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Raman spectroscopic study of ceramic $Sr_2Bi_4Ti_5O_{18}$*

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Raman spectra of ceramic $Sr_2Bi_4Ti_5O_{18}$ (SBTi5) are reported to consist of four different Raman bands. Temperature-dependent spectra reveal the relationship between the lattice vibration and the material's structure. There appears a relatively large change in structure of the material at about 273K. The anharmonic potential of the material has a great influence on its phonon mode full width at half maximum (FWHM), which can be expressed by a function of temperature. Theoretical fittings of the FWHMs for the two modes at around 312 cm^{-1} and 464 cm^{-1} indicate that the latter phonon mode is more anharmonic than the former one.

Keywords: Raman spectra, anharmonic potential, superposition, phonon mode
PACC: 7780, 7830

1. Introduction

Recently, there has been a growing interest in the study of the bismuth layer-structured ferroelectric materials. They have important applications in non-volatile random access memory owing to their good ferroelectric properties.[1−3] Their ceramic structures are also useful for piezoelectric sensors and pyroelectric materials, which have many advantages.[4−7]

Bismuth titanate, $Bi_4Ti_3O_{12}$ (BTO), the prototype of layer-structured ferroelectrics has a large spontaneous polarization, low switching field and high Curie temperature, which make it attractive in scientific research. But BTO bears high dielectric loss and poor fatigue properties.[8−10] Compared with BTO, $Sr_{n-3}Bi_4Ti_nO_{3n+3}$ ceramics and thin films with n=4, 5 and 6 have superior fatigue properties due to the fact that the additional Sr-Ti-O ferroelectric blocks are much more stable than the Bi-Ti-O ones.[11] The remnant polarization (P_r) of SBTi5 was reported to be at least twice larger than that of $Sr_{n-3}Bi_4Ti_nO_{3n+3}$ with n= 4 and 6.[11] So the investigation of SBTi5 will be very fascinating.

As a member of the Aurivillius phase family with the formula $[Bi_2O_2]$ $[A_{n-1}B_nO_{3n+1}]$,[12] SBTi5 (A=Sr, Bi, B=Ti and n=5) has a perovskite-like unit $[Sr_2Bi_2Ti_5O_{16}]^{2-}$ between two neighbouring $[Bi_2O_2]^{2+}$ layers along the c-axis in one unit cell. Raman scattering has been proved to be a valuable technique to study structures of ferroelectric materials. The interaction potential within SBTi5 should be anharmonic, which has the effect of temperature broadening of FWHMs for phonon modes.[13] Study of such an effect is needed and interesting, which may provide valuable information on the understanding of the interaction potential in materials. Meanwhile, the ferroelectric and dielectric properties of ceramic SBTi5 have been reported elsewhere.[8,14,15] But its Raman reports are few and mainly focus on the cases of high temperatures.[16] The authors have given a brief experimental Raman report on ceramic SBTi5.[17] In the present work, temperature-dependent Raman shifts and FWHMs for the different phonon modes at low temperatures are studied further; effects of both the anharmonic potential and orientational relaxation are also discussed. The FWHMs of the modes at around 312 cm^{-1} and 464 cm^{-1} are fitted from theory, showing that the latter mode is more anharmonic.

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2. Experiment

A ceramic sample of SBTi5 was obtained by using the conventional solid-state reaction method with TiO_2, $SrCO_3$, and Bi_2O_3 used as the precursor materials. Details of the preparation method were described elsewhere,[17] in which the Bi_2O_3 was 25% more than its stoichiometric requirement with the aim of compensating its loss during the process. By using a Rigaku x-ray diffractometer with nickel filtered Cu $K\alpha$ radiation, the x-ray diffraction measurements were performed to confirm the phase formation of SBTi5. The x-ray pattern is given in Fig.1, showing that the sample is polycrystalline. The Raman spectra of SBTi5 were measured on a Raman spectrometer (JY LabRam HR 800) in the backward scattering geometry configuration, by taking the 488 nm line of an Ar-ion laser as the excitation source. Temperature of the sample was controlled within 0.1 K (THMS600/HFS91).

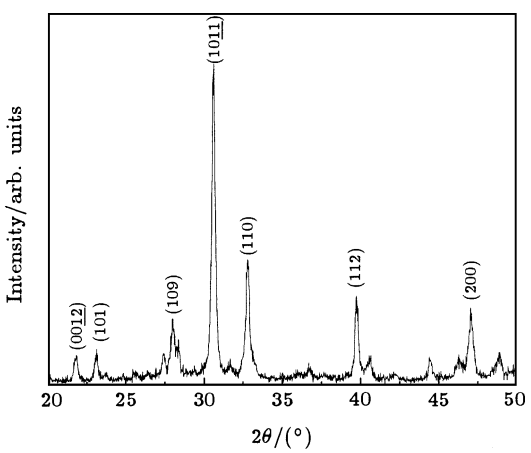


Fig.1. XRD pattern of ceramic SBTi5.

3. Results and discussion

Figure 2 shows that there is no obvious narrowing in Raman bands at temperatures of 80 K and 300 K. There is almost no additional phonon mode given out at a lower temperature, either, which is apparently different from the Raman spectra of ceramic BTO.[18,19] This originates from the difference between their microstructures. The numbers of the TiO_6 octahedral in one unit cell and of the ions at the A site in their perovskite-like structures are different. Compared with BTO, the two additional Sr-Ti-O blocks in one unit cell of SBTi5 increase the anisotropy in structure, which can also lead to the broadening of Raman bands.

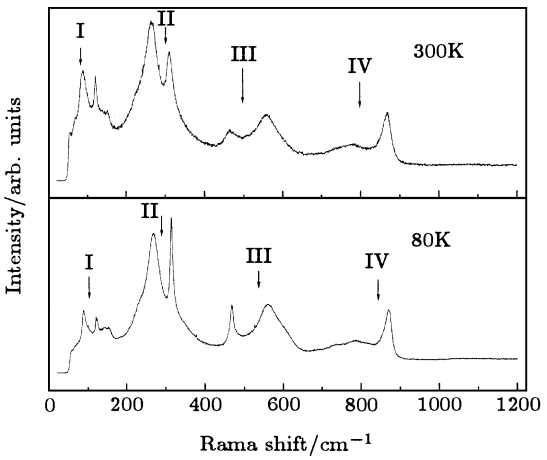


Fig.2. Raman spectra of ceramic SBTi5 at 80 K and 300 K.

The Raman spectra of SBTi5 can be clearly divided into 4 different Raman bands: I, II, III and IV as marked in Fig.2. Herein, Raman band I is related to two different Bi sites.[19,20] The modes below 105 cm^{-1} are correlated with those Bi^{3+} in the Bi_2O_2 rigid layers, while the modes between 105 and 180 cm^{-1} result from the movement of those Bi^{3+} in the perovskite-like units. We believe that Sr^{2+} at the A site also can make a contribution to this Raman band. The last Raman band IV corresponds to the O–Ti–O symmetric stretching, which can be assigned to be A_{1g} phonon mode. While Bands II and III are related to the different bending and rotating vibrations of the TiO_6 octahedral.[21] It is also noted from Fig.2 that these two bands are broad and enveloped, which can be seen as the superposition of series of Raman lines

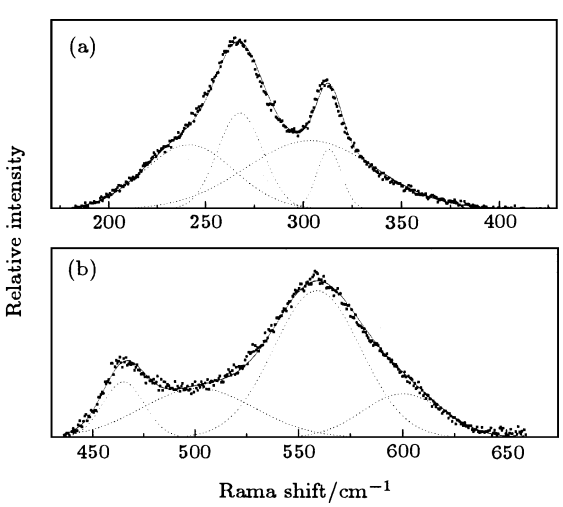


Fig.3. Raman spectra of ceramic SBTi5 showing the superposition of different Raman lines at 300 K. (a) and (b) are for Band II and band III respectively.

with Gaussian shape, a better approximation for ceramic SBTi5. After making Bose–Einstein correction to the original spectra, they have been deconvoluted into four different Raman lines, with varying Raman shift, FWHM and intensity, as shown in Figs.3(a) and (b). The temperature-dependent Raman shifts and FWHMs of these different phonon modes are presented in Figs.4 (a)–(d).

The four phonon modes P1, P2, P3 and P4 labelled in Figs.4(a) and (b) in the Raman band II correspond to the movement of the O-Ti-O bending and the inherent subtle tilting and rotating of the TiO_6 octahedral. Both the Raman shift and the FWHM of the mode P2 are almost independent of temperature, apparently showing the A_{1g} mode character. It is noticed that this mode has also been observed in the Nd doped BTO.[22] The assignment of this mode is different from that in Ref.[17]. However, it is believed that the present assignment after deconvolution of the original spectra is more appropriate. The other three modes P2, P3 and P4 have small fluctuations in FWHM, while their Raman shifts are almost unchanged when the temperature changes from 80 to 300K. It is also noticed that the FWHM of the mode P4 increases gradually with the temperature increasing; this mode is related to the O–Ti–O bending. Compared with the modes P2 and P4, the modes P1 and P3 have large FWHMs correlated with the inherent subtle tilting and rotating of the TiO_6 octahedral.[21]

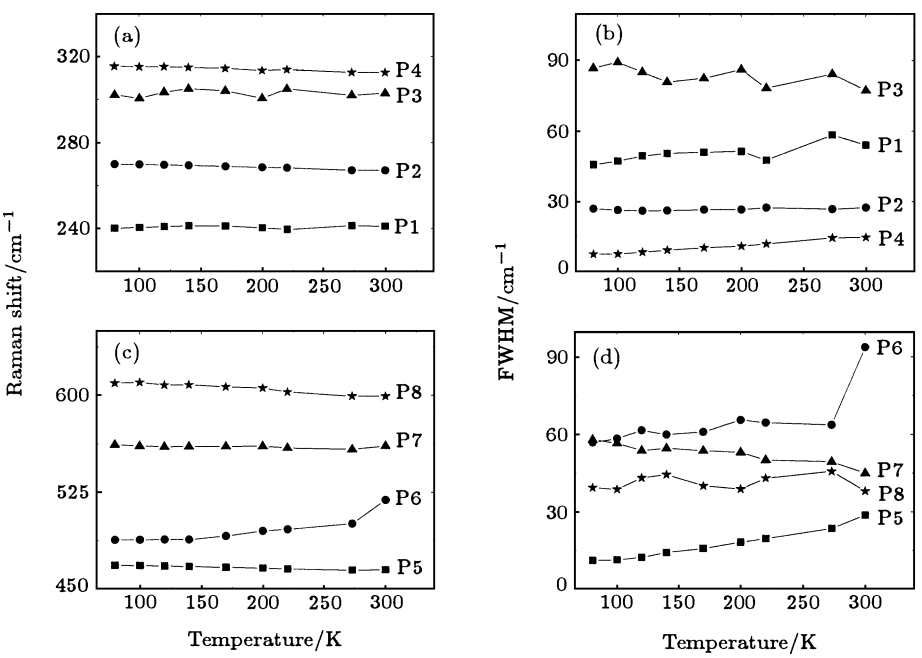


Fig.4. Temperature-dependent Raman shifts and FWHMs for different phonon modes in ceramic SBTi5. (a) and (b) are for Band II; (c) and (d) are for Band III. At 300K, the peak positions of the different phonon modes from P1 to P8 are at 241, 267, 302, 312, 464, 519, 561 and 599 cm^{-1}, respectively. The error bars in the figure are too small to be seen.

Figures 4(c) and (d) show that the Raman shifts of the modes P5, P7 and P8 are almost independent of temperature, while that of the mode P6 has a large change at 273 K. These four modes are correlated with torsions and rotations of the TiO_6 octahedral.[14,21] Compared with Raman band II, the FWHM of this band is obviously dependent on the temperature. The tendency to change the FWHM of the mode P5 is almost the same as that of the mode P4. The FWHMs of the other three modes P6, P7 and P8 change gradually with temperature until a large change takes place at a temperature of 273 K. This change indicates that there exists a structural change in the TiO_6 octahedral around this temperature, though it needs further studying. It is noted that a subtle phase transition has also been revealed in ceramic BTO below room temperature, of which compound belongs to Bi-layered perovskites and has odd Sr–Ti–O blocks as SBTi5.[18]

The above analysis shows that the FWHMs of the modes P4 and P5 have temperature-broadening character. This reflects the effect of anharmonic potential as well as the orientational relaxation effect on the Ra-

man spectra.[23] In SBTi5, the A site of the perovskite-like unit can be occupied by Sr^{2+} and/or Bi^{3+}; the position competition proceeds when the temperature changes. Meanwhile, the ions at the A site and B site tend to have displacements in the same direction within ferroelectric phase.[24] All these ion motions can contribute to the anharmonicity of the potential. Herein, the anharmonicity effect on the rigid layer modes at low frequencies can be ignored based on the rigid ion model. [25]So the anharmonic potential mainly affects those modes originating from the TiO_6 octahedral vibration. The modes P4 and P5 are selected as objects of our study in the present paper. Temperature broadening of FWHMs due to this effect can be expressed in a linear term approximately, which can reflect the degree of anharmonicity for phonon modes. As a fundamental quantity, the FWHM can also provide information on the orientational relaxation effect in materials.[23] In fact, those ion motions mentioned above can also make the orientation of the TiO_6 octahedral change whose manifestation in the Raman spectra just embodies the different vibration properties of phonon modes. The contribution of this effect to FWHM can be expressed by an exponential term appropriately. So the FWHM of phonon mode can be written as

$$\Gamma = a + bT + c\exp\left(-\frac{\hbar\bar{\omega}}{k_{\mathrm{B}}T}\right), \qquad (1)$$

where a, b, and c are the parameters to be fit, Γ is the FWHM, k_{B} is the Boltzmann constant, $\bar{\omega}$ is the mean value of the phonon frequency related to the mode concerned, and T is the absolute temperature in K. Herein, the term a reflects the harmonic vibration contribution, which can be determined from the FWHM measured at a very low temperature;[26] while the term bT corresponds to the anharmonic vibration contribution. After fitting Eq.(1) to FWHMs of the two modes P4 and P5, the results are shown in Figs.5(a) and (b), respectively. The obtained values of the three parameters a, b and c in Eq.(1) are $6.378\,\mathrm{cm}^{-1}$, $0.01190\,\mathrm{cm}^{-1}\mathrm{K}^{-1}$ and $20.87\,\mathrm{cm}^{-1}$, respectively for the mode P4, and $8.521\mathrm{cm}^{-1}$, $0.03074\,\mathrm{cm}^{-1}\mathrm{K}^{-1}$ and $89.08\,\mathrm{cm}^{-1}$, respectively for the mode P5. The goodness of the fitting is reasonable with the root mean squared error of the fitting is 0.3142 for the mode P4, and 0.7615 for the mode P5. By analysing the fitting results of the modes P4 and P5, it can be found that the contributions of anharmonicity and orientational terms, as well as the ratio of the exponential term to the overall FWHM all increase with the temperature increasing. This reflects the effect of the anharmonic thermal expansion of the lattice on phonon modes, as well the effect of orientational relaxation on the directional changing of the TiO_6 octahedral in SBTi5. It is also in accordance with the common knowledge that the role of the orientational effect becomes more dominant with the temperature increasing. The value of the parameter b for the mode P5 is about triple larger than that for the mode P4, which indicates that the mode P5 is more sensitive to the anharmonicity in material than the mode P4. This is closely correlated with the different vibration properties of the two modes, which are related to the bending and torsion of TiO_6 octahedral for the modes P4 and P5, respectively.

There still exists another model of fitting FWHM of phonon modes in literature,[27,28] in which the assumption has been pointed to be inappropriate (for further detail see Ref.[29]). And the associated fitting results are given in Figs.5(a) and (b), indicating that the theoretical results are in good agreement with our results. The analysis of this model fitting also can conclude that the mode P4 is less anharmonic than the mode P5, which indicates that our fitting results are reasonable from another aspect.

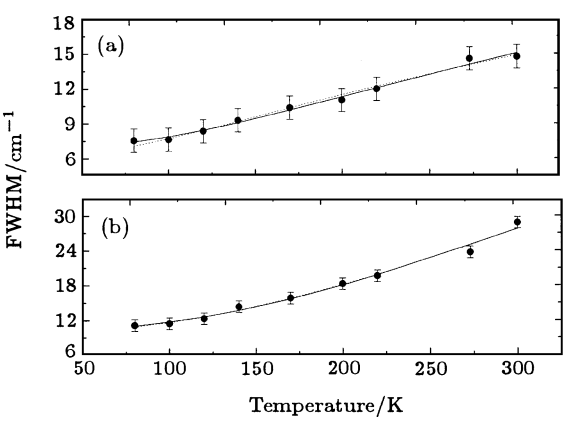


Fig.5. Theoretical fittings of FWHM as a function of temperature. (a) is for the mode P4 (around $312\,\mathrm{cm}^{-1}$); (b) is for the mode P5 (around $464\,\mathrm{cm}^{-1}$). Circled dots denote the experimental results. The solid and dotted lines represent the theoretical fittings of Eq.(1) and Ref.[26], respectively.

4. Conclusion

The broad and enveloped Raman spectra of ceramic SBTi5 can be seen as the superposition of series of Raman lines. The large change in Raman spectrum from 430 to $650\mathrm{cm}^{-1}$ reveals a structural change of the material at about 273 K. Theoretical fittings to

FWHMs provide information about the anharmonic potential as well as the orientational relaxation effect on phonon modes within SBTi5. It reveals that the mode at around 312 cm^{-1} is less anharmonic than that of the mode at around 464 cm^{-1}. The present work gives a new prospect of understanding properties of the material.

References

[1] Araujo C A Paz de, Cuchlaro J D, McMillan L D, Scott M C and Scott J F 1995 *Nature* (London) **374** 627

[2] Qiang F, Zhu J, Mao X Y and Chen X B 2005 *Acta Phys. Sin.* **54** 5422 (in Chinese)

[3] Song Z T, Ren W, Zhang L Y and Yao X 1998 *Chin. Phys.* **7** 292

[4] Schulman H S, Testorf M, Damjanovic D and Setter N 1996 *J. Am. Ceram. Soc.* **79** 3124

[5] Takenaka T and Sakata K 1984 *J. Appl. Phys.* **55** 1092

[6] Reaney I M and Damjanovic D 1996 *J. Appl. Phys.* **80** 4223

[7] James A R, Kumar G S, Suryanarayana S V and Bhimasankaram T 1996 *Ferroelectrics* **198** 91

[8] Srinivas K and James A R 1999 *J. Appl. Phys.* **86** 3885

[9] Joshi P C and Krupanidhi S B 1993 *Appl. Phys. Lett.* **62** 1928

[10] Park B H, Kang B S, Bu S D, Noh T W, Lee J and Jo W 1999 *Nature* (London) **401** 683

[11] Zhang S T, Yang B, Webb J F, Chen Y F, Liu Z G, Wang D S, Wang Y and Ming N B 2002 *J. Appl. Phys.* **92** 4599

[12] Graves P R, Hua G, Myhra S and Thompson J G 1995 *J. Solid State Chem.* **114** 112

[13] Dragoman D and Dragoman M 2002 *Optical Characterization of Solids* (Berlin: Springer)

[14] Lu W P, Mao X Y and Chen X B 2004 *J. Appl. Phys.* **95** 1973

[15] Zhu J, Lu W P, Mao X Y, Hui R and Chen X B 2003 *Jpn. J. Appl. Phys.* Part 1 **42** 5165

[16] Zou G T, Liu J J, Cui Q L and Yang H B 1994 *Phys. Lett.* A **189** 257

[17] Wang J, Cheng G X, Zhang S T, Cheng H W and Chen Y F 2004 *Physica* B **344** 368

[18] Idink H, Srikanth V, White W B and Subbarao E C 1994 *J. Appl. Phys.* **76** 1819

[19] Du Y Lei, Chen G and Zhang M S 2004 *Chin. Phys. Lett.* **21** 1819

[20] Jeon M K, Kim Y, Sohn J M and Woo S I 2004 *J. Phys. D: Appl. Phys.* **37** 2588

[21] Sugita N, Tokumitsu E, Osada M and Kakihana M 2003 *Jpn. J. Appl. Phys.* Part 2 **42** L944

[22] Melgarejo R E, Tomar M S, Bhaskar S, Dobal P S and Katiyar R S 2002 *Appl. Phys. Lett.* **81** 2611

[23] Carabatos-Nédelec C and Becker P 1997 *J. Raman Spectrosc.* **28** 663

[24] Phillpot S R and Gopalan V 2004 *Appl. Phys. Lett.* **84** 1916

[25] Born M and Huang K 1968 *Dynamical Theory of Crystal Lattice* (Oxford: Clarendon)

[26] Schwarz U T and Maier M 1997 *Phys. Rev.* B **55** 11041

[27] Sakurai T and Satõ T 1971 *Phys. Rev.* B **4** 583

[28] Ravindran T R, Arora A K and Mary T A 2003 *Phys. Rev.* B **67** 064301

[29] Menéndez J and Cardona M 1984 *Phys. Rev.* B **29** 2051