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Polarons, oxygen vacancies, and hydrogen in $Ba_xSr_{1-x}TiO_3$

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Abstract

The role of hydrogen in strontium titanate and barium strontium titanate is analysed, for both ceramics and single crystals. New infrared and second-harmonic generation (SHG) experiments show the relationship between hydrogen and oxygen vacancies. The infrared data exhibit strong absorption in the 3000–6000 cm^{-1} region due to polarons. The SHG data exhibit rather strong signals at room temperature (nominally forbidden). These data are correlated with the temperature dependence of activation enthalpies from Steinsvik (Oslo), and it is found that the latter are characterised by a universal exponent of 7/4 for the dependence upon vacancy concentration, in agreement with the predictions for a cubic lattice in percolation theory. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The presence of hydrogen in strontium titanate and in related isostructural materials such as BST — Ba_xSr_{1-x} TiO_3 — has become important for two completely unrelated reasons (1) In ceramic thin-film BST hydrogen enters the ferroelectric both from residual organics in the MOD processing and from the forming-gas anneal and spoils the switching process in the ferroelectric,[1–3] as studied carefully by Ashida et al. at Fujitsu.[4] The primary effect is a significant decrease in remanent polarisation and hence switched charge. Very recently it has been found that this catalysis[5] of H by Pt (and the subsequent catalysis of oxygen vacancies by H-ions) can be minimised by using a TiN/Al metalisation scheme.[6] The strongly detrimental effects of even small amounts ($<4\%$) of H_2 on PZT and SBT were detailed very recently[6] and include the fact that in the presence of H, Pt-electroded SBT partially decomposes into elemental Bi (as first reported by Hartmann, Scott et al.) and PZT partially decomposes at 823 K to yield 0.3% Pb. (2) In pure strontium titanate hydrogen may contribute to dielectric and ultrasonic loss peaks and spontaneous strain at cryogenic temperatures from 8 to 65 K, most notoriously at 37 K.[7,8]

2. Loss mechanisms in pure $SrTiO_3$ at low-T

Measured at 8 MHz, the 37 K ultrasonic and dielectric relaxation in strontium titanate has some resemblance to the Snoek mechanism of relaxation in metals such as hydrogen in iron, tantalum, or niobiu.m. Snoek mechanisms, however, involve interstitial solutes, whereas H in $SrTiO_3$ goes only into oxygen sites (as OH hydroxyl ions) and not interstitially; e.g.[9] the true chemical formula should be written as $WO_{3-x}(OH)_x$ instead of H_xWO_3. H in metals generates relaxation in only the (S_{11}–S_{12}) compliance, and not, e.g. in S_{44}.; this simple fact makes it relatively difficult to relate to recent measurements of mechanical relaxation in $SrTiO_3$, which was measured in terms of Young's modulus, C_{11}, etc., not S_{ij}. It is noteworthy, however, that the hydrogen Snoek peak in Fe, Nb, and Ta at ca. 10 MHz lies at $T_0 = 120$ K (10.8 meV) and exhibits an activation enthalpy of $h = 128$ meV. This ratio of $h/k_BT_0 = 11.9$ is very nearly that (11.5 ± 0.2) observed[10] for all the low temperature relaxations in strontium titanate, including that at 37 K. The activation enthalpy of 128 meV (1033 cm^{-1}) may correspond to a localized vibration of metal-hydrogen, and in general we expect that such relaxations in strontium titanate or BST will be optical-phonon-driven. By comparison, the activation enthalpy for H in $SrTiO_3$ is known[11] to be 0.40 ± 0.02 eV (400 meV), about 3× the value typical of hydrogen in metals and, notably, less than half the activation enthalpy for oxygen vacancies.

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Furthermore, the hydroxyl reaction is exothermic, so that locally a kind of avalanche might be expected, leading to OH clusters rather than randomly isolated OH defects. It is possible to hydrogenate perovskite structures fully to 100% hydroxyl ions, as in bernalite $Fe(OH)_3$.

The relaxations measured near 8 MHz by Scott and Ledbetter[12] in $SrTiO_3$ were primarily longitudinal at 65 K and transverse at 37 K. This is not compatible with the original 1937 theory of phonon-assisted relaxation by Landau and Rumer, which predicts a negligible attenuation of transverse modes, due to wave-vector conservation restriction in three-phonon processes involving only acoustic phonons. But this restriction is not applicable to $SrTiO_3$, however, since it is known[13] that in this material the soft transverse optic phonon has a relaxation time of 1.3×10^{-10} s, a full order of magnitude faster than acoustic processes. Thus the inference is that optical phonon relaxations are dominant in strontium titanate at cryogenic temperatures, which is the fundamental point of Scott and Ledbetter, viz. $\omega_{ac}(q) \rightarrow \omega_{op}^{(1)}(q_0 + q) - \omega_{op}^{(2)}(q_o)$, where $\omega_{op}^{(1)}$ and $\omega_{op}^{(2)}$ are the ferroelectric and antiferro-distortive soft optic modes, respectively.

3. Interaction between *H* and oxygen vacancies

It greatly complicates matters that the hydrogen concentration in oxide ferroelectrics acts as a catalyst to produce oxygen vacancies and other positive charge centers.[14–17] This was studied carefully by Takatani. et al.[18] and Kanaya et al.[19] This means that the problem of hydrogen in perovskite oxide ferroelectrics cannot be cleanly separated from the problem of oxygen vacancies. The activation enthalpy for OH in strontium titanate is only 0.40 ± 0.02 eV, about half that of oxygen vacancies. The activation energy to *move* an oxygen vacancy in strontium titanate is 0.82 eV; this is about 15% of the activation enthalpy to *create* an oxygen vacancy, which is known with great precision to be 5.76 eV (133 kcal/mol). And the reaction is exothermic. Thus, local avalanche-like runaway reactions can occur, producing hydrogen-defect clusters and also oxygen-vacancy clusters. Information on proton mobilities in oxide ferroelectrics can also be found in a rather different context: that of proton-conducting ferroelectrics.[20]

Oxygen vacancies in $SrTiO_{3-x}$ self-order[11] into $2\times2\times1$ super-lattices at a critical concentration $x_c = 7\%$. As the vacancy concentration increases from zero, where the activation enthalpy H is 2.0 eV, H drops[11] from 2.0 to zero eV, signalling a phase transition. The dependence of H upon x is given empirically (present work), as shown in Fig. 1, with $\gamma = 1.78 \pm 0.10$ in the equation

$$H = H_0(x_c - x)^\gamma \quad (1)$$

We note that the percolation exponent[21] for a three-dimensional model (simple cubic) is $\gamma = 7/4$, which agrees with the experimental value in Eq. (1) and with Prosandeev's idea of cluster-polarisation.

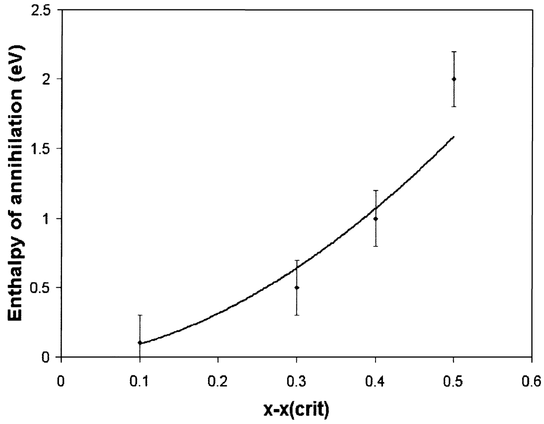

Fig. 1. Graph of activation enthalpy[11] for displacement of oxygen vacancies in strontium titanate vs. vacancy concentration, showing percolation exponent of 7/4.

4. Tetragonality and electric field effects

Below ca. $T_0 = 105$ K pure strontium titanate is tetragonal with a doubled unit cell.[22] Oxygen vacancies and other charged defects can shift this transition temperature significantly. Oxygen vacancies make the system less tetragonal; that is, they shift the transition temperature T_0 to lower temperatures. An oxygen vacancy concentration of $n = 10^{20}$ cm^{-3} is sufficient to lower T_0 by 25 to 80 K; highly reduced $SrTiO_3$ has T_0 as low as 40 K.[23,24] This effect is not due to carrier concentration per se; making strontium titanate heavily *n*-type by adding 10^{19} cm^{-3} Nb donors has no effect on T_0.; hence this downward shift in T_0 is due only to vacancies; but these oxygen vacancy concentrations have relatively little effect on the temperature of the ferroelectric phase transition (which is incipient only — occurring at negative temperatures — although Curie–Weiss law extrapolations of dielectric constant or soft-mode frequencies give a fictitious $T_C' = 35.5$ K). By comparison, adding Ca substitutional for Sr raises the actual ferroelectric transition temperature T_C (as high as 40 K);[25] that is, Ca-doped $SrTiO_3$ is ferroelectric at cryogenic temperatures, whereas pure $SrTiO_3$ is not (even in thin-film form[26]). Adding Bi also makes $SrTiO_3$ "more tetragonal" (raises T_0), as evidenced in the greatly increased intensity of the Raman superlattice modes which become allowed due to the cell-doubling cubic-tetragonal phase transition at T_0.[27]

The Brillouin intensity studied at 9 K.[28] has an unexplained dip at 2.7 kV/cm, which is unrelated to the ferroelectric transition field (1.9 kV/cm) at this temperature. The dielectric loss tangent for the relaxation mode (peak "A") that is field dependent peaks sharply at[29] 5 kV/cm. The latter effect seems to be due to a mode crossing of a field-independent mode (mode III at 23 cm^{-1}) with the field-dependent mode which is driven upward from 8 cm^{-1} at $E = 0$–23 cm^{-1}. These are not the field values at which the ferroelectric soft modes cross the antiferrodistortive soft modes at 9 K. The latter crossings are at 1.0 kV/cm for E_u/E_g components and ca. 17 kV/cm for A_{1g}/A_{2u} components.[30]

5. Infrared data

In at attempt to study H in $SrTiO_3$ and BST we have employed infrared spectroscopy of the OH-stretching region. A single crystal of pure strontium titanate was used as the calibration benchmark. Spectra for this specimen are shown in Fig. 2. This is a nominally pure strontium titanate crystal, which should exhibit no OH-vibrations. Fig. 2 compares these OH-stretching regions with data on MOD (metal organic decomposition) barium strontium titanate (samples from Symetrix Corp. and from Aachen gave the same results). A broad shoulder tentatively assigned to OH was observed at 3100 cm^{-1} in addition to a strong polaron absorption band at 4000 cm^{-1}; the polaron band is modelled (notation of Ref. 14) with known longitudinal optical long-wavelength LO phonon energy $\omega_p = 815$ cm^{-1}; $W = 3440$ cm^{-1}; and $E = 240$ cm^{-1}. This gives a ratio of $W/\omega_p = 4.2$, which is true in most perovskite oxide polarons. 3100 cm^{-1} is the OH frequency in hydroxyl perovskites[12] such as bernalite $Fe(OH)_3$. The BST results are nearly identical to those reported on PZT,[31] showing that oxygen vacancies, not Pb vacancies or Pb^{+3}, are the likely culprits. The principal conclusions from these data are that BST exhibits the same self-trapped polarons at oxygen vacancies as does PZT, and single-crystal $SrTiO_3$ exhibits no measurable density of such vacancy polarons. The temperature dependences and donor and acceptor concentration dependences of these BST polarons will be reported in a separate paper.

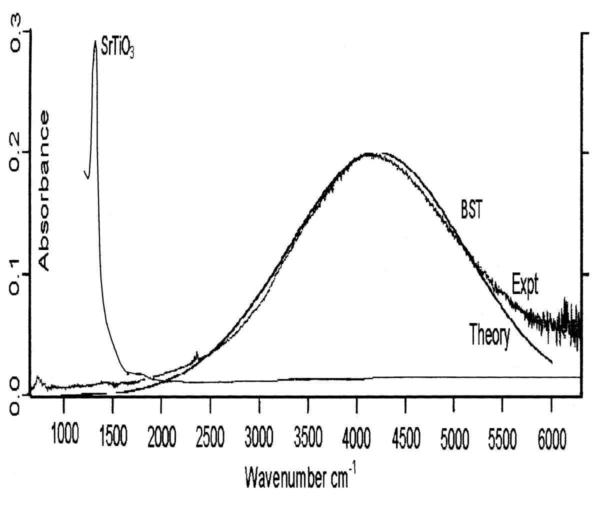

Fig. 2. Infrared data at 292 K of self-trapped polaron absorption associated with oxygen vacancies in 290 nm BST ceramic film (Brüker IFS113v spectrometer) and for a $SrTiO_3$ crystal, showing the known strong phonon peak at 1280 cm^{-1} but no polaron absorption.

6. Second-harmonic generation (SHG) data

Second-harmonic generation is a very useful technique for demonstrating the local breaking of symmetry in a centrosymmetric crystal. This occurs in our single-crystal strontium titanate and in BST films (Fig. 3) not only at surfaces, but also in the interior of the crystal. This is probably due to oxygen vacancy clusters but may also involve twin boundaries, mosaic spread, etc. — basically most kinds of local symmetry-breaking. However, in order to produce SHG the symmetry-breaking must be of odd parity and extend over a wavelength of visible light (ca. 500 nm), so that point defects, unless correlated (e.g. clusters) should not be efficacious. Note that long-range strains usually are not parity-breaking[32] and hence also should not produce SHG. However, infrared-absorption from nominally forbidden LO (longitudinal optical) phonons at surfaces ("Berreman modes") is well known.[32] The most important aspect of SHG in strontium titanate or BST is that oxygen vacancy clusters will permit[33] strong SHG in a nominally centric crystal of ABO_3 perovskite structure and that the SHG signal is linearly proportional to mean cluster polarisation size $<p(T)>$ (not physical cluster diameter). Thus the regions in the interior of single-crystal strontium

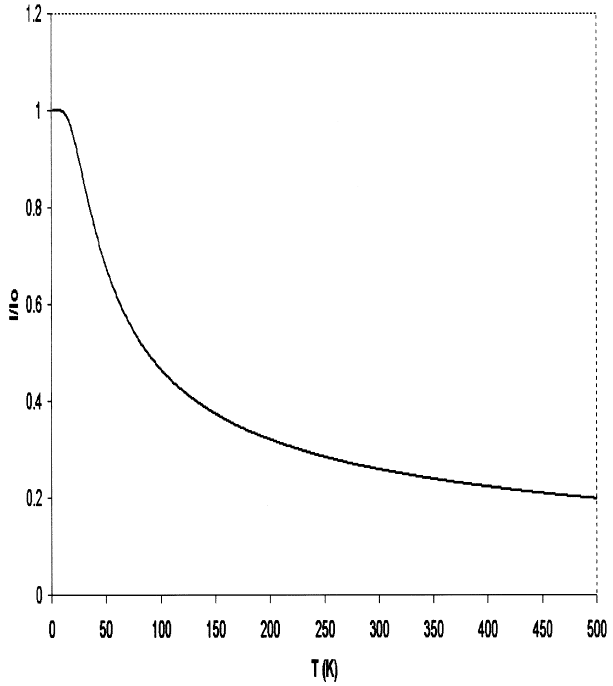

Fig. 3. Second-harmonic generation intensity theory from Ref. 33.

titanate specimens that exhibit strong SHG are likely to be clusters of oxygen vacancies, and these may in turn arise from local hydrogen concentrations.

References

1. Hase, T., Noguchi, T. and Miyasaka, Y., Analysis of the degradation of PZT and $SrBi_2Ta_2O_9$ thin films with a reductive process. *Integr. Ferroelectr.*, 1997, **16**, 29–40.
2. Scott, J. F., Limitations on ULSI-FeRAMs. *IEICE Trans. Elec. (Japan)*, 1998, **E81-C**, 477–487.
3. Aggarwal, S. et al., Recovery of forming gas damaged Pb(Nb, Zr,Ti)O_3. *Appl. Phys. Lett.*, 2000, **76**, 918–920.
4. Ashida, H. et al., Evaluation of electrical properties and SIMS profiles of forming-gas (N_2+H_2) annealed Pt/PZT/Pt capacitors. *Integ. Ferroelec.*, 1998, **21**, 97–105.
5. Shimamoto, Y. et al., H_2 damage of PZT thin-film capacitors. *Appl. Phys. Lett.*, 1997, **70**, 3096–3097.
6. Hong, S.-K. et al., (preprint); Hartmann, A. J. et al., Electronic and microstructure characterization of SBT thin films. *J. Korean Phys. Soc.*, 1998, **32**, S1329–1331; Shimakawa, Y. and Kubo, Y., Degradation of ferroelectric SBT under reducing conditions and their reaction with Pt electrodes. *Appl. Phys. Lett.*, 1999, **75**, 2839–2841.
7. Chen, A., Scott, J. F., Yu Zhi, Ledbetter, H. and Baptista, J., Dielectric and ultrasonic anomalies at 16, 37 and 65 K in $SrTiO_3$. *Phys. Rev.*, 1999, **B59**, 6661–6664.
8. Kityk, A. V., Schranz, W., Sondergeld, P., Havlik, D., Salje, E. and Scott, J. F., Low-frequency superelasticity and nonlinear elastic behavior of $SrTiO_3$ crystals. *Phys. Rev.*, 2000, **B61**, 946–956.
9. Salje, E. and Hoppmann, G., Small-polaron absorption in $W_xMo_{1-x}O_3$. *Phil. Mag.*, 1981, **B43**, 105–114.
10. Scott, J. F., Comment on the physical mechanisms of the 37 K and 65 K anomalies in strontium titanate. *J. Phys. Condens. Mater.*, 1999, **11**, 8149–8153.
11. Steinsvik, S., PhD thesis, Oslo, 1999.
12. Scott, J. F. and Ledbetter, H., Interpretation of elastic anomalies in $SrTiO_3$ at 37 K. *Z. Phys.*, 1997, **B104**, 61–70.
13. Barrett, H. H., *Physical Acoustics*, Vol. 6, ed. W. Mason and R. Thurston. Academic, New York, 1970.
14. Fujisaki, Y., Kushida-Abdelghafar, K., Shimamoto, Y. and Miki, H., The effects of the catalytic nature of capacitor electrodes on the degradation of ferroelectric PZT thin film during reductive ambient annealing. *J. Appl. Phys.*, 1997, **82**, 341–344.
15. Han, J.-P., Guo, X. and Ma, T. P., Memory effects of $SrBi_2Ta_2O_9$ capacitors on silicon with a silicon-nitride buffer. *Integ. Ferroelectr.*, 1998, **22**, 213–221.
16. Warren, W. L. et al., Relationships among fatigue, electronic charge trapping, defect-dipoles, and oxygen vacancies in perovskite oxides. *Integ. Ferroelectr.*, 1997, **16**, 77–84.
17. Al-Shareef, H., Dimos, D., Warren, W. L. and Tuttle, B. A., A model for optical and electrical polarization fatigue in $SrBi_2Ta_2O_9$ and Pb(Ti,Zr)O_3. *Integ. Ferroelectr.*, 1997, **15**, 53–67.
18. Takatani, S., Kushida-Abdelghafar, K. and Miki, H., Effect of H_2 annealing on a Pt/PZT interface studied by X-ray photoelectron spectroscopy. *Jpn. J. Appl. Phys.*, 1997, **36**, L435–L438.
19. Kanaya, H. et al., Hydrogen induced imprint mechanism of Pt/PZT/Pt capacitors by low-temperature hydrogen treatment. *Integ. Ferroelectr.*, 1999, **25**, 575–584.
20. Scott, J. F., A comparison of Ag- and proton-conducting ferroelectrics. *Solid State Ionics*, 1999, **125**, 141–146.
21. Balescu, R., *Statistical Dynamics*. Imperial College Press, London, 1997 pp. 238..
22. Fleury, P. A., Scott, J. F. and Worlock, J. M., Soft phonon modes and the 110 K phase transition in $SrTiO_3$. *Phys. Rev. Lett.*, 1968, **21**, 16–19.
23. Deis, D. W., Hulm, J. K. and Jones, C. K., (abstract). *Bull. Am. Phys. Soc.*, 1969, **14**, 61.
24. Scott, J. F., Raman spectroscopy of structural phase transitions. In *Light Scattering Near Phase Transitions*, ed. H. Z. Cummins and A. Levanyuk. North-Holland, Amsterdam, 1983, pp. 291–358.
25. Kleeman, W., Albertini, A., Kuss, M. and Lindner, R., Optical detection of symmetry breaking on a nanoscale in $SrTiO_3$:Ca. *Ferroelectrics*, 1997, **203**, 57–74.
26. Xi, X. X. et al., Dielectric loss of strontium titanate thin films on different substrates. *Integ. Ferroelectr.*, 1999, **25**, 239–246. .
27. Chen, A. et al., Dielectric polarization process in Bi:$SrTiO_3$. *J. Phys. Chem. Sol.*, 2000, **61**, 191–196.
28. Watanabe, M., Yagi, T. and Yamaguchi, M., Brillouin scattering study of quantum paraelectric $SrTiO_3$ under electric field. *J. Korean Phys. Soc.*, 1998, **32**, S556–S558.
29. Chen, A., Bhalla, A. S., Guo, R. and Cross, L. E., Dielectric loss of $SrTiO_3$ single crystals under direct current bias. *Appl. Phys. Lett.*, 2000, **76**, 1929–1931.
30. Worlock, J. M., Scott, J. F. and Fleury, P. A., Soft phonon modes and the 110 K phase transition in $SrTiO_3$. In *Light Scattering in solids*, ed. G. B. Wright. Springer-Verlag, New York, 1969, pp. 689–696.
31. Guettler, B., Bismayer, U., Groves, P. and Salje, E., Fatigue mechanisms in thin film PZT memory materials. *Semicond. Sci. Technol.*, 1995, **10**, 245–248.
32. Scott, J. F., Lattice perturbations in $CaWO_4$ and $CaMoO_4$. *J. Chem. Phys.,* 1968, **48**, 874–876; Dipole–dipole interactions in tungstates. *J. Chem. Phys.*, 1968, **49**, 98–100.
33. Prosandeev, S. A., Stabilization of the dipole state of a polaron near an oxygen vacancy in oxides of the perovskite family. *Sov. Phys. JETP*, 1998, **83**, 747–758.