Anelastic relaxation in SrTiO$_3$ with O vacancies and H

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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 $\mu$m 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 temperature dependences of $\sigma$ 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 $\lambda$ [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 $\omega$ provides a direct measure of the hopping rate $\tau^{-1}$ 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 $\times$ 0.5 cm $\times$ 0.05 cm) were obtained by cutting and polishing.

The introduction of a sizeable concentration of O vacancies ($\delta > 0.001$) in SrTiO$_3$$_{3-\delta}$ requires extremely low O$_2$ partial pressure (therefore a reducing atmosphere) or temperatures exceed-
Fig. 1. O vacancy with the ellipsoid representing the anisotropic elastic dipole $\lambda$; the jump indicated by the arrow reorients $\lambda$ by $90^\circ$. Also indicated is the ring of four positions of H around a Ti–O bond.

Fig. 2. Elastic energy loss of SrTiO$_3$ 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.
3. Discussion

To our knowledge, no direct measurement of the hopping rate of VO in pure SrTiO₃ exists, but there are various evidences that the hopping barrier should be close to 1 eV, as in other Ti-based perovskites [5]: the activation energy of the VO mobility has been estimated as 0.86 eV on the basis of a series of experiments of electrical conductivity in variously doped SrTiO₃ [4]. Early isotope exchange measurements [11] indicated an activation energy of the tracer diffusion coefficient of 1.1 eV between 850 and 1350 °C in annealed crystals, which dropped to 0.67 eV in unannealed crystals; the lower value was attributed to faster diffusion along dislocations. A direct measurement of a VO hopping rate is probably contained in the dielectric spectra of Sr₁₋₁₅₅Bi₂TiO₃ where a relaxation process with activation energy of 1–1.1 eV is found [12]; in that case, however, the rate has to be attributed to a VO reorienting around a Bi substitutional cation or Sr vacancy, otherwise no reorientation of dielectric dipole would occur. Since τ₀ ~ 10⁻¹³ s for point defects, we expect that VO hopping with E = 1 eV gives rise to a peak around 566 K for ω/2π = 2 kHz, which is exactly the temperature of the peak labeled VO.

Fig. 4 shows the anelastic spectrum after reduction measured at two frequencies and fitted with four peaks of the form (1) with the parameters reported in Table 1; the comparison between fit and data evidences the presence of an additional peak labeled P₂.

All the peaks are compatible with point defect reorientation except P₄, which has a value of τ₀ more characteristic of a collective type of motion. They are also considerably broader than pure Debye relaxations, and peak P₂ has an intensity that increases with temperature, reproduced in terms of relaxation between asymmetric states.

It is clear that a VO has no electric dipole but may have an anisotropic elastic quadrupole δ (generally called elastic dipole) but there is great uncertainty on the expected magnitude of its anisotropic component Δλ. In fact, several first principle calculations indicate small atomic displacements around a VO in SrTiO₃ and PbTiO₃, mainly determined by the electrostatic interactions between the ions, and almost negligible and symmetric long range distortions [13]. This would imply negligible Δλ in Eq. (1) and therefore hardly detectable anelastic relaxation due to VO hopping, but it has recently been observed that calculations with larger supercells yield larger displacements [14,15]; the exaggerated cation displacements in Fig. 4 are based on these works.

Peak VO has two unexpected features. The first is that it is already observed in the as-prepared state, with an intensity only five times smaller than after the reduction treatment (open symbols in Fig. 2), but it is possible that some VO were already present after preparation in order to compensate some acceptor impurities and Sr vacancies [4]. If this is the case, from the lack of temperature shift of the peak, it can be concluded that the hopping rate of the VO is little affected by the presence of the acceptor defects, even though it is likely bound to them at the relatively low temperature of 600 K where the peak is observed (for example, the binding energy of VO to Sr is calculated as Eᵥ₅/KB = 4000 K [13] and that to FeTi₃ is found to be 3100 K [16]).

The other interesting feature of peak VO is its width; due to experimental difficulties, there is a large error on the measurements of the 5th flexural mode, and it cannot be ascertained whether the peak broadening is due to Curie–Weiss–like interactions among the VO elastic dipoles, as in Ru-1212 [17], or if it is inhomogeneous broadening, but in both cases the idea that VO are confined within a surface layer is supported. Such a confinement would be due to surface strains, whether due to dislocations [2,3] or to surface effects in the otherwise perfect crystallites [8,18]. The strained layer is reported to extend to depths of tens of microns in perfect single crystals [18], a distance much larger than the average grain size in our samples, while highly defective layers are reported to be 5–10 μm thick [2]. In both cases, if the observations reported for large crystals are valid also for the crystallites in the ceramic, one concludes that such crystallites must be highly strained. Such strains are reported to rise the temperature of the cubic-to-tetragonal instability by tens of Kelvin [8,19], and this might be the reason why the E(T) curve of the as-prepared sample (Fig. 4) indicates Tc > 110 K, while it is generally reported Tc = 105 K in single crystals. Such internal strains might well be responsible for an inhomogeneous broadening of peak VO, but even if its broadening were due to interactions among the VO elastic dipoles, the latter should be somehow clustered in order to have a locally high concentration. This deduction derives from a comparison with RuSr₂GdCu₂O₈₋ₓ, where the peak due to the hopping of 6 ~ 0.02–0.03 O vacancies was 200 times more intense (Qmax ≃ 0.011) than peak VO in SrTiO₃ if (Qmax ≃ 5 × 10⁻⁵). Since both the intensity of the peak due to the elastic dipole reorientation and the interaction strength among the dipoles are proportional to δ × (Δλ)², a peak as small as peak VO in Fig. 4 could not present significant interaction effects, unless the dipoles were confined in regions with δ much higher than the average value.

The peaks at lower temperature must be due to H defects certainly introduced by reduction in H₂ atmosphere and possibly to polarons connected with both VO and H. Hydrogen is generally introduced in acceptor-doped perovskites ABO₃ treated in H₂O, and it is proposed to form an OH⁻ ion, with H within the plane perpendicular to the B–O bonds [20] almost at the center of a A₂B₂ tetrahedron (Fig. 4). There are four of these positions around a same B–O bond, and H might perform fast rotational hopping within such a ring, while long range diffusion requires hopping to a different ring. The barrier for changing B–O bond has been estimated from ac conductivity experiments in SrTiO₃ doped with 5% Sc as 0.41 eV and from molecular dynamics simulations as 0.5 eV [21]. We propose that peak P₂ is due to

<table>
<thead>
<tr>
<th>Parameters used for the fit of Fig. 4</th>
<th>E (eV)</th>
<th>A (eV)</th>
<th>t₀ (s)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO</td>
<td>0.98</td>
<td>0</td>
<td>1 × 10⁻¹³</td>
<td>0.7</td>
</tr>
<tr>
<td>P₁</td>
<td>0.85</td>
<td>0</td>
<td>1 × 10⁻¹⁴</td>
<td>0.76</td>
</tr>
<tr>
<td>P₂</td>
<td>0.61</td>
<td>0.08</td>
<td>2 × 10⁻¹⁴</td>
<td>0.5</td>
</tr>
<tr>
<td>P₄</td>
<td>0.29</td>
<td>0</td>
<td>2 × 10⁻¹³</td>
<td>1</td>
</tr>
</tbody>
</table>
such jumps, and the difference in the barrier, $E = 0.61 \text{ eV}$ in the present case, may be attributed to the influence of Sc doping. None of the peaks in Fig. 4 may be attributed to fast hopping about a same Ti–O bond, which probably causes anelastic relaxation at much lower temperature, while peak $P_1$ may be compared with peak B in the dielectric spectrum of Bi-doped SrTiO$_3$, attributed to some polaronic mechanism [12].

4. Conclusions

Although in this preliminary experiments it was not possible to introduce a sufficiently high concentration of O vacancies without the complication of additional H defects, an anelastic relaxation peak with an activation energy of 1 eV has been found, which most likely constitutes the first direct measurement of the hopping rate of VO in pure SrTiO$_3$. The considerable peak width supports the view that a large fraction of VO is confined within a highly defective surface layer in SrTiO$_3$ crystals. Other four peaks with smaller activation energies are present in the anelastic spectrum, some of which are attributed to the presence of OH$^-$ complexes, since the sample reduction was performed in H$_2$ atmosphere. The hopping rates of both VO and H defects deduced from the anelastic spectrum of pure SrTiO$_3$ are close to those found with other techniques in SrTiO$_3$ doped by cation substitution.

References