedral distortion in lower concentration; with increasing Ba concentration, the structure gradually modifies towards higher symmetry but the rhombohedral symmetry remains present within the studied compositions. Moreover, with increasing temperature, these modes undergo no substantial shift in their wave number but as expected, they show thermal broadened. The presence of an asymmetric O–B–O bending vibration mode at 420 cm^{-1} (Fig. 5) with F_{1u} symmetry provide further evidences to confirm the existence of rhombohedral distortion.[29] In fact, the mode evolves as stronger and prominent as the Ba concentration increases. It remains to be stronger with increasing temperature

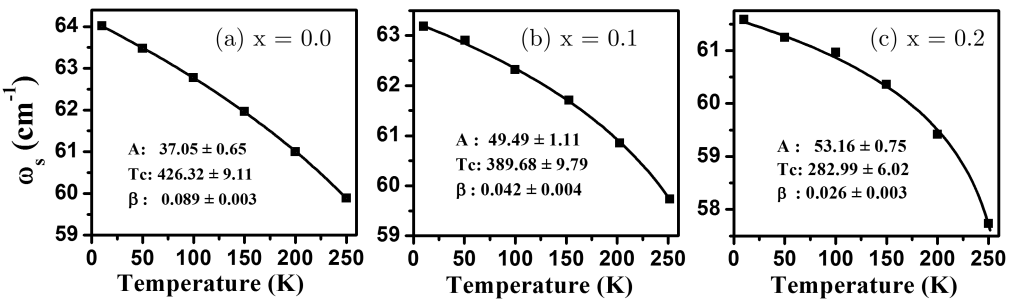

Fig. 3. Temperature-dependent of frequency of F_{2g} mode at 60 cm^{-1}. The scatter point are the experimental data and the solid line is the fitting curve to the power relation.

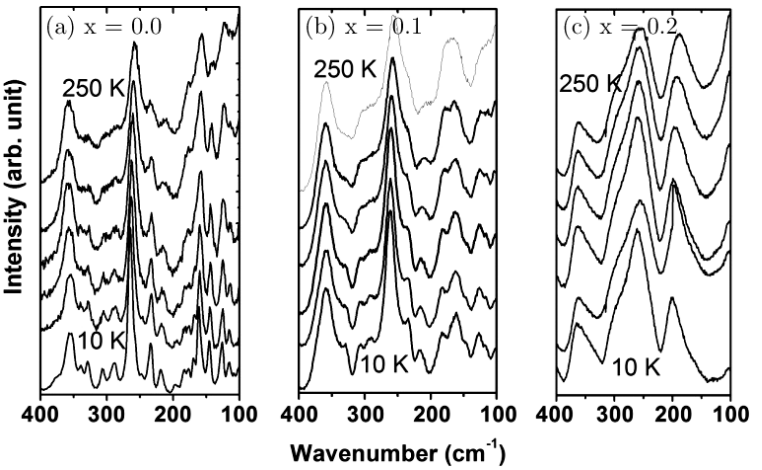

Fig. 4. Temperature-dependent Raman spectra in the frequency range 400–100 cm^{-1}.

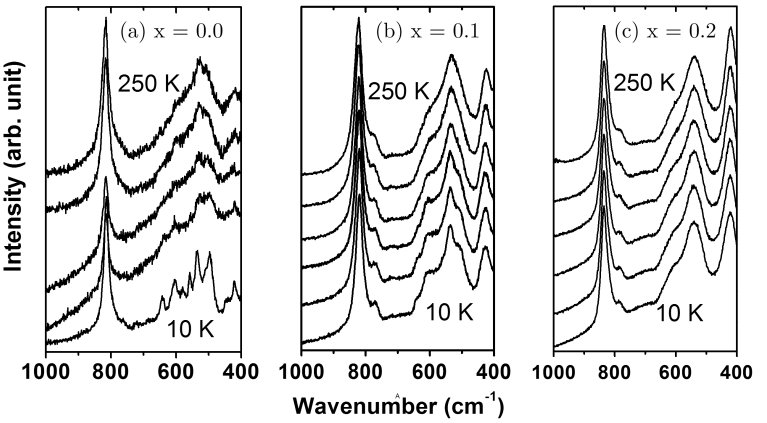

Fig. 5. Temperature-dependent Raman spectra in the frequency range 1000–400 cm^{-1}.

suggesting the persistence of rhombohedral symmetry in those samples, which is one of the reasons for the increase in diffuseness. Hence, the present observations are considerably in accordance with the earlier prediction of a morphotropic phase boundary i.e., the coexistence of more than one structural phases at the composition $x = 0.2$ as per the dielectric study.

Figure 5 plots the Raman spectra in the frequency range 1000–400 cm^{-1} and displays two strong and characteristic peaks at $\approx 535\,cm^{-1}$ and $835\,cm^{-1}$. The former is assigned to F_{2g} symmetric bending of BO_6 octahedra and later is assigned to the A_{1g} mode arises due to the movement of oxygen atoms along B′–O–B″ with cations at rest. Usually, this high frequency A_{1g} mode is a measure of B-site ordering in complex perovskites.[26] The shifting of this mode indicates a change in the degree of ordering due to the size mismatch at A-site as Pb is substituted by Ba in this present system. In analogy to the earlier dielectric studies, the B-site ordering decreases with increasing Ba concentration. However, the mode undergoes no change with increasing temperature maintaining the short range ordering in the temperature range studied. Nevertheless, the high frequency F_{1g} mode shifts towards lower frequency side with increasing temperature. Though the shift is observed in all the samples, the level of shifting gradually decreases with Ba concentration. This may be due to the fact that the FE phase transitions are gradually showing relaxor type behavior in Ba substituted compounds though at low temperatures all the samples exhibit FE phase. Also, there is possible modification in antiferroelectric coupling of Pb^{2+} cations and ferroelectric coupling of B-site cations as the system crossover from antiferroelectric to ferroelectric and then to RFE with increasing Ba concentration.

4. Summary

Single phase $(Pb_{1-x}Ba_x)(Yb_{0.5}Ta_{0.5})O_3$, $x = 0.0, 0.1$ and 0.2 ceramics were prepared by solid state reaction method and Raman spectra were recorded on those samples in the frequency range 1000–40 cm^{-1} at low temperatures 250–10 K. The spectra revealed orthorhombic symmetry for the antiferroelectric PYT and the structure gradually changed to a pseudo-cubic symmetry. The existence of rhombohedral

distortion was also evidenced in the PYT sample and the distortion further increased with increase of Ba concentration. The low frequency F_{2g} mode at $\approx 60\,cm^{-1}$ showed soft mode behavior in all compositions suggesting ferroelectric phase at low temperature. The mode clearly fit into a power law and the T_c values obtained from each fit match well with the phase transition temperature observed in dielectric measurements of those samples.

References

[1]L. E. Cross, Relaxor ferroelectrics, *Ferroelectrics* **76**, 241 (1987).
[2]H. Fu and R. E. Cohen, Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics, *Nature* **403**, 281 (2000).
[3]A. A. Bokov and Z.-G. Ye, Recent progress in relaxor ferroelectrics with perovskite structure, *Front. Ferroelectricity* **41**, 31 (2006).
[4]B. Mihailova, B. Maier, T. Steilmann, E. Dul'kin and M. Roth, Electric-field-induced local structural phenomena in Pb-based ABO_3-type relaxor ferroelectrics, *IEEE Trans.* **62**, 7 (2015).
[5]D. J. Goossens, Local ordering in lead-based relaxor ferroelectrics, *Acc. Chem. Res.* **46**, 2597 (2013).
[6]V. V. Shvartsman and D. C. Lupascu, Lead-free relaxor ferroelectrics, *J. Am. Ceram. Soc.* **95**, 1 (2012).
[7]G. Burns and F. H. Dacol, Crystalline ferroelectrics with glassy polarization behavior, *Phys. Rev. B* **28**, 2527 (1983).
[8]Z. Trybuła, S. Miga, S. Łoś, M. Trybuła and J. Dec, Evidence of polar nanoregions in quantum paraelectric $KTaO_3$, *Solid State Commun.* **209**, 23 (2015).
[9]D. Rout, V. Subramanian, K. Hariharan, V. Sivasubramanian and V. R. K. Murthy, Dielectric study of the phase transitions in $(Pb_{1-x}Ba_x)(Yb_{1/2}Ta_{1/2})O_3$ ceramics, *Ferroelectrics* **300**, 67 (2004).
[10]C. Stock, P. M. Gehring, H. Hiraka, I. Swainson, G. Xu, Z. G. Ye, H. Luo, J. F. Li and D. Viehland, Evidence for anisotropic polar nanoregions in relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$: A neutron study of the elastic constants and anomalous TA phonon damping in PMN, *Phys. Rev. B* **86**, 104108 (2012).
[11]F. Li, Z. Xu and S. Zhang, The effect of polar nanoregions on electromechanical properties of relaxor-$PbTiO_3$ crystals: Extracting from electric-field-induced polarization and strain behaviors, *Appl. Phys. Lett.* **105**, 122904 (2014).
[12]K. Hirota, Z. G. Ye, S. Wakimoto, P. M. Gehring and G. Shirane, Neutron diffuse scattering from polar nanoregions in the relaxor Pb $(Mg_{1/3}Nb_{2/3})O_3$, *Phys. Rev. B* **65**, 104105 (2002).
[13]I. K. Jeong, T. W. Darling, J. K. Lee, T. Proffen, R. H. Heffner, J. S. Park, K. S. Hong, W. Dmowski and T. Egami, Direct observation of the formation of polar nanoregions in $Pb(Mg_{1/3}\ Nb_{2/3})O_3$ using neutron pair distribution function analysis, *Phys. Rev. Lett.* **94**, 147602 (2005).
[14]M. E. Manley, J. W. Lynn, D. L. Abernathy, E. D. Specht, O. Delaire, A. R. Bishop, R. Sahul and J. D. Budai, Phonon localization drives polar nanoregions in a relaxor ferroelectric, *Nature Commun.* **5**, 3683 (2014).
[15]W. Kleemann, J. Dec and S. Miga, The cluster glass route of relaxor ferroelectrics, *Phase Transitions* **88**, 234 (2015).
[16]B. E. Vugmeister and H. Rabitz, Dynamics of interacting clusters and dielectric response in relaxor ferroelectrics, *Phys. Rev. B* **57**, 7581 (1998).
[17]R. Pirc and R. Blinc, Spherical random-bond–random-field model of relaxor ferroelectrics, *Phys. Rev. B* **60**, 13470 (1999).
[18]V. Westphal, W. Kleemann and M. D. Glinchuk, Diffuse phase transitions and random-field-induced domain states of the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$, *Phys. Rev. Lett.* **68**, 847 (1992).
[19]K. Tani, Dynamics of displacive-type ferroelectrics–soft modes, *J. Phys. Soc. Japan* **26**, 93 (1969).
[20]A. Nabereznov, S. Vakhrushev, B. Dorner, D. Strauch and H. Moudden, Inelastic neutron scattering study of the relaxor ferroelectric $PbMg_{1/3}Nb_{2/3}O_3$ at high temperatures, *Eur. Phys. J. B-Condens. Matter Complex Syst.* **11**, 13 (1999).
[21]P. M. Gehring, S. Wakimoto, Z.-G. Ye and G. Shirane, Soft mode dynamics above and below the burns temperature in the relaxor Pb $(Mg_{1/3}Nb_{2/3})O_3$, *Phys. Rev. Lett.* **87**, 277601 (2001).
[22]S. Wakimoto, C. Stock, R. J. Birgeneau, Z.-G. Ye, W. Chen, W. J. L. Buyers, P. M. Gehring and G. Shirane, Ferroelectric ordering in the relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ as evidenced by low-temperature phonon anomalies, *Phys. Rev. B* **65**, 172105 (2002).
[23]D. Rout, V. Subramanian and V. Sivasubramanian, Temperature dependence Raman spectroscopic studies of $Pb(Yb_{0.5}Ta_{0.5})O_3$, *Vib. Spectrosc.* **46**, 22 (2008).
[24]D. Rout, V. Subramanian, K. Hariharan, V. Sivasubramanian and V. R. K. Murthy, Raman spectroscopic study of $(Pb_{1-x}Ba_x)(Yb_{1/2}Ta_{1/2})O_3$ ceramics, *J. Appl. Phys.* **98**, 103503 (2005).
[25]U. Bismayer, V. Devarajan and P. Groves, Hard-mode Raman spectroscopy and structural phase transition in the relaxor ferroelectric lead scandium tantalate, $Pb(Sc_{0.5}Ta_{0.5})O_3$, *J. Phys. Condens. Matter* **1**, 6977 (1989).
[26]I. G. Siny, R. Tao, R. S. Katiyar, R. Guo and A. S. Bhalla, Raman spectroscopy of Mg-Ta order-disorder in $BaMg_{1/3}Ta_{2/3}O_3$, *J. Phys. Chem. Solids* **59**, 181 (1998).
[27]A. Hushur, Y. Akishige and S. Kojima, Soft optical phonon in Ba-doped $Sr_2Nb_2O_7$ ceramics, *Ceram. Int.* **30**, 2023 (2004).
[28]G. A. Samara, The relaxational properties of compositionally disordered ABO_3 perovskites, *J. Phys.: Condens. Matter* **15**, R367 (2003).
[29]B. Mihailova, U. Bismayer, B. Guttler, M. Gospodinov and L. Konstantinov, Local structure and dynamics in relaxor-ferroelectric $PbSc_{1/2}Nb_{1/2}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$ single crystals, *J. Phys: Condens. Matter* **14**, 1091 (2002).