Nonmonotonic dependence of the positron lifetimes on the dopant content in La-doped BaTiO$_3$

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The positron-lifetime spectra and the resistivity in La-doped BaTiO$_3$ have been measured at room temperature for La content of 0–0.8 at. %. It was found from the experiments that with increasing La content, the variation of both the positron-lifetime parameters and the resistivity are nonmonotonic. The nonmonotonic dependence of positron-lifetime parameters on the La content is explained by an associated-defect model, in which a small critical region of La content is proposed. With an increase of La content Ba vacancies induced by La doping appear mainly in isolated form below the critical region, while above the critical region the associated defect $(2La_{Ba}^{\cdot}V_{Ba}'')$ forms quickly. The associated defect may have no ability to trap positrons.

I. INTRODUCTION

Since the positive temperature coefficient of resistivity (PTCR) in donor-doped barium titanate was discovered[1] this material has been studied extensively. It is well known that (a) the resistivity of donor-doped BaTiO$_3$ ceramics at room temperature exhibits a nonmonotonic variation with increasing dopant content, and there is a smaller range of dopant content (generally below about 0.5 at. %) in which BaTiO$_3$ ceramics exhibit n-type semiconduction; (b) the PTCR effect occurs only in donor-doped n-type semiconducting BaTiO$_3$ ceramics, and does not appear in BaTiO$_3$ single crystals and undoped BaTiO$_3$ ceramics; and (c) the PTCR effect is linked directly to the ferroelectric-paraelectric phase transition. These facts have shown that doping, grain boundaries, and spontaneous polarization play important roles in the conduction mechanism and the PTCR effect. In order to understand these properties, a large number of investigations have been performed by means of electrical property measurements,[2–13] thermogravimetric analysis,[14] electron microscopy,[15] internal friction,[16] and electron paramagnetic resonance.[17] From these studies some models have been proposed; among them the model suggested by Heywang[2,3] and developed by Jonker[4] and Daniels *et al.*[6] is the most satisfactory. However, there are still some subjects needing further investigation; for example, the importance of intrinsic disorder, nonstoichiometry, charge trapping, compensation of dopant, configuration of defects, and interactions between dopant and defect or between defects. We note that direct microscopic experimental observation for the configuration and distribution of defects and the electrical structure of grain boundaries in BaTiO$_3$ ceramics is still lacking.

The positron annihilation technique (PAT) has been proved to be a useful tool for studying lattice defects and microstructure in metals and alloys.[18] Perhaps due to the complexity of ceramics there were few positron annihilation studies in ceramics until recently. A few years ago the discoveries of high-temperature superconductivity in perovskitelike ceramics prompted not only a resurgence of research activity in the superconducting field, but also the application of PAT in high-temperature superconductors[19,20] and other ceramics.[21,22] These studies have shown that positron annihilation is also sensitive to vacancy-type defects and variations of microstructure in ceramics.

In the present work we have performed a positron-lifetime study in La-doped BaTiO$_3$ ceramics. In the study, a low dopant content (< 1 at. %) was used, and the samples exhibited a nonmonotonic dependence of resistivity on dopant content and evident semiconducting behavior. Our aim is to investigate defects and their variations in the BaTiO$_3$ ceramics due to doping by analyzing variations of positron-lifetime parameters. In this paper, the experimental results are reported and discussed.

II. EXPERIMENTAL

The BaTiO$_3$ ceramic samples were prepared in accordance with the conventional solid-state synthesis technique. The starting powder materials were BaCO$_3$, TiO$_2$, and La$_2$O$_3$, which were weighed following the overall formula $(Ba_{1-x}La_x)TiO_3$ (x from 0 to 0.8 at. %). To improve sintering, all samples were given an excess of 1 at. % titania. The starting powder materials were mixed with agate milling balls for 48 h in rolling PVC bottles, and after drying and sifting the mixed powders were presintered for 2 h in air at 1150 °C. Then the sintered mixtures were again reground for 48 h, dried, sifted, and pressed into sheets of ϕ25 mm $\times$ 3 mm; finally the sheets were sintered for 4 h in air at 1350 °C and used for measurements.

The resistance of the samples at room temperature was measured. The average size of the grains was observed by scanning electron microscopy. The positron-lifetime spectra in the samples were measured at room temperature by using a fast-fast coincidence spectrometer with a resolution of 260 ps. About 10-μCi ^{22}NaCl source was used. Each spectrum contains total counts of 1×10^6. The lifetime spectra were analyzed with three components by using the program POSITRONFIT-EXTENDED.

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The average positron lifetime τ in each sample is found from

$$\tau = (I_1\tau_1 + I_2\tau_2)/(I_1 + I_2) . \tag{1}$$

III. RESULTS AND DISCUSSION

For the convenience of analysis, the resistivity ρ and the average positron lifetime τ are shown as a function of La content in Figs. 1(a) and 1(b), respectively. As a comparison the average positron lifetime in $BaTiO_3$ ceramics doped with Gd_2O_3 (Ref. 23) is demonstrated in Fig. 1(c). In Fig. 2, τ_1, τ_2, and I_2 are shown as functions of La content. The lifetime τ_3 (2.0 ± 0.2 ns) of the long-lived component with the intensity I_3 (1.9–2.5 %), is independent of La content and is not shown in the figure.

As shown in Fig. 1(a), when the La content x is increased from 0 to 0.2 at. %, the resistivity ρ decreases; in the region of $x = 0.2$–0.3 at. % ρ reaches a minimum value; and above 0.3 at. % ρ increases quickly. This non-monotonic variation of resistivity is in agreement with earlier work.[24]

It can be seen from Fig. 1 that the variation of the average positron lifetime with increasing dopant content is nonmonotonic in our work, but monotonic in Ref. 23. In fact, the difference occurs mainly in the range of lower
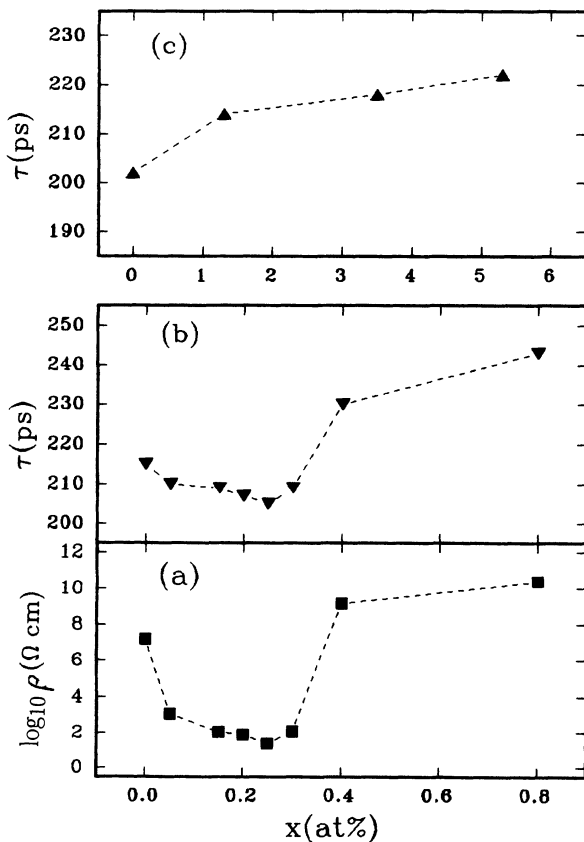

FIG. 2. Positron lifetime parameters (a) τ_1, (b) τ_2, and (c) I_2 as functions of the La content x in La-doped $BaTiO_3$.

FIG. 1. (a) Logarithm of resistivity $\log_{10}\rho$ and (b) average positron lifetime τ as functions of the La content x in La-doped $BaTiO_3$; and (c) the average positron lifetime τ as a function of the Gd content x in Gd-doped $BaTiO_3$ (Ref. 23).
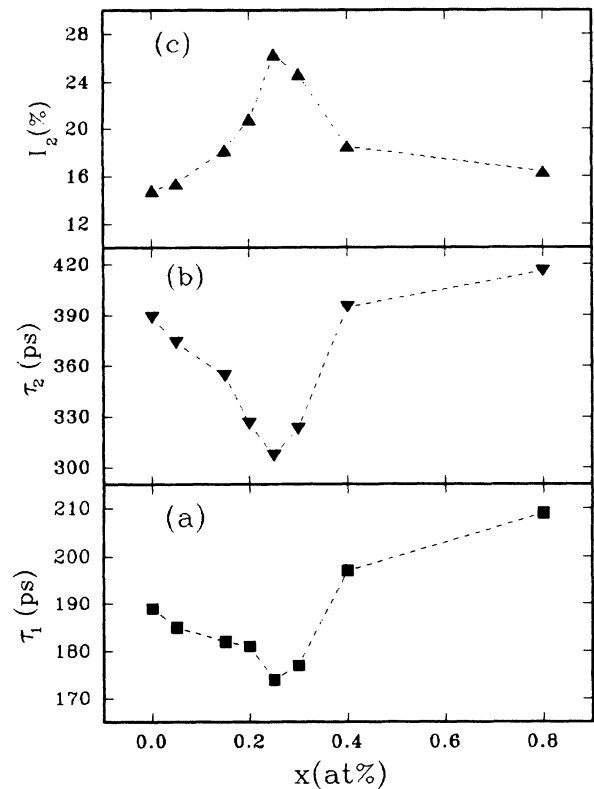
dopant content (< 0.4 at. %), in which Ref. 23 did not give any experimental data. In our results, if the data for $x = 0.05$, 0.15, 0.2, 0.25, and 0.3 are ignored, the variation of τ vs x is also monotonic. Thus the range of lower dopant content, in which $BaTiO_3$ ceramics exhibit semi-conducting behavior, must be specially considered.

It is seen from Fig. 2 that the dependences of the positron lifetimes τ_1 and τ_2 and the intensity I_2 on the La content are also nonmonotonic. In order to explain this nonmonotonic dependence of the positron-lifetime parameters, it is worth summarizing the former knowledge about the influence of dopants on $BaTiO_3$ ceramics.

It is known that[2] in the donor-doped $BaTiO_3$ ceramics the bulk of the grains is low Ohmic and their boundaries are high Ohmic, and the resistivity of the material is contributed together by bulk and boundaries. It is also known that[6] in La-doped $BaTiO_3$ most of the La ions are expected to substitute only for Ba ions, and the La ions incorporated at Ba sites carry an excess positive charge which, for the maintenance of electric neutrality, can be compensated in two different ways. On the one hand conducting electrons (electron compensation) may result from $Ti^{4+} \rightarrow Ti^{3+}$, and on the other hand Ba vacancies may be formed to compensate the excessive electrons (vacancy compensation). Daniels et al.[6] pointed out that in an atmosphere of air electron compensation predominates for $T > 1500\,°C$, mixed Ba vacancy and electron compensation takes place in the range of $1220 < T < 1500\,°C$, and Ba vacancy compensation is

predominant below 1220 °C. In the present work, the samples were sintered in air at 1350 °C; thus certainly mixed compensation takes place. According to this compensation mechanism we can infer that the electron density and the Ba vacancy concentration both increase with increasing dopant content. Considering these ideas, below we discuss mainly the causes of the nonmonotonic variation of τ_2 with La content.

In polycrystalline materials such as ceramics, grain boundaries cannot be neglected as defects trapping positrons. Thus in analyzing the behavior of positrons in La-doped $BaTiO_3$ ceramics, two kinds of defects, Ba vacancy and grain boundary, need to be considered. Referring to earlier work, where in Gd-doped $BaTiO_3$ $\tau_2 = 310-350$ ps was regarded as the lifetime of positrons in isolated Ba vacancies,[23] and in La-doped $PbTiO_3$ the positron lifetime in Pb vacancies was measured to be 304 ps,[25] in the present work τ_2 can be regarded as the weighted average lifetime of positrons in Ba vacancies and at grain boundaries.

In an undoped sample the τ_2 of 389 ps is evidently contributed by positrons at grain boundaries and in other open-volume defects. In the range of $0 < x < 0.25$ at. %, with an increase of La content x, mixed compensation takes place, and both electron density and Ba vacancy concentration increase. An increase of Ba vacancy concentration results certainly in a decrease of τ_2, because τ_2 is contributed by Ba vacancies and grain boundaries and other open-volume defects together, and because the positron lifetime in Ba vacancies is less than the lifetime at grain boundaries and other open-volume defects (389 ps). An increase of I_2 reflects just this variation of Ba vacancies.

When $x > 0.25$ at. %, variations of the positron-lifetime parameters are just contrary to that in the former range; τ_2 becomes large and I_2 becomes small. Now we meet a problem. It is known that as the La content increases the Ba vacancy concentration becomes large. This should result in an increase of I_2, but the observed I_2 decreases. This contradiction forces us to consider other mechanisms. In this case a possible explanation is that when the Ba vacancy concentration and La ion concentration become large enough, La ions form pairs with Ba vacancies (this is called an associated defect below), and these associated defects do not trap positrons. A similar associated defect has been observed in Eu-doped $SrTiO_3$ by site-selective laser spectroscopy.[26] It is evident that each double-ionizable Ba vacancy (V''_{Ba}) can compensate for two $La^{.}_{Ba}$ ions. Thus the most possible configuration of the associated defect is $(2La^{.}_{Ba}V''_{Ba})$. From the point of view of positron annihilation, formation of the associated defect, in fact, makes the Ba vacancy lose the ability to trap positrons. In order to explain the variation of the positron-lifetime parameters by using the associated-defect model, we assume the following case. Near $x = 0.25$ at. % there is a small critical region of x, below which La ions and Ba vacancies are isolated from each other due to their lower concentration. When the value of x is in the critical region, if there are two isolated La ions and one isolated Ba vacancy in a small volume, with increase of x two new La ions enter into this volume and introduce one new Ba vacancy; then there are four La ions and two Ba vacancies in this small volume, so that two associated defects form due to the large enough concentration of La ions and Ba vacancies. Thus, above the critical region, with increasing x the contribution of Ba vacancies to τ_2 decreases so that the intensity I_2 decreases and τ_2 rises toward the longer lifetime in the grain boundaries and open-volume defects.

IV. CONCLUSIONS

Defects and their variations in $BaTiO_3$ ceramics can be probed by using the positron-lifetime technique. In La-doped $BaTiO_3$, with increasing La content, the concentration of Ba vacancies increases continuously. Ba vacancies can appear in two forms: either isolated or associated with La ions. There is a small critical region of La content near $x = 0.25$ at. %; below the critical region the isolated Ba vacancies are predominant, and above this region the associated defects predominate. The associated defects may not trap positrons, and their most probable configuration is $(2La^{.}_{Ba}V''_{Ba})$.

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