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## A positron annihilation study of SrTiO<sub>3</sub>-based ceramics

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**Abstract.** The dielectric properties and positron annihilation spectra of the SrTiO<sub>3</sub> ceramics doped with the trivalent elements La and Bi were measured. The results show that the dielectric properties are strongly correlated to the defect structure, which is dependent on the kind of doping element and its content. The study of positron annihilation lifetime spectra provides direct evidence for defect structures in the trivalent-element-doped SrTiO<sub>3</sub> ceramics. The correlation between the dielectric properties and the defect structure was further described by means of the complex-defect model.

### 1. Introduction

Perovskite-structure oxide ceramics have received further considerable attention especially after the discovery of high-temperature superconductivity. Various methods have been adopted to study the structure and the defects, as well as their influence on the relevant physical properties [1, 2] of oxide ceramics. Perovskite-structure strontium titanate (SrTiO<sub>3</sub>) exhibits superconductivity [3], semiconductivity [4] and various phase transitions [5]. In particular, trivalent-element-doped SrTiO<sub>3</sub> ceramics show excellent dielectric properties for practical use and an interesting dielectric relaxation behaviour with significant increased permittivity [6]. However, the defect structure of doped SrTiO<sub>3</sub> ceramics has been rarely investigated.

Recently the positron annihilation technique has been developed so that it is an efficient probe of the defect structure and electronic structure in solids [7]. Positron annihilation has now been used to characterize the DL2 defect in GaAs [8], as well as the oxygen vacancies in high-temperature superconducting ceramics [9]. In the present paper, the positron annihilation technique is adopted to study the defect structure and its influence on the dielectric properties in La- and Bi-doped SrTiO<sub>3</sub> ceramics.

### 2. Experiments

The samples were prepared by means of solid state reaction. Their nominal compositions are firstly (Sr<sub>1-x</sub>La<sub>x</sub>)TiO<sub>3</sub>, where  $x = 0, 0.0005, 0.001, 0.002, 0.01, 0.02$  or  $0.06$  and secondly (Sr<sub>1-y</sub>Bi<sub>(2/3)y</sub>)TiO<sub>3</sub>, where  $y = 0, 0.06, 0.11, 0.16, 0.21, 0.25, 0.29, 0.33$  or  $0.36$ . The dielectric parameters were measured at 25 °C and 1 MHz using an HP4275A LCR meter. X-ray diffraction using Cu K $\alpha$  radiation was carried out on samples to determine the crystallographic structure.

The positron annihilation lifetime spectra of samples were measured. A 10  $\mu\text{Ci}$   $^{22}\text{Na}$  positron source was sandwiched between two pieces of identical samples. The lifetime spectra were analysed for three components using a standard computer program POSITRONFIT EXTENDED [10]. Each spectrum contains total counts of one million events.

### 3. Results and discussion

#### 3.1. Dielectric properties and defect structure

**3.1.1. Resistivity.** In the La- and Bi-doped  $\text{SrTiO}_3$  ceramics used in the present work, only a single cubic perovskite structure of solid solutions was observed for all samples by x-ray diffraction patterns. This indicated that the low-content La and Bi ion can substitute for Sr sites separately as a solid solution because of the similarity of the ionic radii and electronegativities of La, Bi and Sr. The trivalent elements La or Bi located at Sr sites carry excess positive charges which, for maintenance of electric neutrality, can be compensated in two different ways: on the one hand by the formation of electrons, whose concentration will then be equal to the concentration of the incorporated donor ions (electron compensation) and on the other hand by strontium vacancies to compensate the excess electrons (vacancy compensation). They are illustrated as follows:

$$D_{\text{Sr}} = D'_{\text{Sr}} + e' \quad \text{electron compensation} \quad (1)$$

$$2D_{\text{Sr}} = 2D'_{\text{Sr}} + V''_{\text{Sr}} \quad \text{vacancy compensation} \quad (2)$$

where  $D_{\text{Sr}}$  represents a donor occupying an Sr site, and  $V_{\text{Sr}}$  represents a strontium vacancy. At room temperature, electron compensation will lead to semiconductive or conductive ceramics, whereas vacancy compensation is likely to lead to an insulator. This semiconducting theory of the ceramics explains the donor-doped  $\text{BaTiO}_3$  system ceramics very well [11].

Figure 1 shows the curve of the electrical resistivity of  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples as a function of La content  $x$ . The resistivity of the La-doped samples decreased for  $x \leq 0.001$  and increased significantly for  $x > 0.001$ . This curve shows a similar U-type curve to that in the La-doped  $\text{BaTiO}_3$  system ceramics [12]. However, the reduced resistivity for La-doped  $\text{SrTiO}_3$  ceramics is relatively high compared with that for La-doped  $\text{BaTiO}_3$  semiconducting ceramics [12], i.e. the concentration of electrons ionized by La is very small in the  $\text{SrTiO}_3$  system as derived from the resistivity. Thus it is reasonable to assume that the incorporated lanthanum ions are compensated by both electrons and vacancies, i.e. equations (1) and (2) coexist at low dopant concentrations in the La-doped  $\text{SrTiO}_3$  ceramics, which is the case of mixed compensation of electrons and vacancies; this is the reason why the semiconductive  $\text{SrTiO}_3$  ceramics with a low resistivity cannot be obtained only by donor doping. For higher donor concentrations ( $x \geq 0.02$ ), the resistivity is independent of the dopants. So the vacancies are the predominant defect and may progressively increase with increasing La content while the electrons produced by the donors can be neglected.

In summary, two kinds of defect (weakly bonding electrons and vacancies) may explain the resistivity curve for the  $\text{SrTiO}_3$  system ceramics based on the semiconducting theory of the ceramics.

**3.1.2. Dielectric properties.** The curves of relative permittivity  $\epsilon$  and dielectric dissipation factor  $\tan \delta$  versus lanthanum content for  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples are

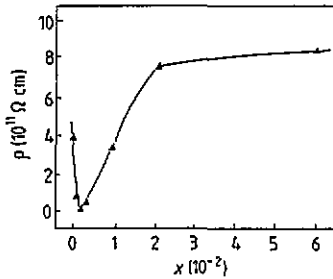


Figure 1. Resistivity  $\rho$  as a function of  $x$  for  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples.

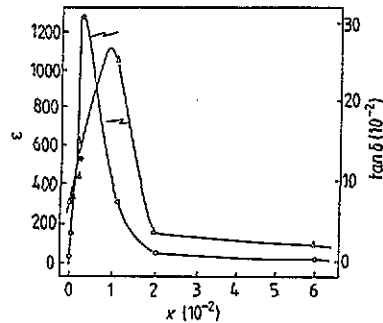


Figure 2. Relative permittivity  $\epsilon$  and dissipation factor  $\tan \delta$  as functions of  $x$  for  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples.

given in figure 2. For  $0.0005 \leq x \leq 0.01$ ,  $\epsilon$  and  $\tan \delta$  reach maximum values at  $x = 0.01$  and  $x = 0.001$ , respectively. According to the above discussion on the resistivity in the mixed-compensation region, electrons and vacancies coexist. It is reported that the barium (strontium) vacancies were originally formed at the grain boundary and diffused to the grain centre in  $\text{BaTiO}_3$  ( $\text{SrTiO}_3$ ) ceramics [13]. The electrons and strontium vacancies are inhomogeneously distributed in the grains and grain boundaries from the viewpoint of the ceramic microstructure. Thus, two kinds of conducting phase occur: one is mainly compensated by electrons and the other is mainly compensated by vacancies, and this results in space-charge polarization which contributes to the dielectric constant. Dielectric relaxation behaviour is observed in a frequency range of  $10^5$ – $10^7$  Hz [14]. For  $0 < x \leq 0.001$ , the higher the content  $x$ , the higher is the electron concentration, and the higher is the dissipation factor caused by the enhanced electrical conduction. The maximum value of  $\tan \delta$  occurred at  $x = 0.001$  corresponding to the minimum resistivity in figure 1. As the lanthanum content increases further, the proportion of vacancy compensation is increased and the space-charge polarization increases; therefore,  $\epsilon$  still increases when  $x$  exceeds 0.001 and shows a maximum value at  $x = 0.01$  as shown in figure 2. The increased permittivity and dissipation factor for  $x < 0.01$  are attributed to the space-charge polarization caused by the inhomogeneous distribution of electrons and vacancies. For  $0.02 \leq x \leq 0.06$ , the vacancy compensation mechanism is dominant. The quasi-free electrons can be neglected and the strontium vacancies are homogeneously distributed. The space-charge polarization is eliminated. So both  $\epsilon$  and  $\tan \delta$  are reduced compared with the corresponding values in the region  $0.0005 \leq x \leq 0.01$ .

The composition dependence of the relative permittivity  $\epsilon$  and dissipation factor  $\tan \delta$  of the  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  system is shown in figure 3. For  $y = 0.06$ , both  $\epsilon$  and  $\tan \delta$  are greater than the corresponding values for pure  $\text{SrTiO}_3$ ; there was an obvious dielectric relaxation at a low frequency (about  $10^5$  Hz) [15]. This is in accordance with the case of La-doped  $\text{SrTiO}_3$  discussed above. For  $0.11 \leq y \leq 0.36$ , a maximum in  $\epsilon$  was observed, but  $\tan \delta$  is very small;  $\epsilon$  and  $\tan \delta$  are approximately independent of frequency from  $10^2$  to  $10^7$  Hz and the relaxation peak may occur at about  $10^8$  Hz [6], which is different from the dielectric polarization and relaxation properties of the La-doped  $\text{SrTiO}_3$  system for high lanthanum contents. These high-quality dielectric properties in the  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  samples for  $0.11 \leq y \leq 0.36$ , which was not observed in the La-doped  $\text{SrTiO}_3$  samples, may be attributed to the influence of the different defect structure of the highly Bi-doped  $\text{SrTiO}_3$  samples.

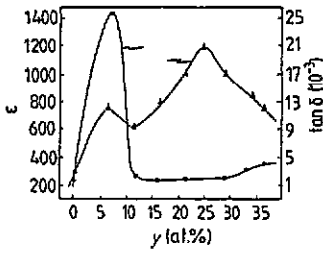


Figure 3. Relative permittivity  $\epsilon$  and dissipation factor  $\tan \delta$  as functions of  $y$  for  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  samples.

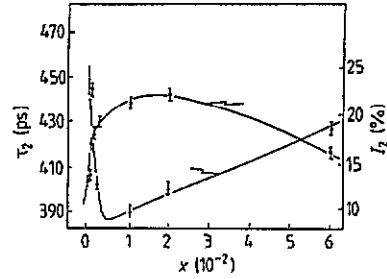


Figure 4. Positron annihilation lifetime  $\tau_2$  in the defect state and its intensity  $I_2$  as functions of  $x$  for  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples.

The above discussion on figures 2 and 3 shows that the dielectric properties are correlated to the different kinds of dopant (La and Bi) as well as their concentrations, which may correspond to different kinds of defect and their concentrations.

### 3.2. A positron annihilation study of defect structure

Three positron lifetime components were resolved from all the lifetime spectra obtained. It is well known that the intermediate-lived component  $\tau_2$  is assigned to the positron annihilated in the defect state and  $I_2$  is its intensity. So the following discussion is mainly concerned with this lifetime component.

**3.2.1. La-doped  $\text{SrTiO}_3$  system.** In  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples,  $\tau_2$  exhibits a minimum value at about  $x = 0.005$ , and  $I_2$  shows a maximum near  $x = 0.02$ , as shown in figure 4. The bulk lifetime  $\tau_b$  was found from the values of the lifetime and the intensity of the first two components by the equation

$$\tau_b^{-1} = (I_1/\tau_1 + I_2/\tau_2)/(I_1 + I_2). \quad (3)$$

The calculated values of  $\tau_b$  are plotted in figure 5. It is known that  $\tau_b$  is associated with the bulk characteristics of the materials. The rapid decrease in  $\tau_b$  means an increase in the electronic density of the materials for low La contents  $x$ ; the increase in  $\tau_b$  means a decrease in the number of electrons and an increase in the number of vacancies with increasing  $x$ . For  $0.002 < x < 0.01$ , there is a valley in the curve of  $\tau_b$  versus  $x$  (figure 5); this is a competitive result of the two compensation mechanisms. The  $\tau_2$  versus  $x$  curve shows a similar variation in the low-La content region. It is reasonable to assume that  $V_{\text{Sr}}$  begins to appear obviously for  $x > 0.005$ , where the minimum values of  $\tau_b$  and  $\tau_2$  occur. For  $x > 0.005$ , the intensity  $I_2$  still increases and its maximum occurs at  $x = 0.02$ ; this implies that the defect concentration is constantly increasing in this region of  $x$ . For  $0.02 < x < 0.06$ ,  $\tau_b$  reaches a saturation value, which indicates that the electron concentration decreases to a constant value and the predominant defect is vacancies. The vacancies may pair with each other to form double vacancies, which will lead to an increase in the positron lifetime component  $\tau_2$  because the Sr ion cores are missing and the density of electrons at this site is reduced, and will also lead to a decrease in the positron annihilation density  $I_2$ .

**3.2.2. Bi-doped  $\text{SrTiO}_3$  system.** The positron annihilation lifetime  $\tau_2$  and its intensity  $I_2$  in  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  samples are shown in figure 6. It can be seen that, for  $y \leq 0.06$ ,  $\tau_2 = 450$  ps, and then there is a sharp drop in the range  $0.06 \leq y \leq 0.11$

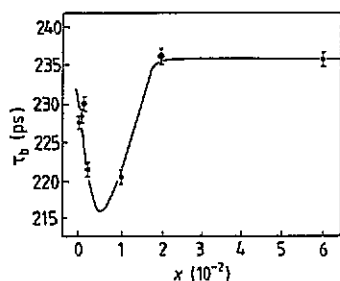


Figure 5. Curve of bulk lifetime  $\tau_b$  versus La content  $x$  for  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples.

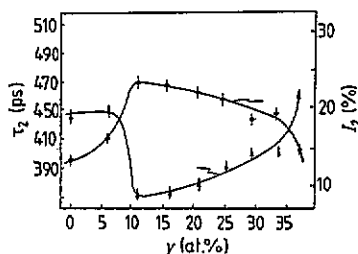


Figure 6. Positron annihilation lifetime  $\tau_2$  in the defect state and its intensity  $I_2$  as functions of  $y$  for  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  samples.

in the curve of  $\tau_2$  versus Bi content  $y$ . For  $0.11 < y \leq 0.36$ , a linear increase in  $\tau_2$  and a decrease in  $I_2$  occurs as the bismuth content is increased.

The discussion in section 3.1 indicated that the dielectric properties of the solid solutions are closely related to the kinds of dopant and their contents and may be attributed to the different defect structures caused by the dopants. The above results on the positron annihilation spectra provide further information about the defect structure.

In the low-bismuth-content range,  $\tau_2 = 450$  ps which indicates the existence of divacancies or vacancy clusters.

For  $y \geq 0.06$ , the vacancy compensation mechanism in equation (2) is predominant as in the case of  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  samples. As the Bi content increases, the number of Sr-site vacancies increases, and the concentrations of the defects  $\text{Bi}_{\text{Sr}}$  and  $\text{V}_{\text{Sr}}$  may become high (estimated to be  $10^{21}$ – $10^{22}$   $\text{cm}^{-3}$ ), so that the defects pair with each other as follows:



We call these pairs complex defects. The lifetime of the positron annihilated in the complex defect  $[\text{Bi}_{\text{Sr}}\text{V}_{\text{Sr}}]$  is shorter than that of the Sr-site divacancy or Sr-site vacancy cluster because of the increase in the local electronic density which is due to the core electrons of Bi atoms. So the occurrence of the complex defect  $[\text{Bi}_{\text{Sr}}\text{V}_{\text{Sr}}]$  results in a sharp drop in  $\tau_2$  for  $0.06 \leq x \leq 0.11$ . Generally, the intensity of the positron lifetime component corresponds to the defect concentration to some extent; the concentration of the defect is increased in this region. So the intensity  $I_2$  is increased as the bismuth content increases for  $0.06 \leq x \leq 0.11$  as shown in figure 6.

When the bismuth content increases further, for  $x > 0.11$ , the concentration of the complex defect  $[\text{Bi}_{\text{Sr}}\text{V}_{\text{Sr}}]$  increases. Further pairing of the complex defect  $[\text{Bi}_{\text{Sr}}\text{V}_{\text{Sr}}]$  may occur; its form can be described as  $[\text{Bi}_{\text{Sr}}\text{V}_{\text{Sr}}]_n$  (here  $n \geq 2$ ). The pairing of the complex defect will make the lifetime of the positron annihilated in  $[\text{Bi}_{\text{Sr}}\text{V}_{\text{Sr}}]_n$  longer; so the positron lifetime component  $\tau_2$  in the  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  samples increases with increasing  $y$  in the range  $0.11 \leq y \leq 0.36$ . As the concentration of the complex defect and the pair of the complex defect is enhanced, the concentration of free strontium vacancies is decreased quickly because of defect accumulation. Consequently, the total defect concentration is decreased, and correspondingly the intensity  $I_2$  is decreased.

Because of the perovskite structure of  $\text{SrTiO}_3$ , the occurrence of the complex defect causes distortion of the oxygen octahedron, makes the internal field stronger and produces more than one 'non-central' site for the weakly binding Ti ions. This

kind of Ti ion is easy to be activated by thermal motion so that it moves over the small potential barrier and provides a high permittivity and low dissipation factor in a frequency range from  $10^2$  to  $10^7$  Hz [15]. This agrees with the hypothesis and the calculation of Skanavi *et al* [6] for which the activation energy is low (0.2–0.3 eV) and the relaxation time is about  $10^{-8}$  s at room temperature. The high  $\epsilon$  and low  $\tan \delta$  for Bi-doped  $\text{SrTiO}_3$  samples are mainly attributed to the occurrence of complex defects  $[\text{V}_{\text{Sr}}\text{Bi}_{\text{Sr}}]_n$ ; this has a different influence on the dielectric properties which are superior to those of La-doped  $\text{SrTiO}_3$  samples.

The positron annihilation lifetime spectra provide evidence of the pairing of the complex defect and confirm that its concentration increases and the concentration of free defects decreases with increasing bismuth content  $y$  from 0.11 to 0.36 in  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  ceramics.

#### 4. Conclusion

The dielectric properties and polarization mechanism of La- and Bi-doped  $\text{SrTiO}_3$  dielectric ceramics are closely related to the defect structure which depends on the kind of dopant and the dopant content. In the region of different La or Bi contents, the dielectric properties are quite different; this was attributed to different defect structures. The positron annihilation spectra give information about the defect structures in La- and Bi-doped  $\text{SrTiO}_3$  ceramics. They indicate that the concentration of strontium vacancies begins to increase when the dopant content exceeds about 0.005 in  $(\text{Sr}_{1-x}\text{La}_x)\text{TiO}_3$  ceramics and that the complex defect is formed in Bi-doped  $\text{SrTiO}_3$  ceramics. The picture of 'hopping-ion' relaxation polarization given by Skanavi *et al* was further described by the structure of the complex defect, which is favourable for the excellent dielectric properties observed for  $(\text{Sr}_{1-y}\text{Bi}_{(2/3)y})\text{TiO}_3$  ceramics.

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