Anelastic spectroscopy for studying O vacancies in perovskites

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Abstract

We present the results of anelastic relaxation experiments (2–30 kHz) on ceramic $SrTiO_3$ subjected to reduction in H_2 atmosphere, which yield a balance between 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 $V_O –(OH)^-$ defects in pure $SrTiO_3$.
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1. Introduction

Oxygen vacancies (V_O) are considered as one of the most common defects in perovskites, and are held responsible for a variety of effects, often undesired, such as fatigue, aging, doping of charge carriers in ferroelectric and dielectric materials; they are also introduced on purpose in order to obtain ionic conduction and are thought to play an important role in determining the physical properties of earth's lower mantle, whose prevalent phase is a perovskite. Yet, the microscopic parameters of V_O in perovskites, such as the activation energy for diffusion, are generally known with great uncertainty. Strontium titanate is an emblematic case; it has been studied for over 50 years as a model system where the quantum paraelectric state prevents ferroelectricity, and superconductivity may be induced by doping,[1] generally with O vacancies; in addition, it is used in various technological applications, notably film substrates and capacitors. The mobility of V_O in $SrTiO_3$, however, is poorly characterized, as demonstrated by a recent compilation of O chemical diffusion data.[2] Even more striking are the recent indications that the V_O introduced by high temperature reduction are not uniformly distributed over the bulk, as generally assumed for both crystals and ceramics, but would form clusters[3] or might

form only in highly defective near-surface layers.[4] Such observations put into discussion much of the past research on $SrTiO_3$, especially on polaronic effects, including the belief that it supports a metal-insulator and superconducting transition at very low densities of carriers.

Here, we discuss how the anelastic spectroscopy, namely the measurement of the complex dynamic elastic modulus $M = M' + iM''$ or compliance $s = s' - is'' = M^{-1}$, may significantly contribute to the study of the mobility and ordering of V_O in perovskites. In fact, a V_O has a quadrupolar symmetry that is in principle associated with a tetragonal strain reorienting by $90°$ after each jump (see Fig. 1), whereas the associated electric dipole is null in a perfect cubic perovskite. Then, 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 for dielectric spectroscopy, but without the contribution of free charges to the relaxation spectrum.

After introducing an interpretative framework and reviewing the few existing data in the literature, preliminary results will be presented on the hopping dynamics of V_O in $SrTiO_3$ reduced in H_2 atmosphere.

2. Anelastic and dielectric relaxation from O vacancy hopping

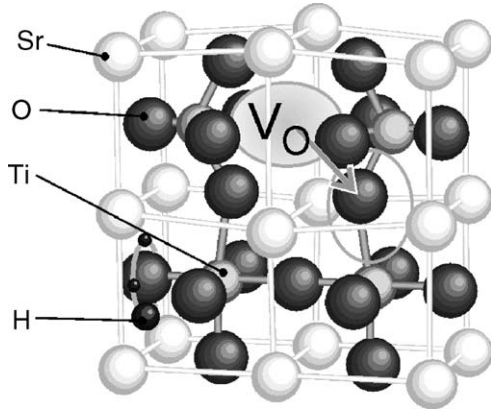An O vacancy in a cubic perovskite ABO_3 has tetragonal symmetry, with quaternary axis along the direction of the nearest

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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.

neighbour B atoms, as shown in Fig. 1. Therefore, a uniform concentration c_x of V_O with tetragonal axis x will give rise to an anisotropic strain

$$\varepsilon = c_x \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda2 \end{bmatrix} = c_x \lambda^{(x)} \tag{1}$$

and similarly for the other orientations $\alpha = y, z$, where $\lambda^{(\alpha)}$ is called elastic dipole tensor,[5] by analogy with the electric and magnetic dipole, although it is actually a quadrupole. The uniaxial strains along the tetragonal axis, λ_1, and in the perpendicular plane, λ_2, are negative in case of compression and positive in case of expansion. Fluctuations in the populations c_α of the three types of orientations are reflected as strain fluctuations, since $\varepsilon = \Sigma_\alpha c_\alpha \lambda^{(\alpha)}$; for the cubic case, the fluctuating symmetric strains are of tetragonal symmetry, $\varepsilon^t = 2\varepsilon_3 - \varepsilon_1 - \varepsilon_2$, and orthorhombic symmetry, $\varepsilon^o = \varepsilon_1 - \varepsilon_2$ (using the notation $\varepsilon_1 = \varepsilon_{xx}$, etc.). The tetragonal strain is coupled to fluctuations of the type $c_z = c/3 + \delta c$ and $c_{x,y} = c/3 - \delta c/2$, giving rise to $\varepsilon^t = 2\delta c(\lambda_1 - \lambda_2)$, and similarly for the orthorhombic strain; clearly, the strain fluctuations are proportional to the anisotropic component $\Delta\lambda = \lambda_1 - \lambda_2$ of the elastic dipole. Both strains are related to the corresponding stresses through the elastic compliance $s_{11} - s_{12}$, as $\varepsilon^{t,o} = (s_{11} - s_{12}) \sigma^{t,o}$. The application of a periodic stress σ with angular frequency ω perturbs the elastic energies of the various dipoles and therefore their populations, resulting in a strain response out of phase of ϕ with respect to stress; then, the compliance acquires a complex relaxational component[5]

$$\delta(s_{11} - s_{12}) = \frac{2}{3} \frac{cv_0}{k_B T} (\Delta\lambda)^2 \frac{1}{1 + i\omega\tau} \tag{2}$$

where τ is the relaxation time, related to the hopping rate Γ of a V_O to a specific nearest neighbour position through $\tau^{-1} = 12\Gamma$. The imaginary part produces absorption, and the elastic energy loss coefficient, or reciprocal of the mechanical Q, is $Q^{-1} = \tan\phi = s''/s'$ or, neglecting the relaxational contribu-

tion to s' and setting $s' = s_{11} - s_{12}$,

$$Q^{-1} = \frac{2}{3} \frac{cv_0(\Delta\lambda)^2}{(s_{11} - s_{12})k_B T} \frac{\omega\tau}{1 + (\omega\tau)^2} \tag{3}$$

which is peaked at $\omega\tau = 1$. Measurements are generally made as a function of temperature at the fixed frequencies determined by the sample or transducer resonances. The factor 2/3 in the above equation is valid for application of $\sigma^{t,o}$ stresses to a single crystal; for a polycrystal, it should be reduced due to angular averaging and porosity. Note that the dielectric relaxation is given by the same expressions with electric dipoles **p** instead of elastic quadrupoles λ, dielectric susceptibility χ instead of the compliance s and possibly slightly different factors relating the relaxation time to the hopping rates.[6] When interpreting dielectric experiments, it is customary to neglect the temperature dependence of the relaxation strength, which is simply set to $(\varepsilon_0 - \varepsilon_\infty)/\varepsilon_\infty$.

To our knowledge, no measurements of the elastic quadrupole tensor λ of V_O in perovskites exist, but first principle calculations indicate small atomic displacements around an V_O in $SrTiO_3$ and $PbTiO_3$, mainly determined by the electrostatic interactions between the ions, and almost negligible and isotropic long range distortions,[7] although more recent calculations on larger supercells indicates more substantial displacements[8,9]; the exaggerated cation displacements in Fig. 1 are based on these works. It is therefore possible that the anisotropic component $\Delta\lambda = \lambda_1 - \lambda_2$ and therefore the amplitude of the anelastic relaxation due to V_O hopping are rather small. Yet, V_O hopping in a perovskite is in principle detectable by anelastic relaxation, while it is not by dielectric relaxation. In fact, there is no electric dipole associated with a V_O, unless some chemical disorder exists; for example, if a V_O is trapped at a Fe^{3+} substituting a Ti^{4+} in $SrTiO_3$, then an electric dipole is created within the Ti^{4+}–V_O–Fe^{3+} cluster. In this case, however, one measures the hopping rate around the dopant and not in the regular lattice.

2.1. Jumps between inequivalent sites

If for simplicity, we consider a small amount of acceptor dopants in the B sublattice of ABO_3 inducing the formation of V_O, e.g. Fe_{Ti}, the potential profile for V_O hopping should appear as in Fig. 2. Hopping between O sites far from the dopants occurs over a barrier E_f with a mean rate Γ_f, while hopping around the dopants occurs over a barrier E_t with a mean rate Γ_t; also indicated in the figure is the binding energy E_b of the complex dopant-V_O. Jumps of the type $3 \rightarrow 2$ for the vacancy

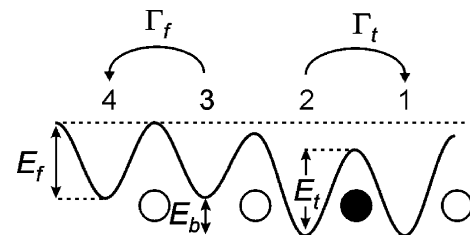Fig. 2. Potential energy profile felt by an O vacancy hopping near a trapping donor impurity (black circle).