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Raman scattering study on ferroelectric $(Ba_{0.32}Sr_{0.68})_2Nb_2O_7$ ceramics

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Abstract

Raman scattering technique was applied to examine the Ba-doping effect to the two low temperature phase transitions of $Sr_2Nb_2O_7$ (SN) in the temperature range from −190 to 600 °C. The line shape of Raman spectra can be well fitted by multidamped harmonic oscillator model. We did not observe any soft mode related to the two low temperature phase transitions corresponding to those of the pure SN. It is correlated to the disappearance of the incommensurate phase in $(Ba_{0.32}Sr_{0.68})_2Nb_2O_7$ ceramics. However, the temperature dependence behavior of the three low frequency modes indicates another new structural phase transition around 270 °C. It is considered that the reduction of the interlayer interaction caused by partial replacement of Sr-site by Ba-site, whose ionic radius is larger than that of Sr, may be the reason for the disappearance of the incommensurate phase transition in $(Ba_{0.32}Sr_{0.68})_2Nb_2O_7$ ceramics.

Keywords: Soft mode; Structural phase transition; Raman scattering; $Sr_2Nb_2O_7$; Ferroelectric

1. Introduction

Lead-based ferroelectric materials with perovskite structure, PZT and PMN-PT, have a good ferroelectric and piezoelectric properties and thus widely used as electromechanical devices. However, lead may affect natural environment. The development of lead-free ferroelectric materials required from the viewpoint of environmental problems. In recent years, a significant effort has been made to manufacture new lead-free ferroelectric or piezoelectric materials.

SN is the highest T_c ferroelectric with the perovskite slab structure [1]. Low coercive field, low permittivity and high-heat resistance of this material enables its solid solutions $Sr_2Ta_xNb_{2-x}O_7$ to be used as Pb-free non-volatile ferroelectric memory devices based on field effect transistors and capacitors, and optical waveguides [2–4]. Furthermore, its lead-free character has received much more attention as green materials in its application. The spontaneous polarization, $P_s = 9 \times 10^{-6}$ C/cm^2, is parallel to the c-axis and the coercive field is $E_c = 6$ kV/cm at room temperature [5]. The structure of SN have perovskite slabs parallel to (0 1 0), consists of an NbO_6 octahedra and Sr atoms. It was known that the octahedra distort and tilt on cooling and SN undergoes three phase transitions at 1342, 215 and −156 °C, $Cmcm \rightarrow Cmc2_1 \rightarrow Pbn2_1 \rightarrow Pb11$ [6,7]. The dynamics of phase transitions has been studied mainly by means of Raman scattering [8–11], ESR [12], and polarized far-infrared reflectivity and transmission measurements [13]. The ferroelectric soft mode was found in $b(cc)\bar{b}$ scattering geometry below $T_c = 1342$ °C. Below 215 °C another soft mode appears showing the displacive character of this normal to incommensurate phase transition. Further decreasing the temperature, the soft mode coupled with another low-frequency mode, an intensity transfer occurs between the two modes. Raman, ESR and polarized far-infrared reflectivity and transmission results showed a non-classical behavior of the incommensurate order parameter with critical exponents $\beta = 0.38$, 0.34 and 0.3, respectively. As for Ba-doped SN, $(Sr_{1-x}Ba_x)_2Nb_2O_7$, the T_c decreases from 1342 °C with respect to x [6]. For $x = 0.32$ crystals, dielectric measurements show that the low temperature ferroelectric transition temperature disappears and a new structural phase transition occurs at 192 °C [14].

Our high temperature Raman scattering study on $(Ba_{0.32}Sr_{0.68})_2Nb_2O_7$ (BSN) ceramics revealed that the soft mode frequency related to the order parameter of this $Cmcm \rightarrow Cmc2_1$ high temperature ferroelectric phase transitions shows a non-classical behavior, and the critical exponent

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connected to the increase of the order parameters obtained as $\beta = 0.377$. From the relation of the soft mode frequency with temperature, it is also found that the ferroelectric phase transition temperature T_c decreases from 1342 to 1058 °C with Ba concentration ($x = 0.32$) [15]. In this paper, we report our Raman scattering study of the Ba effect to another two low temperature phase transitions.

2. Experimental

Raman scattering are excited using a diode-pumped solid-state laser at a wavelength of 532 nm and a power of about 100 mW. The light beam, passing through a narrow band pass filter, a half wavelength plate, and a polarizer, is focused onto a sample by lens. Scattered light from a sample is then collected by another lens using the backward scattering geometry, and analyzed by a triple-grating spectrometer of additive dispersion (Jobin Yvon T64000). The spectral resolution was about 2 cm^{-1}. The room temperature spectra were measured in the range of 7–1000 cm^{-1}. Low frequency spectra from −80 to 200 cm^{-1} were obtained at the wide temperature range from −190 to 600 °C. The sample was inserted into a cryostat cell (THMS600, Linkham), whose temperature stability was ±0.1 °C from −190 to 600 °C in temperature-dependent Raman measurements.

3. Results and discussion

Whole Raman spectra measured from 7 to 1000 cm^{-1} at room temperature are shown in Fig. 1. At room temperature 22 distinct bands have been observed. Factor group analysis of the high temperature ferroelectric phase of SN have been done by Buixaderas et al. [13]. However, they did not show the contribution of different ions to the lattice modes. In order to clarify this, we also did the factor group analysis using the structural data from the 3D X-ray diffraction [1], it gives 66 lattice modes at the centre of the Brillouin zone (Γ), with the atoms in the 4*a* and 8*b* Wickoff-sites, 19 of A_1 symmetry, 14 of A_2 symmetry, 14 of B_1 symmetry, and 19 of B_2 symmetry. The contribution of Sr and Nb ions to the lattice modes is $\Gamma_{Sr} = \Gamma_{Nb} = 4A_1 + 2A_2 + 2B_1 + 4B_2$, and from oxygen ions is $\Gamma_O = 11A_1 + 10A_2 + 10B_1 + 11B_2$. The total lattice modes are $\Gamma_{Sr_2Nb_2O_7} = 19A_1 + 14A_2 + 14B_1 + 19B_2$. The acoustic modes are $A_1 + B_1 + B_2$. The A_1, B_1 and B_2 modes are both Raman and infrared active, while A_2 mode is only Raman active.

In a low temperature phase, the decrease in structure symmetry produces more Raman active modes. Although the number of the Raman modes observed at room temperature in present study is less than the theoretical mode number, mode counting in the Raman spectra of ceramic samples is very difficult due to the possible overlapping and broadening of the bands. Bands formally allowed but too weak to observe. The lowest mode was observed at 24.8 cm^{-1}. The strongest and sharpest mode was observed at 60.7 cm^{-1}. Two shoulder peaks were observed at 43.1 and 52.4 cm^{-1}. As the temperature increases, the Raman modes become broad and intense up to measured temperature as shown in Fig. 2. However, some modes disappear completely at certain temperature, which corresponds to the new structural phase transition. For example, the lowest peak at 24.8 cm^{-1} at room temperature disappears above $T_r \sim 250$ °C. The mode at 52.4 cm^{-1} approaches to the mode at the 43.1 cm^{-1} in the spectra, an intensity transfer between the two modes occur. Then the peak at 43.1 cm^{-1} shows softening for increasing temperature. It is

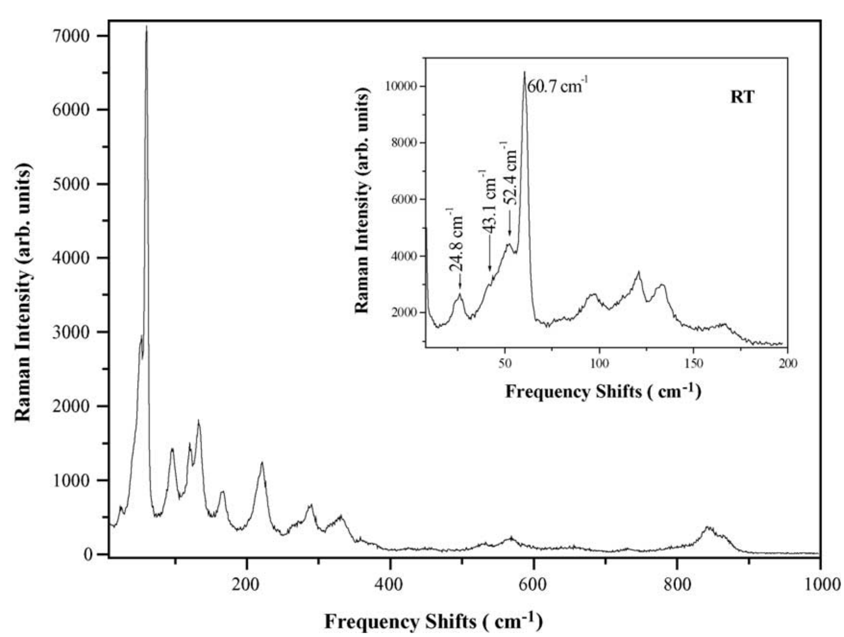

Fig. 1. Raman spectra of $(Ba_{0.32}Sr_{0.68})_2Nb_2O_7$ at room temperature from 7 to 1000 cm^{-1}. Inset: for 7–200 cm^{-1}.