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Dielectric properties and structural defects in $BaTi_{1-x}Sn_xO_3$ ceramics

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Abstract. As a function of Sn doping concentration x, dielectric properties and X-ray diffraction measurements were carried out on $BaTi_{1-x}Sn_xO_3$ (BTS_x) ceramics fabricated by the solid-state reaction route. Positron annihilation lifetime spectroscopy and coincident Doppler-broadening spectroscopy were also measured for the evaluation of defects in the BTS_x ceramics. Dielectric properties measurement reveals that the permittivity of BTS_x ceramic gradually increases with increasing Sn dopant content for x≤3%, and then decreases. This change of permittivity is found to agree well with the relative defect concentration estimated using two positron annihilation techniques. The S-W plot indicates that the defect species do not change with Sn doping. The variation correlations between defects and dielectric properties further proves that BTS_x ceramics with the higher relative defect concentration present a lower permittivity.

1. Introduction

As one of the most important lead-free dielectric ceramics, barium titanate ($BaTiO_3$)-based ceramics have been attracting extensive interests for about 50 years, owing to their excellent dielectric properties and wide range of applications.[1-3] However, in order to meet the broad application in advanced electronics nowadays, the constant research of its structure defect and modification is in demand.[4] The $BaTiO_3$-based ceramics are of perovskite structures with an ABO_3 formula. Unique electric/dielectric properties of $BaTiO_3$-based materials can be carried out by varying the preparation conditions and by doping with various isovalent cations on both A (Ba) and B (Ti) sites.[5-6]

Recently, solid solution $BaTi_{1-x}Sn_xO_3$ (BTS_x) is attracting enormous attention due to the applications of capacitors, relaxors, sensor and the advantages of low internal stresses, low production costs and the possibility to design systems from lead-free materials.[7-8] Wei et al. reported the dielectric relaxation in paraelectric phase of $Ba(Ti,Sn)O_3$ ceramics.[9] Markovic et al reported BTS_x materials have high values of dielectric permittivity, which depends on the Sn content.[6] It is shown that the partial replacement of titanium by tin improve the dielectric behavior.[4] Besides, partial isovalent substitution of Ti^{4+} by Sn^{4+} leads to a shifting of the paraelectric–ferroelectric phase transition (Curie point, Tc) to lower temperatures.[6, 10] These researches mainly aimed at the influences of doping and preparation conditions on the dielectric properties. It is known that the properties of $BaTiO_3$-based ceramics might strongly depend on defects that exist in large concentrations.[11] The substitution of Ti^{4+} by Sn^{4+} ions in the BTS_x lattice might cause the lattice mismatch due to the different atomic radii. The research on the variation of structure defects and its influence on the dielectric properties induced by Sn dopants were necessary. Unfortunately, the microstructure defects doped with Sn content observation, to our knowledge, still required further investigation.

Positron annihilation spectroscopy (PAS), due to its sensitivity and selectivity to crystal defects, is well suited to the nondestructive study of structural defects in solid materials.[12-13] In recent years, a

lot of significant results have been achieved by applying positron annihilation techniques into ceramics defects studies.[14-15] In this work, the structural defects and dielectric properties in the BTS_x ceramics were studied. We tried to understand the relationship between the defect mechanisms and the dielectric properties with different Sn dopant content.

2. Experimental Procedures

All the BTS_x ceramic samples in this literature were provided by the group of the Meilei Zhao in Shandong University. BTS_x ceramics with x (Sn doping concentration) =0.00, 0.01, 0.03 and 0.05 were prepared by the conventional solid-state reaction route. The starting powder materials were $BaCO_3$ (99.9%), TiO_2 (99.9%) and SnO_2 (99.9%), which were of analytical grade and were weighed following the overall formula ($BaTi_{1-x}Sn_xO_3$) (x from 0 to 0.05). The starting powder materials were mixed and ball-milled with alcohol for 12 h, subsequently dried, sifted, and pressed into sheets and pre-sintered for 4 h in air at 1050 ^{0}C. Then the sheets were again reground for 12 h, dried, sifted and pressed into sheets of φ13mm×2mm with the addition of a little organic adhesive; finally the sheets were sintered for 2 h in air at 1240 ^{0}C and used for measurements.

The structure and composition of the samples were characterized by X-ray diffraction (XRD) technique using X' PERT PRO diffractometer. The dielectric constants at room temperature were determined at 1 kHz, 10 kHz and 1 MHz using an Agilent 4292A precision impedance analyzer with the environmental temperature was 300 K.

The positron annihilation spectroscopy (PAS) measurements were performed at room temperature. Two PAS techniques were carried out for the evaluation of defects in the BTS_x ceramics. The positron lifetime spectra (PLS) were measured using a conventional ORTEC fast-slow coincidence system with a resolution of 185 ps. A 20 μCi ^{22}Na positron source was sandwiched between two pieces of identical samples. Each spectrum contains total counts of 2×10^6. In order to obtain more information about defects, the coincident Doppler-broadening spectroscopy (CDBS) measurements were undertaken using two HPGe Detectors. Each spectrum was collected with a total count over 8×10^6.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the BTS_x ceramic samples with x=0.00, 0.01, 0.03 and 0.05, respectively. The structural analysis mainly indicates that the samples consist of single perovskite phase without any other impurity phases. The diffraction patterns of $BTS_{0.00}$ (Pure $BaTiO_3$) ceramic sample shows that the peak nearby 2θ=45° splits into (002) and (200) reflections, however, a single (111) peak at 2θ=39°, which are characteristic to $BaTiO_3$ tetragonal phase. Compared with the $BTS_{0.00}$ ceramic sample, the diffraction patterns of BTS_x ceramic samples with x=0.01, 0.03 and 0.05 shows that the (002)/(200) double peak of each sample still remains but is not obvious. This suggests that a low content of cubic phase is interfused accompanying the Sn doping. Besides, it can be observed from XRD patterns that increasing of Sn content causes slightly systematic shift of peaks towards lower 2θ angles. This shift is because that the substitution of Ti^{4+} (0.068 nm) by Sn^{4+} (0.071 nm) ions increases the unit cell volume.

A detailed study of the microstructural defects in the BTS_x ceramics was performed by positron annihilation lifetime measurements. Each lifetime spectrum was fitted by LIFETIME9 program with three-component fitting procedure. The longest lifetime τ_3 and its intensity I_3 were around 2.4 ns and below 1.2% respectively, without significant variation for all compositions. This component is attributed to the ortho-positronium (o-Ps) annihilation in the source or at the surfaces among the grains in the ceramics and is neglected in the following discussion. The shortest lifetime component τ_1 is around 140-150 ps, while the second lifetime τ_2 has a value between 206-248 ps. τ_1 might be attributed to the average value of free positron lifetime and the lifetime in smaller cation vacancies like V_O. τ_2 can be regarded as the weighted average lifetime of the positron in the mono-vacancies (like V_{Ba}, V_{Ti})[16].

Average lifetime $\tau_m=(\tau_1 I_1+\tau_2 I_2)/(I_1+I_2)$ could synthetically reflect the material microstructure. It is because that the value of τ_m could present an overall reflection on the defect traps in crystal lattice of materials. Therefore, it could provide the details of the electronic structure and defect distribution in the materials. The variation of average positron lifetime τ_m as a function of the x for BTS_x is presented in figure 2. It is seen that the average lifetime τ_m gradually decreases with the increase of x up to 3%. While the x exceeds 3%, the average lifetime τ_m begins to increase. This indicates that doping small

amount of Sn content could reduce the defects of $BaTiO_3$. However, the structure defects in the BTS_x increased when the Sn doping concentration exceeds 3%.

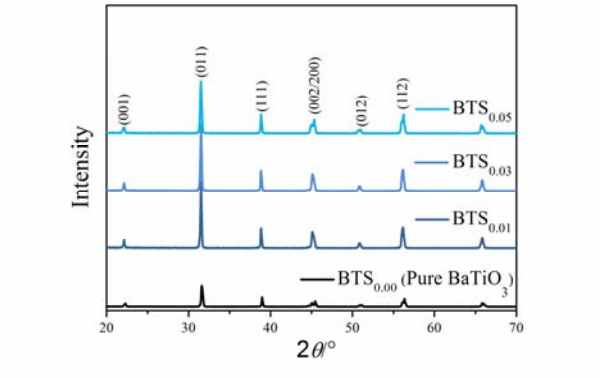

Figure 1. X-ray diffraction patterns of BTS_x ceramics

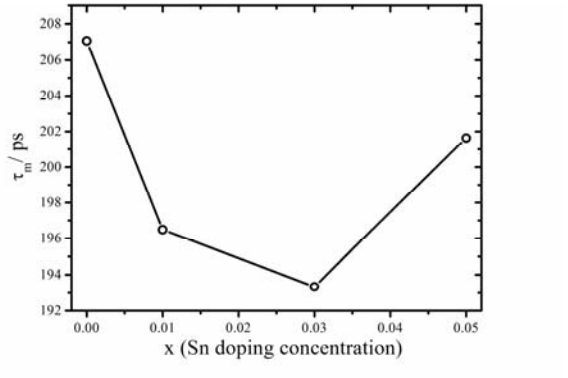

Figure 2. Average lifetime as a function of the x for BTS_x ceramics

In order to obtain more information about structural defects, we carried out CDBS measurements in BTS_x ceramics samples. The S-parameter as a function of the x is shown in figure 3. It is clear from figure 3 that the S-parameter drops with increasing Sn doping concentration when the x is below 3%. For samples with Sn doping concentration of exceeding 3%, the S-parameter increases slowly. The variation of S-parameter with x gives a preliminary idea of the changing defective state of the samples. The coincident Doppler-broadening is characterized by the S- and W-parameter. The S-parameter reflects the annihilation probability of positrons with the low-momentum valence electrons. Therefore, it suggests that the main origin of a decrease in S-parameter is due to a decrease in the relative concentrations of defects in the material. Therefore, the same conclusion about the defects evolution can be obtained in both PLS measurement and CDBS measurement.

Positron annihilation correlation plots of the S-parameter and its complementary W-parameter are found to be useful in distinguishing various defect species or the chemical surrounding of the defects. It can be seen in figure 4, the data points fall on a straight line, suggesting that the defect species do not change with Sn doping.

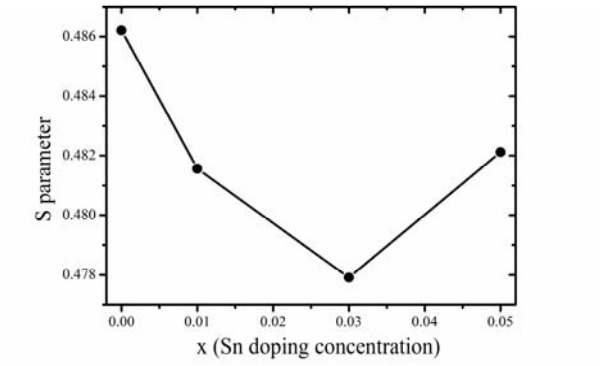

Figure 3. The S-parameter as a function of the x for BTS_x ceramics

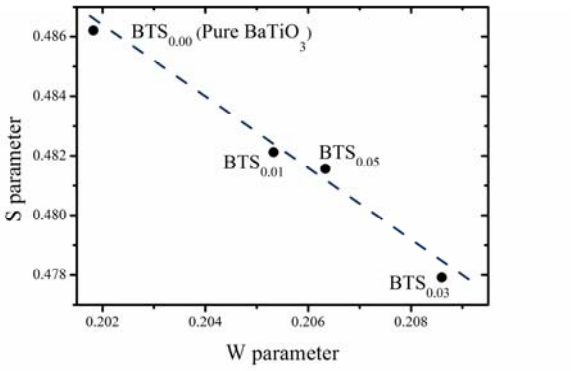

Figure 4. The variation of S- versus W-parameter for BTS_x ceramics

The variations of relative permittivity of BTS_x ceramic samples with Sn doping concentration x, at various frequencies (1 kHz, 10 kHz and 1 MHz.) are shown in figure 5. The permittivity of the sample decreases with the increasing frequency. The variation of the permittivity with the corresponding frequency can be qualitatively explained by the Debye's theory. At every frequency, the permittivity of BTS_x ceramic samples gradually increases to about 4000 with Sn doping concentration (when Sn doping concentration is below 0.03). With more Sn doped (x>0.03), the permittivity of BTS_x ceramics decreases. Compared figure 5 with figure 2 and figure 3, it can be discovered that BTS_x ceramic samples with the higher relative defect concentration present a lower permittivity.

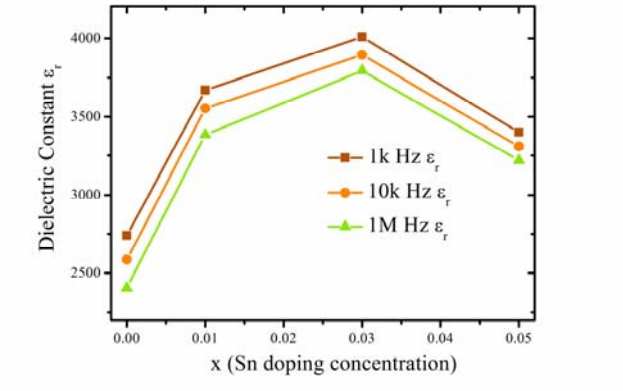

Figure 5. Permittivity for BTS_x ceramic versus x at various frequencies

4. Conclusion

In summary, a detailed study of the variation of the X-ray diffraction, dielectric constant and positron annihilation spectra have been carried out on BTS_x ceramics for x from 0.00 to 0.05 fabricated by the conventional solid-state reaction route. The following conclusions have been observed:

(1) A low content of cubic phase is interfused into $BaTiO_3$ tetragonal phase accompanying the Sn doping. Besides, increasing Sn content causes slightly systematic shift of peaks towards lower 2θ angles. This shift is because that the substitution of Ti^{4+} (0.068 nm) by Sn^{4+} (0.071 nm) ions increases the unit cell volume.

(2) The permittivity of BTS_x ceramics in the same x decreases with increasing frequency. However, at each measuring frequency, the permittivity of BTS_x ceramic gradually increases with Sn dopant content for x≤3% and decreases after it.

(3) The results of the positron annihilation lifetime spectroscopy and coincident Doppler-broadening spectroscopy agree well with the variation of the dielectric property. The S-W plot indicates that the defect species do not change with Sn doping. The variation correlations between defects and dielectric properties further proves that BTS_x ceramic with the higher relative defect concentration present a lower permittivity.

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