

Visualization of highly graded oxygen vacancy profiles in lead-zirconate-titanate by spectrally resolved cathodoluminescence spectroscopy

Atsuo Matsutani, Zhenhua (Jerry) Luo, Soodkhet Pojprapai, Mark Hoffman, and Giuseppe Pezzotti

Citation: *Appl. Phys. Lett.* **95**, 202903 (2009); doi: 10.1063/1.3245317

View online: <http://dx.doi.org/10.1063/1.3245317>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v95/i20>

Published by the [American Institute of Physics](http://www.aip.org).

Additional information on *Appl. Phys. Lett.*

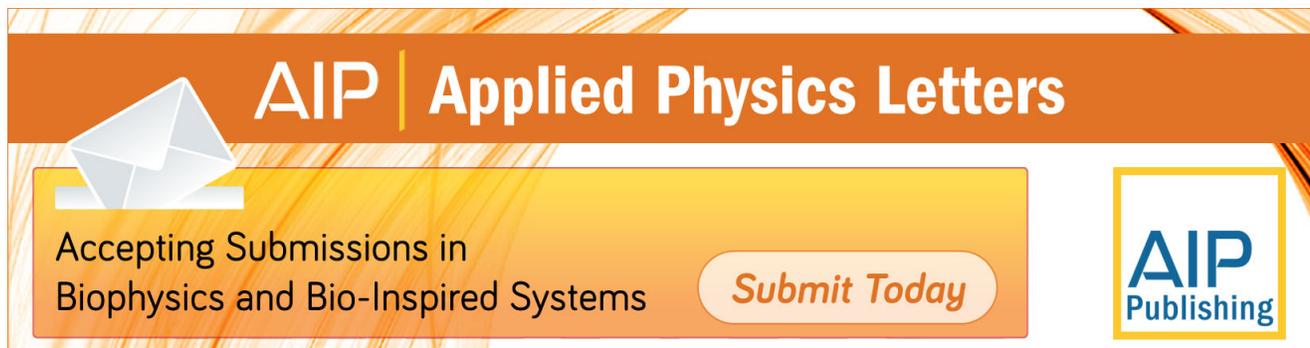
Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



AIP | Applied Physics Letters

Accepting Submissions in
Biophysics and Bio-Inspired Systems

Submit Today

AIP
Publishing

Visualization of highly graded oxygen vacancy profiles in lead-zirconate-titanate by spectrally resolved cathodoluminescence spectroscopy

Atsuo Matsutani,¹ Zhenhua (Jerry) Luo,² Soodkhet Pojprapai,² Mark Hoffman,² and Giuseppe Pezzotti^{1,a)}

¹*Ceramic Physics Laboratory and Research Institute for Nanoscience, RIN, Kyoto Institute of Technology, Sakyo-ku, Matsugasaki, 606-8585 Kyoto, Japan*

²*School of Materials Science and Engineering, UNSW Sydney, New South Wales 2052, Australia*

(Received 29 June 2009; accepted 31 July 2009; published online 18 November 2009)

The ultraviolet and visible cathodoluminescence (CL) emitted at room temperature from bulk hard lead-zirconate-titanate polycrystalline perovskite has been systematically collected before and after an annealing cycle conducted in a reducing atmosphere. Spectroscopic assessments have been made of the in-depth stoichiometric profile developed upon annealing from the sample surface toward the subsurface. Trapping of electronic charge and local atomic scale distortions in the perovskite oxygen octahedron influences the variation observed in visible CL emission, while lattice distortions upon annealing directly arise from the formation of oxygen vacancies. © 2009 American Institute of Physics. [doi:10.1063/1.3245317]

Since Jaffe *et al.*¹ reported the piezoelectric behavior of lead-zirconate-titanate [Pb(Zr_xTi_{1-x})O₃ (PZT)] perovskites, a large amount of research has been performed to explain the reasons for the unusually high piezoelectric response of their polycrystalline structures.² Nowadays, the high number of possible polarization directions around the morphotropic phase boundary is believed to be one major factor for effectively increasing the polarization directions. However, the presence of oxygen vacancies has also been proved to play a fundamental role and vacancy concentration can be used for finely tuning the piezoelectric response of PZT materials.³ Vacancies have a tendency to stabilize the domain motion resulting in ferroelectrically harder materials (i.e., with higher coercive field strengths, lower permittivity, and lower losses). In most recent applications,⁴ the presence of oxygen vacancies has been related to the imprint mechanism of ferroelectric memory through their effect on interface charge density and, in turn, on the offset bias. Despite the importance of the vacancy issue, however, local vacancy gradients are hard to visualize and quantify with high spatial resolution. Most recently, Zhang *et al.*⁵ have reported a depth-profiling characterization of defects in SrTiO₃ single-crystal films by cathodoluminescence (CL) spectroscopy. In this study, we propose the use of a spectrally resolved (visible) CL method as a means to elucidate, on the microscopic scale, the topographic location of electrically active point defects in PZT.

A polycrystalline unpoled hard PZT [Pb(Zr_{0.52}Ti_{0.48})O₃] on the tetragonal side of the morphotropic phase boundary with 5 μm of grain size (K270, Piezo Technologies, Indianapolis, IN) was used in this investigation. A heat-treatment at 600 °C in a reducing Ar/H₂ atmosphere (4% H₂ gas composition; also simply referred to as annealing cycle, henceforth) was carried out for 4 h in order to create a chemical gradient from the bulk toward the sample surface. A further reannealing cycle in air (4 h at 600 °C) was made on a piece of the Ar/H₂ annealed sample, in order to check about the

reversibility of the vacancy gradient. The sample was confirmed to be a pure perovskite phase before and after annealing by x-ray diffraction analysis. A field emission gun scanning electron microscope (FEG-SEM) device (S-4300SE, Hitachi, Tokyo, Japan) equipped with a high-sensitivity CL detector unit (MP-32FE, Horiba Ltd., Kyoto, Japan) was employed for CL spectroscopy measurements. Spectra were always collected at room temperature. Throughout the experiments the FEG-SEM magnification was kept at 20 K, the acceleration voltage used was 10 kV, and the spectral accumulation time was 15 s. A 600 grooves/mm grating was used for the analysis of the luminescence emission. Under these experimental conditions, the spatial resolution of the electron probe was of the order of 0.58 μm, as calculated according to the Kanaya–Okayama equation.⁶ The collected CL spectra at each location were averaged to obtain a statistically representative morphology for each given location, and then deconvoluted into five symmetrical Gaussian subcomponents.

Figures 1(a) and 1(b) show experimentally retrieved CL spectra and their subband structures after deconvolution [i.e., according to Eqs. (1) and (2)], as collected on the surface of the PZT sample before and after annealing in reducing atmosphere, respectively. A clear morphologic alteration can be observed, especially in a comparison among the five Gaussian subbands before and after annealing. The valence band top in PZT mainly consists of Pb 6s states and the conduction band bottom consists of empty Ti 3d states. The band gap between the valence band top and conduction band bottom is about 3.2 eV, and this wide gap makes the PZT materials transparent to visible light.⁷ The energy gap was located as the subband I in Fig. 1. A broad blue emission band peaking at about 2.6 eV (referred to as subband II, henceforth) was clearly observed; the relative intensity of this latter emission band visibly increased after annealing in reducing atmosphere [cf. Figs. 1(a) and 1(b)]. Such a behavior supports the relation of this Gaussian subband to the presence of oxygen vacancies.⁸ The investigated PZT sample was indeed a “hard” material, thus already containing a large concentration of oxygen vacancies in its as-sintered state, as confirmed by the spectrum in Fig. 1(a), in which subband II

^{a)}Author to whom correspondence should be addressed. Electronic mail: pezzotti@kit.ac.jp.

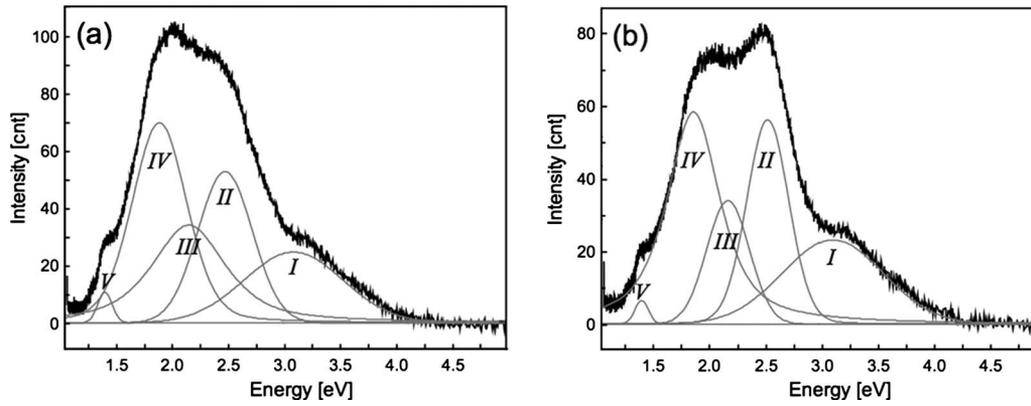


FIG. 1. Experimental CL spectra of the PZT sample and their deconvolution: (a) before and (b) after annealing in reducing atmosphere.

was already pronounced. An increase of the observed blue luminescence is correlated with the increase of the TiO_5 and/or ZrO_5 -type structures, and thus with the resulting population of oxygen-excess defects, whose density should be thus related to the observed intensity of the CL signal. A population of positively charged defects leads to possibly different valence states of the clusters (TiO_5^+ or ZrO_5^+ , and TiO_6^+ or ZrO_6^+); the loss of symmetry associated with the change from sixfold-oxygen coordinated Ti (O_h symmetry) to fivefold-oxygen coordinated Ti (symmetry C_{4v} or D_{4h}) creates new electronic states; consequently, additional CL bands can also be observed.^{9,10} Eglitis *et al.*¹⁰ investigated the photoluminescence of undoped PLZT and reported about a band centered at 552 nm (corresponding to the Gaussian subband III observed in this study at around 2.2 eV). By comparing luminescence, lifetimes and excitation spectral properties of various samples, this band was assigned to structures of octahedral geometry with a sixfold oxygen-coordinated Ti ion. The CL band in the red region at around 1.9 eV (i.e., band IV in Fig. 1) has been suggested to arise as a result of charge-transfer vibronic exciton (CTVE) radiative recombination.¹¹ The CTVE in ABO_3 ferroelectric oxides with partly covalent chemical bonding consists of spatially well-correlated pairs of electronic and hole polarons forming a metastable intrinsic quasicerter due to a bipolaron self-trapping in the strong field of the lattice distortion.^{12,13} Interestingly, the relative intensity of subband IV also decreases upon annealing in reducing atmosphere. As far as the CL subband V, observed in the near-infrared spectral region, is concerned, we might tentatively assign it to self-trapped exciton emission of the oxygen deficient octahedral $\text{Ti}^{3+}\text{V}^\circ$, according to Teepakov *et al.*¹⁴ As shown in Fig. 2, the optical band gap apparently increased (3.22–3.26 eV) with distance from the free surface. On the other hand, no appreciable band shift could be observed for the subband II with increasing distance from the free surface of the heat-treated PZT sample. The intensity trend of the excess-oxygen-related subband II from the edge toward the bulk might be directly assumed to represent a change in concentration of oxygen vacancies, whose density should be related to the diffusion length from the free surface of the sample. It should be noted that, after re-annealing in air a piece of the same sample previously annealed in hydrogen, the intensity of the subband II (i.e., as collected at about 100 μm from the free surface) could be only partly recovered to the initial (low) intensity of the as-sintered sample (subband II and IV show-

ing about the same intensity). Data on the reannealed sample show the possibility of tailoring vacancy concentration gradients using annealing in controlled atmosphere.

The increase in vacancy concentration in the PZT lattice is revealed by the appearance of a shoulder located in the UV region of the CL spectrum, whose intensity increases with increasing vacancy concentration. The observed energy value at shoulder maximum is dictated by the variation in relative intensity of subbands II and, to a minor extent, to the observed variation of band-gap energy (cf. Fig. 2). This latter variation is indeed quite small and can be attributed to a residual stress gradient nearby the free surface. The spectrum collected at the center of the sample was found to systematically coincide with spectra randomly collected on the same sample before annealing. Figure 2 also shows the relative intensity ratio $I_{\text{II}}/I_{\text{IV}}$ retrieved from CL spectra collected from the PZT sample after annealing as a function of distance, x , from the sample edge. This latter plot directly shows how the defect population dramatically changes with annealing the sample.

It is known that conventional photostimulated spectroscopy works poorly for stoichiometric evaluations of ferroelectrics and other wide-band-gap materials because the visible photon energy is much smaller than the band gap. For

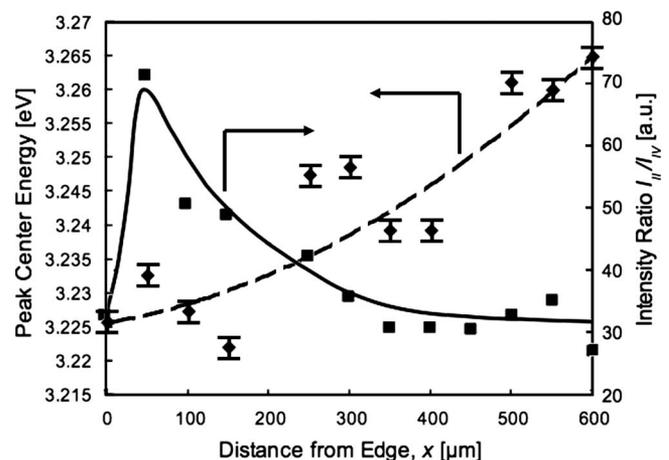


FIG. 2. Apparent optical band gap shift (3.22–3.26 eV) with distance, x , from the free surface (a) and the relative intensity ratio $I_{\text{II}}/I_{\text{IV}}$ retrieved from CL spectra collected from the PZT sample after annealing as a function of distance, x , from sample edge. The scatter in the best-fitting curves was below 5% (at any measurement location) in comparing five profiles collected at different locations.

CL excitation, the excitation energy is above the band gaps of ferroelectrics, leading to a much stronger absorption and to a significantly shorter probe penetration depth; preventing light emission from deep regions allows probing with high spatial resolution. This study demonstrates the feasibility of highly spatially resolved assessment of oxygen vacancy gradients in PZT by means of CL spectroscopy. The CL procedure may be useful for vacancy control, thus enabling fine tuning of macroscopic coercive field strengths and permittivity in PZT materials.

¹B. Jaffe, R. S. Roth, and S. Marzullo, *J. Appl. Phys.* **25**, 809 (1954).

²B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S.-E. Park, D. E. Cox, and G. Shirane, *Phys. Rev. B* **61**, 8687 (2000).

³S. Aggarwal and R. Ramesh, *Annu. Rev. Mater. Sci.* **28**, 463 (1998).

⁴H. Miyazawa, Y. Hamada, T. Higuchi, E. Natori, T. Kijima, T. Shimada, M. Yoshiya, and T. Oguchi, *Mater. Res. Soc. Symp. Proc.* **902E**, 0902–

T10–43.1–6 (2006).

⁵J. Zhang, S. Walsh, C. Brooks, D. G. Schlom, and L. J. Brillson, *J. Vac. Sci. Technol.* **B26**, 1466 (2008).

⁶K. Kanaya and S. Okayama, *J. Phys. D: Appl. Phys.* **5**, 43 (1972).

⁷Y. Shimakawa and Y. Kubo, *Appl. Phys. Lett.* **77**, 2590 (2000).

⁸S. Murakami, M. Herren, D. Rau, and M. Morita, *Inorg. Chim. Acta* **300**, 1014 (2000).

⁹P. S. Pizani, E. R. Leite, F. M. Pontes, E. C. Paris, J. H. Rangel, E. J. H. Lee, E. Longo, P. Delega, and J. A. Varela, *Appl. Phys. Lett.* **77**, 824 (2000).

¹⁰R. I. Eglitis, E. A. Kotomin, and G. Borstel, *Eur. Phys. J. B* **27**, 483 (2002).

¹¹V. S. Vikhnin and E. A. Kotomin, *Phys. Rev. B* **65**, 104304 (2002).

¹²V. S. Vikhnin, *Z. Phys. Chem. (Munich)* **201**, 201 (1997).

¹³V. S. Vikhnin, H. Liu, W. Jia, S. Kapphan, R. I. Eglitis, and D. Usvyat, *J. Lumin.* **83–84**, 10 (1999).

¹⁴V. Teepakov, V. Dimza, L. Zjastrabik, A. Savinov, and Z. Brykhar, *Phys. Status Solidi B* **183**, 299 (1994).