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Soft modes condensation in Raman spectra of (Pb–La)(Zr–Sn–Ti)O_3 ceramics

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Low frequency Raman spectra of $(Pb_{0.97}La_{0.02})(Zr_{0.864}Sn_{0.04}Ti_{0.096})O_3$ ceramic samples have been studied near cubic to antiferroelectric phase transition at about 200° C. A set of low frequency soft modes were observed restoring below the transition point, in addition to the known one above 100 cm^{-1}. These modes show strong damping anomalies at the transition point that supposes considerable intermode interactions via dampings.

Keywords: PZT ceramics; phase transition; Raman scattering; soft mode.

1. Introduction

PZT-like solid solutions are the most extensively studied and technologically important dielectric materials of the perovskite family for more than fifty years.[1] High dielectric characteristics of these materials are normally associated with phase transitions, which makes mechanisms of these transitions of great importance both for basic solid state physics and applications.

Substituting Zr by Sn element and Pb with La dopants results in the obtained (Pb–La)(Zr–Sn–Ti) (PLZST) ceramics having a richer and flexible phase structure, such as ferroelectric (FE), antiferroelectric (AFE) and paraelectric (PE). The phase can be easily adjusted via composition variation. Near the phase boundary, the phase of PLZST ceramics could be influenced easily by external stimulation, such as electric field, temperature, pressure, etc. For example, some PLZST ceramics become FE after poling, whose composition is just on the AFE side of FE–AFE boundary. Under pressure, the internal dipoles are transformed into reverse alignment. At this time, the ceramics is transformed from a FE phase to an AFE phase.[2,3] In addition, by rising temperature, the AFE phase could be transformed to the PE one above Curie temperature.

The temperature- or pressure-induced phase transition could be utilized in energy conversion or harvesting. For example, PLZST ceramics can experience the FE–AFE phase transition by applying external field (electric field, pressure, temperature). Under the action of the compressive shock, the poled PLZST ceramics undergoes FE–AFE phase transition as well and instantly releases a large amount of charge. This energy conversion of mechanical to electrical energy is achieved by phase change under pressure, which can be utilized for power generation. The pulse power generated by impacting the loaded material with explosives is one of the main applications of the FE–AFE phase transformation.[4] Also, the temperature-induced phase transition could have a great impact on the dielectric behavior of PLZST, which has been used for thermal energy harvesting.[5]

In the former study, the phase transition was usually studied by the dielectric behavior, such as the temperature dependence of small signal dielectric constant. To better understand the phase transition in this work, the temperature-induced phase transition of $(Pb_{0.97}La_{0.02})(Zr_{0.864}Sn_{0.04}Ti_{0.096})O_3$ ceramic was studied by Raman spectroscopy and we compared the Raman result with the traditional dielectric behavior. It should be noted that lower frequency part of Raman spectra of pure $PbZrO_3$ single crystals have been studied earlier[7] and one soft mode restoring was found at about 100 cm^{-1}. Recently, Raman spectra of closer composition ceramics were published[8] and similar soft mode was observed, but frequency range below 100 cm^{-1} was not investigated. Same single soft mode was found earlier[9,10] in PLZST ceramics of rather different compositions and phase diagram. While investigations of lattice dynamics of the same single crystals by inelastic neutron scattering above the transition point[11] predicted at least four soft modes restoring below the PE–AFE transition, this lower frequency range of the spectrum assumes a special interest.

2. Experimental

2.1. *Sample preparation*

$(Pb_{0.97}La_{0.02})(Zr_{0.864}Sn_{0.04}Ti_{0.096})O_3$ ceramic was prepared by solid-state reaction technique. The powders of Pb_3O_4, ZrO_2, SnO_2, TiO_2, La_2O_3 were used as the starting raw materials. The mixture was ball-milled for 10 h to improve the homogeneity with the rotating speed at 350 rad/min. After that, calcination was performed at 850°C for 3 h to obtain the pre-sintered powder. After being crushed and pulverized, the powder was subsequently uniaxially pressed into a disc with polyvinyl acetate (PVA) as a binder. This blend was sintered at 1300°C for 2.5 h in a lead-rich environment. Specimens were formed as discs of 12 mm diameter and 1 mm thickness.

Figure 1 shows the XRD pattern of such disc to analyze its phase structure, measured by X-ray diffractometer D/MAX-2400. The sample was scanned at the rate of 2°/min from 10° to 80° at room temperature. Sharp and distinct diffraction peaks show that this ceramic has pure perovskite phase without any secondary phase, such as a pyrochlore one, in agreement with the Jade card.

2.2. *Dielectric measurements*

A sliver paste electrode was applied over the two opposite major surfaces of the ceramic chips for the measurement of electric properties.

The dielectric constant (relative permittivity) and loss tangent as a function of temperature were measured with Agilent E4980A Precision LCR Meter within 100 Hz to 1 MHz frequency range.

2.3. *Raman measurements*

A smaller piece of such unpolarized chip (Fig. 2) without electrodes was used for Raman spectroscopy.

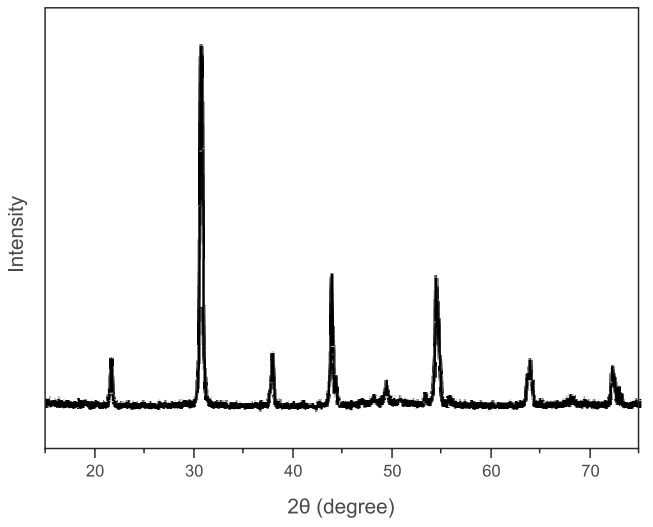

Fig. 1. XRD pattern of obtained $(Pb_{0.97}La_{0.02})(Zr_{0.864}Sn_{0.04}Ti_{0.096})O_3$ ceramics.

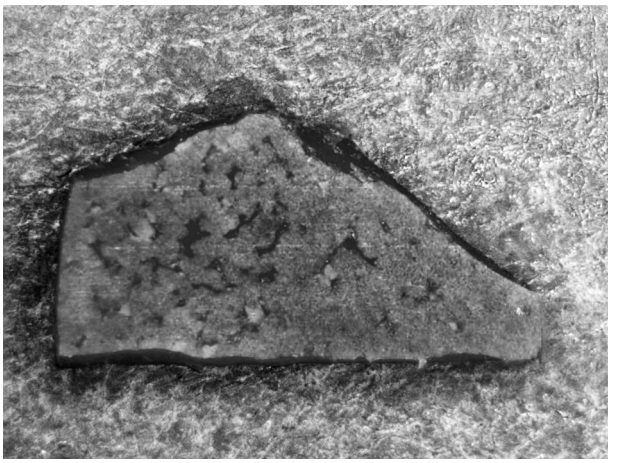

Fig. 2. Sample used for Raman spectroscopy.

The spectra in the backscattering geometry were recorded with Horiba Jobin Yvon T64000 spectrometer equipped with a liquid nitrogen cooled charge coupled device detection system in 10–1600 cm^{-1} range. Ar^+-ion laser Spectra Physics Stabilite 2017 with $\lambda^\circ = 514.5$ nm and power 3 mW at a sample was used as an excitation light source. Experiments were carried out using incident laser beam focused on the sample by a 50× Olympus MPlan objective lens with a numerical aperture (NA) of 0.75. The scattered light was collected by the same objective lens. The spectroscopic measurements were performed in the subtractive dispersion mode to investigate the low wavenumber spectra, which attained a limit of 10 cm^{-1} in the present setup. The deformation of the low-wavenumber spectral edge by an optical slit, that sometimes smears the true features of low-wavenumber spectra, was carefully eliminated by rigorous optical alignment. Temperature measurements were performed using an ARS CS204–X1.SS closed cycle helium cryostat in the temperature range of 8–860 K. The accuracy of temperature stabilization during spectra measurement was < 0.2 K.

3. Experimental Results

3.1. *Dielectric measurements — results*

Figure 3 shows the dielectric properties of the sample at various temperatures. Unpoled sample displays sharp single dielectric peak near 200°C that corresponds to the known AFE–PE phase transition point.

It can be seen that when the sample undergoes an AFE–PE phase transition, the dielectric constant shows a sharp peak, which is the Curie peak.[6] The corresponding phase transition temperature is the Curie temperature (182°C, 455 K). This Curie temperature stays the same within the whole studied frequency range, confirming the nonrelaxor character of the transition.

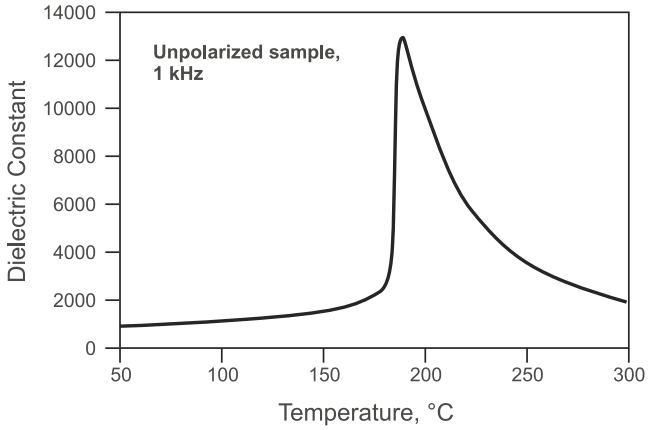

Fig. 3. Dielectric constant of studied ceramics.

3.2. *Raman scattering — results*

Obtained Raman spectra at room and above temperatures are in good agreement with Raman spectra of pure $PbZrO_3$ single crystal (see, e.g., Ref. 2), but all line positions are shifted a bit to lower frequencies and slightly widened. Temperature transformation of the spectrum is shown in Fig. 4.

Wider bands above the transition point are extremely weak as compared to the lower temperature spectra and are obviously induced by second-order processes and lattice disorder.

Softening of several lines is clearly seen in the lower wavenumber part of spectra when heating the sample to the transition point (Fig. 5).

Even better, it is seen at the intensity versus temperature diagram (Fig. 6).

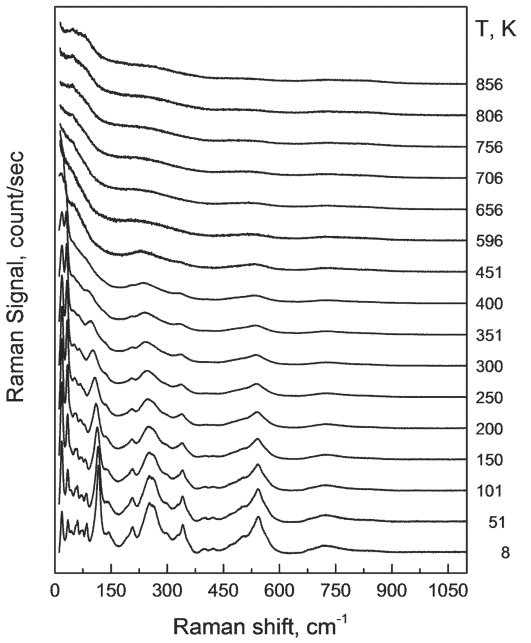

Fig. 4. Temperature transformation of Raman spectrum.

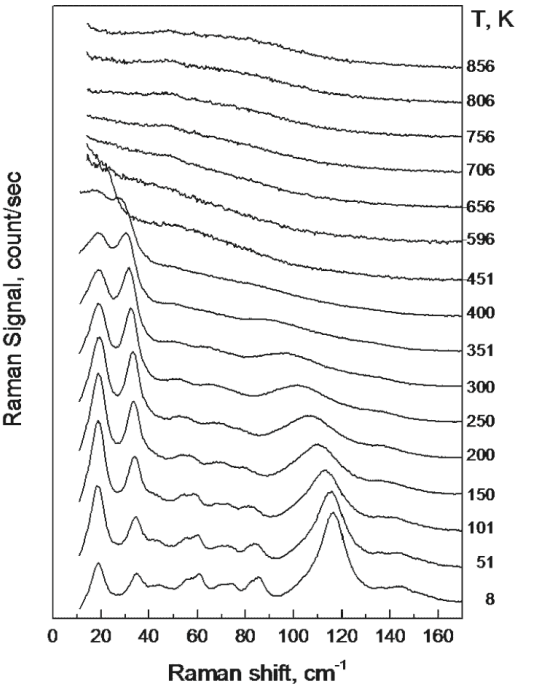

Fig. 5. Lower wavenumber part of Raman spectra.

At least three modes condensing under heating to the transition point are clearly seen in the diagram. It should be pointed out that positions of lowest modes do not change much while their dampings grow drastically (Fig. 7).

This strong damping growing of several low frequency modes in the disordered lattice should result inevitably in their strong interaction and mixing of their eigenvectors. Performed simulation of the lattice dynamics in the AFE phase showed that these two lower frequency modes correspond to Pb and La displacements mainly, while the higher

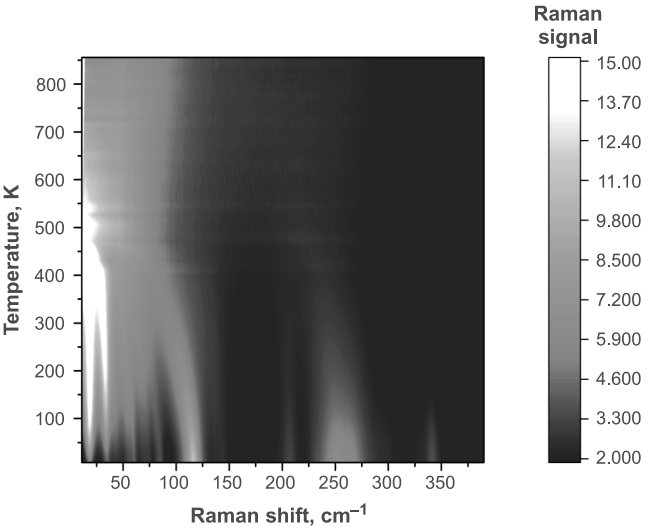

Fig. 6. Raman intensity versus temperature diagram. Softening of the lower frequency modes is clearly seen.

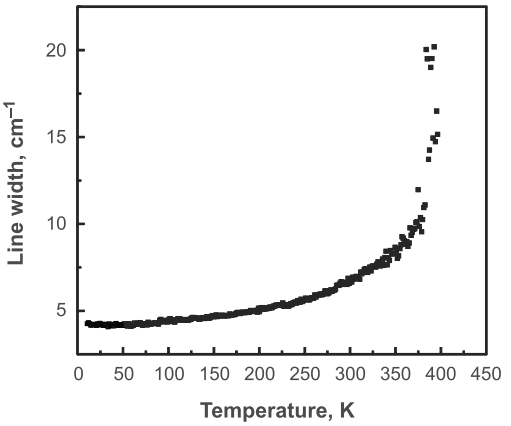

Fig. 7. Line width of the lowest Raman line versus temperature.

frequency ones correspond to rotations of ZrO_6 groups. Supposedly, these motions should be considerably mixed closer to the PA–AFE transition point as a result of strong interaction of several order parameters.

4. Conclusion

Ceramic samples of $(Pb_{0.97}La_{0.02})(Zr_{0.864}Sn_{0.04}Ti_{0.096})O_3$ have been synthesized by traditional hot pressing technique; X-ray analysis confirmed single phase composition of the samples, and dielectric measurements showed single cubic to AFE phase transition at about 200°C. In the low frequency Raman spectra, we observed a set of soft modes restoring below the transition point, in addition to the mode above $100\,cm^{-1}$ observed earlier.[7,8] These modes show strong damping anomalies at the transition point that supposes considerable intermode interactions via dampings.

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