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Materials Science and Engineering A 442 (2006) 55–58

MATERIALS SCIENCE & ENGINEERING A

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Anelastic relaxation in $SrTiO_3$ with O vacancies and H

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Received 29 July 2005; received in revised form 26 December 2005; accepted 26 December 2005

Abstract

We present the results of anelastic relaxation experiments (2–30 kHz) on ceramic $SrTiO_3$ subjected to reduction in H_2 atmosphere, which yields a balance between oxygen vacancy (V_O) and $(OH)^-$ defects. The resulting anelastic spectrum contains, besides the well known structural transformation near 110 K, several thermally activated relaxation processes between 200 and 700 K. The two main elastic energy loss peaks are proposed to provide the first measurement of the hopping rate of V_O and $(OH)^-$ defects in pure $SrTiO_3$.

PACS: 61.72.Ji; 62.40.+i; 66.30.Dn

Keywords: Perovskites; Anelastic spectroscopy; O vacancies

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1. Introduction

Strontium titanate has been studying for over 50 years, due to its quantum paraelectric state preventing ferroelectricity, and its superconductivity induced by doping [1], generally through introduction of O vacancies (V_O). In addition, it is used in various technological applications, like capacitors or film substrates. It has generally been assumed that the V_O introduced by high temperature reduction are uniformly distributed over the bulk, both in crystals and ceramics, but recent works put into discussion this assumption [2,3], together with the belief that $SrTiO_3$ supports a metal-insulator and superconducting transition at very low densities of carriers, and many researches on polaronic effects. It is suggested that it may be impossible to homogeneously reduce $SrTiO_3$ and describe its behavior in terms of standard point defect chemistry, since the reduction would occur only within a thick (5–10 μm for single crystals) highly defective surface layer [2].

Even the evaluation of the diffusivity of V_O in perovskites is not obvious. In fact, the ac dielectric response is insensitive to the motion of a V_O, unless bound to some defect causing an electric dipole, and the extraction of ionic diffusion data from conductivity experiments requires the unraveling of the temperatures dependences of σ from the formation of defects, their ionization, the mobility of the charge carriers [4]. Similarly, the measurements of the O tracer exchange rate may be affected by the surface reaction and diffusion through near surface defective layers [5]. The fact that a V_O is a defect of quadrupolar nature, therefore in principle possessing an anisotropic elastic dipole tensor λ [6] (see Fig. 1), prompted us to investigate the hopping dynamics of V_O in the model system $SrTiO_3$. The measurement of the dynamic compliance at frequency ω provides a direct measure of the hopping rate τ^{-1} through the condition $\omega\tau = 1$ at the absorption maximum, exactly like the dielectric spectroscopy, but without the contribution of free charges.

2. Experimental and results

The samples were prepared by solid-state reaction of $SrCO_3$ (Aldrich, 99.9%) and TiO_2 (Aldrich, 99.9%) mixtures for 6 h at 1100 °C. The resulting powder was milled, sieved and pressed in parallelepipeds with 4 cm height and 1 cm edge, which were sintered in air at 1450 °C. The resulting ceramics showed homogeneous microstructure and a relative density of 97%. Samples suitable for anelastic relaxation experiments (4.5 cm × 0.5 cm × 0.05 cm) were obtained by cutting and polishing.

The introduction of a sizeable concentration of O vacancies ($\delta > 0.001$) in $SrTiO_{3-\delta}$ requires extremely low O_2 partial pressure (therefore a reducing atmosphere) or temperatures exceed-

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doi:10.1016/j.msea.2005.12.087

ing 1200 °C. Here we show the effect of reducing a sample for 3 h in 450 mbar H_2 at 950 °C. The treatment was done in a quartz tube connected to a UHV system and a flux of H_2 was maintained in order to remove the O_2 evolved by the sample and reacted with H_2 to form H_2O. Although this method allows the O_2 partial pressure to be lowered to very low levels (but the actual O_2 partial pressure could not be measured), it has the drawback of introducing H together with O vacancies. The sample color turned from white-yellow to uniform dark gray and exhibited metallic conductivity. The evaluation of δ from the mass loss, $\delta \simeq 0.02$, was not reliable, possibly due to the evaporation of residual conductive silver paint, that was not completely removed before the reduction treatment and is necessary for the anelastic measurements.

The dynamic Young's modulus $E(\omega T) = E' + iE''$ was measured by electrostatically exciting the 1st and 5th flexural modes of the sample suspended with thin thermocouple wires at the nodal lines. The resonance frequencies were $\omega/2\pi \simeq 2$ and 28 kHz, and the temperature variation of the real part E' can be deduced from $E' \propto \omega^{1/2}$, while the elastic energy loss coefficient $Q^{-1} = E''/E'$ contains peaks of the form [6,7]

$$Q^{-1} \propto \frac{(\Delta\lambda)^2}{T\cosh^2(A/2k_{\mathrm{B}}T)}\frac{\alpha(\omega\tau)^{\alpha}}{1+(\omega\tau)^{2\alpha}} \qquad (1)$$

in correspondence with the temperatures at which $\omega\tau = 1$ for defects reorienting their elastic dipole by $\Delta\lambda$ (change in the defect contribution to strain) with relaxation time $\tau = \tau_0 \exp(E/k_{\mathrm{B}}T)/\cosh(A/2k_{\mathrm{B}}T)$, where E is the mean barrier between states differing in energy by A, the Fuoss–Kirkwood parameter $\alpha \le 1$ reproduces a possible peak broadening with respect to the pure Debye form with $\alpha = 1$.

Fig. 2 shows the $Q^{-1}(T)$ curves before and after the reduction treatment; some of the five thermally activated peaks must be connected with H defects. A method for evaluating δ is the determination of the temperature T_{C} of the cubic-to-tetragonal transformation. Such a temperature depends on several factors, including near-surface strains that may cause a gradient in T_{C} [8], but the doping level n should have a major effect, approximately as $\mathrm{d}T_{\mathrm{C}}/\mathrm{d}n = -2400$ [9] or -1800 K/mol [10]. The anelastic measurements were extended to liquid nitrogen temperatures, where the cubic-to-tetragonal transformation occurs, and Fig. 3 shows the effect of the above reduction treatment on the elastic modulus $E(T)$ around T_{C}. Without entering in the problem of determining T_{C} from the $E(T)$ curves, we observe that the reduction treatment shifted the step in the modulus by $\Delta T_{\mathrm{C}} = -10.5$ K, which, assuming $\delta = 0$ initially and $n = 2\delta$ after the treatment, yields $\delta \simeq 0.0025$.

This estimate, however, completely neglects the possible effect of H defects. Indeed, the doping dependence $T_{\mathrm{C}}(n)$ reported in Refs. [9,10] are for samples reduced in atmosphere containing H_2, as in our case, but the resulting doping level n was attributed exclusively to the V_{O}. In addition, it was shown that the charge carrier density n alone does not determine T_{C}, since doping $SrTiO_3$ with Nb produced an increase of T_{C} instead of a decrease [9]. In the absence of further data, we consider the above estimate $\delta \simeq 0.0025$ only indicative, and we assume that also a concentration of H defects comparable with δ is present.

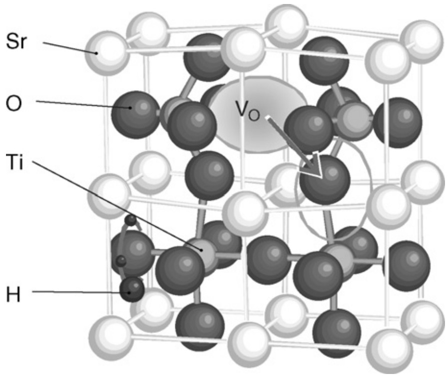

Fig. 1. O vacancy with the ellipsoid representing the anisotropic elastic dipole λ; the jump indicated by the arrow reorients λ by 90°. Also indicated is the ring of four positions of H around a Ti—O bond.

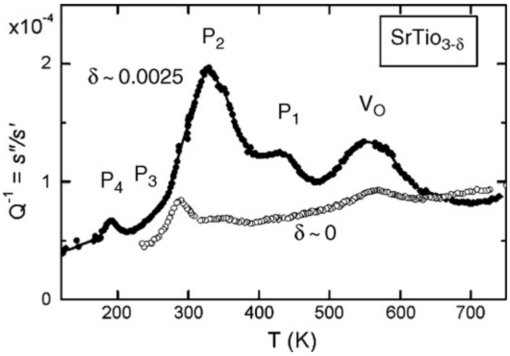

Fig. 2. Elastic energy loss of $SrTiO_{3-\delta}$ measured at $\omega/2\pi = 2$ kHz in the as prepared state ($\delta \simeq 0$) and after reduction in H_2 atmosphere ($\delta \sim 0.0025$).

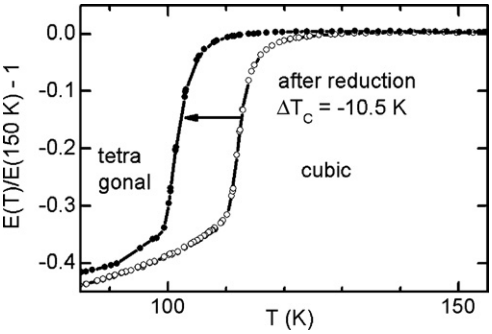

Fig. 3. Young's modulus around the cubic-to-tetragonal transition before (open symbols) and after (closed symbols) the reduction treatment.

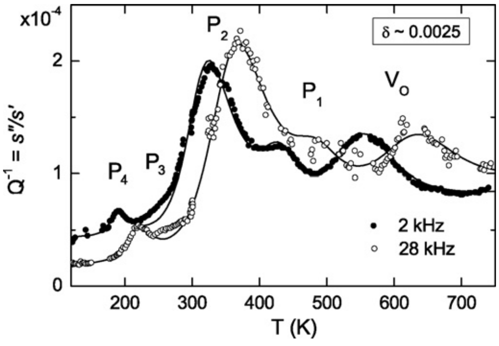

Fig. 4. Fit of the anelastic spectrum of $SrTiO_{3-\delta}$ after reduction in H_2 measured at two frequencies.