

## Cation vacancies in ferroelectric $\text{PbTiO}_3$ and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ : A positron annihilation lifetime spectroscopy study

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Positron annihilation lifetime spectroscopy measurements identify *A*- and *B*-site cation vacancies in ferroelectric perovskite oxides ( $\text{ABO}_3$ ). Crystal  $\text{PbTiO}_3$  and ceramic lead zirconium titanate (PZT) were studied and gave consistent values for the lifetime resulting from positron localization at lead vacancies  $V_{\text{Pb}}$ . Positron trapping to *B*-site vacancies was inferred in PZT. Temperature dependent studies showed that the defect specific trapping rate was higher for  $V_B$  compared to  $V_{\text{Pb}}$ , consistent with the larger negative charge. Doping PZT with Fe increased the fraction positron trapping to  $V_B$  compared to  $V_{\text{Pb}}$ -type defects.

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### I. INTRODUCTION

Vacancies are assumed to be the dominant native defects in ferroelectric perovskite oxide,  $\text{ABO}_3$ , titanates and often influence material properties.<sup>1</sup> The materials are wide band gap,  $\sim 3.5$  eV, semiconductors; point defects can trap and emit charge carriers but can also interact directly with the polarization and can trap domain walls. Aging and fatigue mechanism remain of fundamental importance, and vacancy defects are often implicated. Point defect complexes with a dipole moment such as acceptor dopant oxygen vacancy nearest neighbor pairs, or *A*-site oxygen vacancy complexes, have been considered to be of particular relevance, both for aging and in relaxor ferroelectrics.<sup>2-4</sup> Theoretical studies of lead vacancy oxygen vacancy pair  $V_{\text{Pb}}V_{\text{O}}$  in  $\text{PbTiO}_3$  have been made, but uncertainty remains regarding the stability of the nearest neighbor configuration.<sup>3,4</sup> More recently, the formation energy for the lead vacancy in  $\text{PbTiO}_3$  has been calculated and provides evidence for acceptor behavior in oxygen rich conditions, but deep donor behavior in low oxygen environments.<sup>5</sup> The importance of *B*-site vacancies in the perovskite structure  $\text{ABO}_3$  is unclear; the calculated formation energies suggest concentrations should be low.<sup>5</sup> However, relaxor behavior in La doped  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT) has been attributed to their presence,<sup>6</sup> and a recent study of fatigue inferred the presence of  $V_B$  defects from the activation energy associated with the fatigue induced response.<sup>7</sup>

The primary monovacancy defects in  $\text{PbTiO}_3$  are  $V_{\text{O}}$ ,  $V_{\text{Ti}}$ , and  $V_{\text{Pb}}$ , with ionic model charges of 2+, 4-, and 2-, respectively. The Ti *B*-site vacancy has six oxygen nearest neighbors in octahedral coordination and the *A*-site vacancy 12, see Fig. 1. If cation vacancies have concentrations of the order of an atomic percent or higher, their presence can be inferred from diffraction studies.<sup>8</sup> At lower concentrations, atomic scale characterization methods are required. Electron paramagnetic resonance (EPR) methods provide the required sensitivity, and can give detailed local structure information; however, there has been no unambiguous identification of a cation vacancy in a perovskite oxide. Positron annihilation techniques have specific sensitivity to open volume defects; varying in size from monovacancies to small vacancy clus-

ters. Positrons are trapped by open volume defects, this alters their annihilation characteristics. The methods are well established for the study of metal and semiconductor materials, but application to oxide materials has been limited. Variable energy positron annihilation spectroscopy studies have shown sensitivity to vacancy defects formed due to oxygen deficiency and La doping in PZT capacitor structures.<sup>9</sup> Initial positron annihilation lifetime spectroscopy (PALS) measurements on ceramic PZT showed evidence of a long defect lifetime attributed to lead vacancies;<sup>10</sup> however, these studies were performed with a low resolution spectrometer and with low count spectra. A more recent systematic PALS study has been reported for La and Nb doped rhombohedral  $\text{Pb}(\text{Zr}_{0.6}\text{Ti}_{0.4})\text{O}_3$  ceramics, and a dominant defect lifetime in the region of  $\sim 300$  ps has also been reported.<sup>11</sup>

Here, we measure positron lifetimes in both crystal  $\text{PbTiO}_3$  and in ceramic tetragonal  $\text{Pb}(\text{Zr}_{0.42}\text{Ti}_{0.58})\text{O}_3$  and report atomic superposition method density functional theory (DFT) calculations of positron lifetimes. The lifetime for positrons localized at lead vacancies in  $\text{PbTiO}_3$  is established, and an upper limit for the bulk positron lifetime is determined. The  $V_{\text{Pb}}$  and the *B*-site vacancy positron lifetimes are assigned for PZT, and evidence for the existence of nearest neighbor complexes with oxygen vacancy defects is presented. The specific positron trapping coefficient for  $V_{\text{Pb}}$  defects is shown to be smaller than for the  $V_B$  centers, consistent with the lower negative charge.

The positron annihilates in the material from a state  $i$  with a lifetime  $\tau_i$  and an intensity  $I_i$ . This can be a delocalized

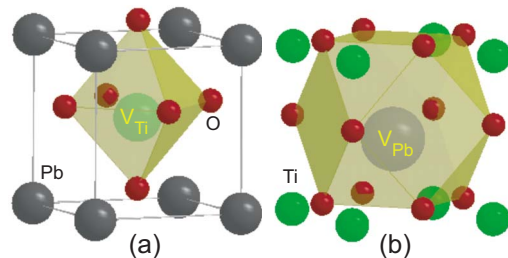


FIG. 1. (Color online) Cation vacancy defect sites for perovskite oxide  $\text{PbTiO}_3$ : (a) *B* site and (b) *A* site.

state in the bulk lattice or a localized state at a vacancy defect. If the average lifetime  $\bar{\tau} = \sum_i I_i \tau_i$  is greater than the bulk lattice lifetime  $\tau_B$ , characteristic of the material, it shows that vacancy defects are present. The rate of positron trapping to a vacancy defect,  $\kappa_d$ , is proportional to concentration  $[d]$ ; the constant of proportionality is the defect specific trapping coefficient  $\mu_d$ . The one-defect simple trapping model (1D-STM) gives (see Ref. 12)

$$\kappa_d = \mu_d [d] = I_2 \left( \frac{1}{\tau_1} - \frac{1}{\tau_2} \right), \quad (1)$$

It predicts two experimental lifetimes;  $\tau_2 = \tau_d$  is the characteristic defect value. The first is reduced from the bulk lifetime by an amount that depends on the rate of trapping to the defect,  $\tau_1 < \tau_B$ . If the 1D-STM is applicable, the bulk lifetime can be calculated from the experimental lifetime components,

$$\tau_B = \left( \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1}. \quad (2)$$

Saturation trapping can occur; as the concentration of the vacancy increases,  $I_2$  can increase to unity, all positrons are annihilating from vacancy defects, and sensitivity to concentration is lost. The  $[d]$  at which this occurs depends on the values of  $\tau_B$  and  $\mu_d$ . Assuming a plausible specific trapping coefficient  $\sim 2 \times 10^{15} \text{ s}^{-1}$  at. for a negatively charged monovacancy,<sup>12</sup> saturation occurs when  $\kappa_d \tau_B = \mu_d [d] \tau_B \approx 10$ , giving a vacancy concentration of order of 50 ppm.

## II. EXPERIMENT

The  $\text{PbTiO}_3$  crystals were grown by a flux solution method at Argonne National Laboratory using a mixture of high purity (99.99%) oxide powders, composed of approximately 60–70 mol %  $\text{PbO}$  and 30–40 mol %  $\text{TiO}_2$ , placed in a platinum crucible and heated to 1100 °C for 5 h in air.<sup>13</sup> They were polydomain but with the majority of domains oriented with the  $c$  axis perpendicular to the main face. The crystals were either gray or light yellow in color; two pairs of similar samples were selected, one pair of yellow crystals (P1) and one pair of gray crystals (P2). All crystals were nominally undoped, but EPR measurements showed trace levels of Fe, Cu, and Pt; the  $[\text{Fe}^{3+}]$  increased from  $\sim 20$  ppm in the yellow crystals to  $\sim 300$  ppm in the gray crystals. The  $\text{Pb}(\text{Zr}_{0.42}\text{Ti}_{0.58})\text{O}_3$  ceramic samples were prepared by a conventional solid state process from oxide precursors;<sup>14</sup> undoped and 0.1, 0.5 and 1.0 at. % Fe doped samples were studied.

The positron lifetime experiments were performed using two conventional fast-fast spectrometers in colinear geom-

etry. One is optimized for room temperature measurements and with a time resolution function of 205 ps, and the second is for variable temperature studies in the range 15–300 K with a resolution function of 275 ps. All spectra contained at least  $5 \times 10^6$  counts. Positron sources were made from aqueous  $\text{NaCl}$  containing  $^{22}\text{Na}$  and were either directly deposited on the material under study or deposited on thin support and protective foils; 1  $\mu\text{m}$  Ni and 8  $\mu\text{m}$  Kapton were both used. Several source strengths were used between  $\sim 200$  and 650 kBq. Two near identical samples sandwiched the positron source between them. The lifetime spectrum is analyzed as a sum of exponential decay components,  $n(t) = \sum_i I_i \exp(-t/\tau_i)$ , convoluted with three Gaussians describing the timing resolution function of the spectrometer. Decay components due to annihilations in the positron source were subtracted in the procedure; direct deposit sources required one component with a lifetime of  $\sim 430$  ps with an intensity that depended on source strength, while foil supported sources required an additional component with a lifetime of  $\sim 380$  ps for Kapton ( $\sim 10\%$ ) or 140 ps for Ni ( $\sim 10\%$ ).<sup>15</sup> Care is required to correctly account for source annihilations; if a direct deposit was not possible, measurements were made with both Kapton and Ni foil sources to establish source independent fittings.<sup>15</sup> This procedure involved a systematic variation of the source correction terms and a minimization of the fit chi-squared and allowed both material and source correction terms to be determined and checked.

Calculations of positron lifetimes were performed using two-component DFT.<sup>16</sup> The electron density of the solid is approximated by the non-self-consistent superposition of free-atom density method, the atomic superposition model, and the potential sensed by the positron is constructed in a similar way.<sup>17</sup> The Schrödinger equation is then solved for the positron eigenenergy and for the positron wave function using a three-dimensional real-space solver.<sup>18,19</sup> The positron lifetimes are obtained from the calculated annihilation rates using the electron density and the positron density and including the enhancement factor that takes into account the pileup of electron density at the positron. The procedure is implemented within the program Doppler in the MIKA package,<sup>19</sup> using the gradient-corrected scheme parametrization of the electron-positron enhancement factor and correlation potential developed by Arponen and Pajanne<sup>20</sup> and Barbiellini *et al.*<sup>21,22</sup> The calculations were made on the  $P4mm$  structures of  $\text{PbTiO}_3$  and  $\text{Pb}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ ,<sup>23,24</sup> without atomic position relaxation, using 1080 atom supercells.

## III. RESULTS AND DISCUSSION

The calculated positron lifetime values for the bulk and for the relevant vacancy defects in  $\text{PbTiO}_3$  and

TABLE I. Calculated positron lifetime values (ps) for  $\text{PbTiO}_3$  and PZT.

Material	Bulk	$V_O$	$V_{O-O}$	$V_B$	$V_{B-O}$	$V_A$	$V_{A-O}$	Ref.
$\text{PbTiO}_3$	147	152		175		280	284	25
$\text{PbTiO}_3$	150	160	170	191	211	278	282	This work
PZT(40/60)	160	165	175	204	221	290	293	This work

TABLE II. Experimental positron lifetime values (ps) for PbTiO<sub>3</sub> and PZT. The one-defect simple trapping model bulk values [Eq. (2)] are also given for PbTiO<sub>3</sub>. The PZT values are the average of those obtained using the different positron sources, after source correction. The PbTiO<sub>3</sub> values were obtained using direct deposit sources and a one-component source correction.

Material	Sample	$\tau_1$	$\tau_2$	$\bar{\tau}$	$\tau_{B(\text{STM})}$
PbTiO <sub>3</sub>	P1	159.0(5)	280(4)	170	165
	P2	139.5(8)	285(2)	191	170
Pb(Zr <sub>0.42</sub> Ti <sub>0.58</sub> )O <sub>3</sub>	Undoped	185(3)	281(3)	239	
	0.1% Fe	186(3)	284(3)	230	
	0.5% Fe	193(3)	293(3)	225	
	1.0% Fe	198(2)	290(3)	211	

Pb(Zr<sub>0.4</sub>Ti<sub>0.6</sub>)O<sub>3</sub> are given in Table I, along with previously reported values for PbTiO<sub>3</sub>.<sup>25</sup> The agreement was, in general, good; however, the *B*-site vacancy lifetime was found to be larger. The calculated increase in lifetime between a cation vacancy and a cation-oxygen divacancy was found to be significantly larger for a *B*-site cation, in agreement with previous calculations for LaCoO<sub>3</sub>,<sup>25</sup> and is consistent with the more open local environment at the *A*-site (Fig. 1).

The measured positron lifetimes for the two pairs of PbTiO<sub>3</sub> crystals using directly deposited positron sources are shown in Fig. 2 and Table II. Only two-component fits gave good chi-squared values. A vacancy defect lifetime of 280(4) ps for P1 and of 285(2) ps for P2 was detected; the first lifetime values were 159 and 139 ps, respectively. The average lifetime obtained increased from 170 ps for pair P1 to 191 ps for P2. The one-defect trapping model bulk lifetime values calculated using Eq. (2) were 165 and 170 ps, respectively. The lead vacancy is predicted to have a lifetime of 280 ps, and the bulk positron lifetime was calculated to be  $\sim 150$  ps, see Table I. The larger calculated model values

given here (Table II) may be due to the presence of a second weakly trapping defect with lifetime close to the bulk value, for example  $V_O$ . Current positron lifetime spectrometers cannot resolve two lifetime components where  $\tau_n \lesssim 1.4\tau_{n+1}$ . Using the intensities for the 280 ps lifetime component, and assuming a one-defect simple trapping model ( $\mu_d = 2 \times 10^{15} \text{ s}^{-1}$ ), vacancy concentrations of  $\sim 3(1)$  and  $17(6)$  ppm for P1 and P2, respectively, result. These values must be treated with caution; the defect specific trapping rate is an estimate and the weak trapping to a second defect is neglected.

The positron lifetime results for the undoped and Fe doped PZT ceramic samples are shown in Fig. 3 and Table II. Two long lifetimes were detected for all samples, consistent

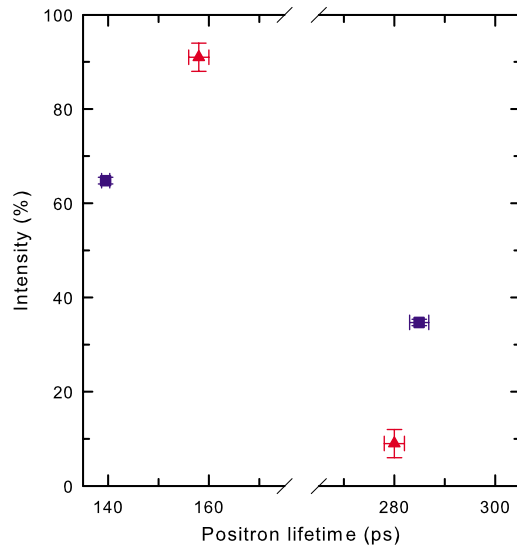


FIG. 2. (Color online) Positron lifetime measurements for two pairs of PbTiO<sub>3</sub> crystals, P1 (square) and P2 (triangle), using directly deposited positron sources. The second, longer lifetime component corresponds to positrons trapping at Pb vacancies.

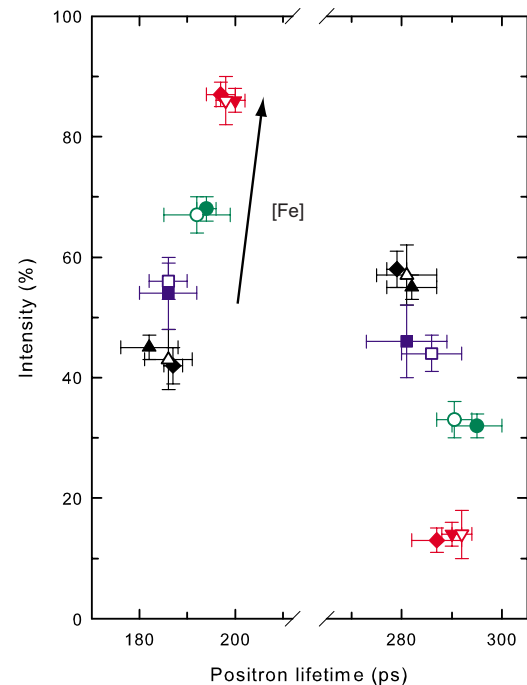


FIG. 3. (Color online) Positron lifetime measurements for Pb(Zr<sub>0.42</sub>,Ti<sub>0.58</sub>)O<sub>3</sub> ceramic samples; undoped (up triangle), 0.1% Fe doped (square), 0.5% Fe (circle), and 1.0% Fe (down triangle). Measurements using Ni (solid) and Kapton (open) foil supported positron sources are shown. Undoped and 1.0% Fe directly deposited positron sources (diamond) were also used.

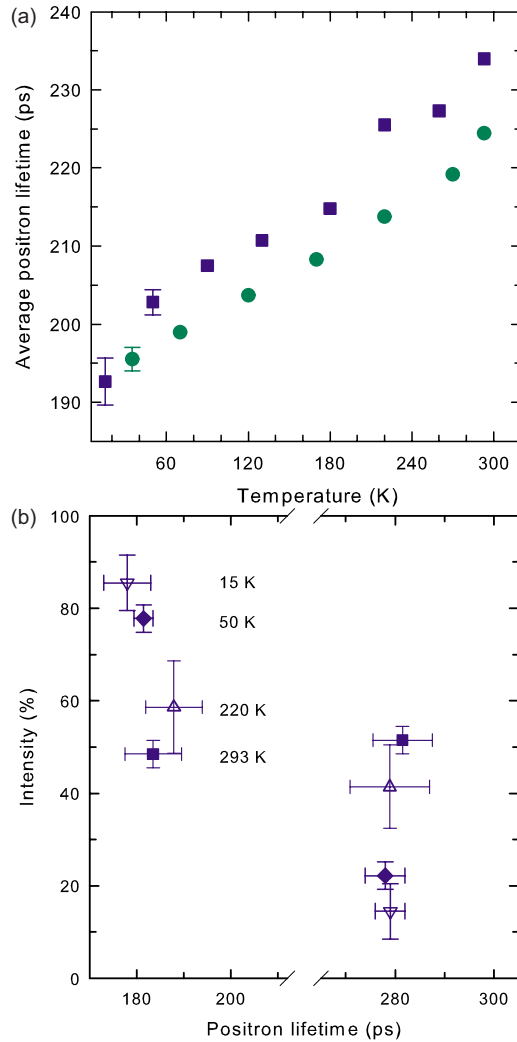


FIG. 4. (Color online) (a) Average positron lifetime of 0.1% (square) and 0.5% (circle) Fe doped Pb(Zr<sub>0.42</sub>,Ti<sub>0.58</sub>)O<sub>3</sub> ceramic samples as a function of measurement temperature. (b) Two-component positron lifetime fit values for the 0.1% Fe doped sample for the temperatures 15 K (triangle down), 50 K (diamond), 220 K (triangle up), and 293 K (square).

with saturation trapping at two types of vacancy defect. The two-defect model in the limit of saturation trapping gives

$$\frac{I_2}{I_1} = \frac{\kappa_{d2}}{\kappa_{d1}} = \frac{\mu_{d2}[d_2]}{\mu_{d1}[d_1]}. \quad (3)$$

The defect lifetimes determined for undoped PZT were 185(3) and 281(3) ps; comparable values of 186(3) and 284(3) ps were obtained for the 0.1 at. % Fe doped sample. The 0.5% and 1.0% doped samples showed an increase in both lifetimes to  $\sim 195$  and  $\sim 291$  ps. The A-site vacancy lifetime is in approximate agreement with the calculated value (Table I) and the value of 295 ps previously reported in rhombohedral phase PZT.<sup>11</sup> The experimental lifetime of 185(3) ps is consistent with, but slightly less than, the calcu-

lated  $V_B$  lifetime of 204 ps given in Table I. The unrelaxed oxygen divacancy calculated to be  $\sim 175$  ps is the only other defect type with a comparable lifetime. These defects could segregate to grain boundaries, but the observation by EPR of only Fe<sub>Ti</sub><sup>3+</sup>-V<sub>O</sub> defect complexes, not isolated Fe<sub>Ti</sub><sup>3+</sup>, suggests that positively charged oxygen vacancies are found dominantly bound in charge compensation complexes.<sup>26</sup> The increase in  $\tau_1$  with increasing [Fe] shown in Fig. 3 suggests an increasing contribution from  $V_B V_O$  divacancies. An average lifetime component would be obtained for a population of both  $V_B$  and  $V_B V_O$  defects. A similar, but smaller, increase was observed for  $\tau_2$ , consistent with the formation of  $V_{Pb} V_O$  defects with increasing [V<sub>O</sub>].

The systematic increase in the ratio  $[V_B]/[V_{Pb}]$  with increasing [Fe] can be inferred from the observed increase in  $I_1$ , the intensity of  $\sim 185$  ps component, and the concomitant decrease in  $I_2$ , associated with positrons trapped at  $V_{Pb}$  defects, shown in Fig. 3 using Eq. (3). To investigate the relative trapping coefficients for the two vacancy defect types, measurements in the range 15–300 K were performed on the 0.1% and 0.5% doped samples and are shown in Fig. 4; a direct deposit source was used for the 0.1% samples and a Kapton foil source for the 0.5% measurements. The average positron lifetime was observed to decrease with decreasing temperature for both samples; the two term fits showed that this was due to an increase in  $I_1$  with respect to  $I_2$ . The trapping coefficient for the  $\sim 185$  ps defects increases more rapidly with decreasing temperature than for  $V_{Pb}$  defects, consistent with the larger negative charge for  $V_B$  centers. Comparing the 0.1% and 0.5% doped temperature dependences suggests that relative change is not significantly influenced by an increase in  $V_{A,B} V_O$  defects.

To explain the observation of only the Fe<sub>Ti</sub><sup>3+</sup>-V<sub>O</sub> defect complexes with Fe doping, it has recently been proposed that additional negative charge compensation due to the formation  $V_{Pb}$  defects occurs.<sup>26</sup> Here, we observe an increase in  $[V_{Pb}]$  with increased [Fe<sup>3+</sup>] for unintentionally doped PbTiO<sub>3</sub> crystals. However, in Fe doped PZT, the increase in the ratio  $[V_B]/[V_{Pb}]$  with increasing [Fe] suggests a charge compensation mechanism involving B-site vacancy formation.

#### IV. CONCLUSIONS

These results show that positron annihilation techniques can characterize cation vacancy defects in perovskite oxide materials. The lead vacancy in PbTiO<sub>3</sub> is identified, the experimental positron lifetime is in agreement with the theoretical value, and an upper limit for the bulk lifetime is established. In PZT, we infer that both the lead vacancy and the B-site vacancy are observed, and evidence for the presence of cation vacancy oxygen vacancy defects is also given.

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