

Role of trivalent Sr substituents and Sr vacancies in tetragonal and polar states of SrTiO₃

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Abstract

Inelastic light scattering is used to study lattice dynamics of strontium titanate (STO) ceramics with several heterovalent dopants (La³⁺, Gd³⁺, Y³⁺), which substitute Sr²⁺ ions. An extraordinary shift of the antiferrodistortive transition temperature (T_a) is ascertained when just a small percentage of any of the dopants is used. T_a is dependent on the tolerance factor (t). In this work, it is clearly shown that, regardless of the dopant used, a common linear dependence of T_a vs. t is obtained if strontium vacancies are taken into account. A vacancy size of ~ 1.547 Å was estimated, which is $\sim 7\%$ larger than the Sr²⁺ radius. The vacancy size obtained can directly explain the increase in lattice parameter with increasing Bi³⁺ content in Bi-doped STO, as opposed to the dopants referred to above. Furthermore, the introduction of La³⁺, Gd³⁺ or Y³⁺ ions at the Sr site causes a considerable stiffening of the transverse optic TO₁ mode at low temperatures, thereby decreasing the phonon contribution to the dielectric permittivity. Thus, no traces of a ferroelectric phase are found for any of the dopants used in this work.

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1. Introduction

Strontium titanate (SrTiO₃; STO), as a member of perovskite structure materials family, has been extensively studied and has drawn the attention of researchers for its distinctive properties, related to both cubic–tetragonal phase transition occurring at $T_a \sim 110$ K [1] and suppression of a ferroelectric state at low temperatures [2]. The former has been understood within the framework of a triply degenerated soft mode at the Brillouin zone boundary associated with the anti-phase rotation of the oxygen octahedral [3]. It has been described within the scope of the Landau theory, wherein long-range strain interactions are considered [4]. On the other hand, suppression of the ferroelectric state

has been attributed to paraelectric state stabilization brought about by quantum fluctuations at low temperatures, from where STO is known as incipient ferroelectric or quantum-paraelectric [2]. Nevertheless, the effect of quantum fluctuations itself does not fully explain the behaviour of STO at low temperatures. Furthermore, first-principle calculations and hyper-Raman measurements [5,6] have indicated that tetragonal distortion, which emerges on entering the antiferrodistortive phase transition, also plays an important role in suppressing the ferroelectric phase.

All previous studies addressing STO have thus far revealed that whenever an electric field [1,7] or strain [8] is applied or dopants [9–16] are introduced into the STO lattice, large changes are evident in the lattice parameters and hence in physical properties. Dopants in particular may induce a variety of phases at low temperatures, ranging from dipolar glass to relaxor and ferroelectric. This

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occurs in isovalent substitution of Sr^{2+} by Pb^{2+} [9], Ba^{2+} [10], Ca^{2+} [11] and Mn^{2+} ions [12], and in heterovalent substitution of Sr^{2+} by Bi^{3+} ion [13,14,16]. It has been reported, however, that a polar state is not induced by La^{3+} incorporation on the Sr^{2+} site [17]. Instead, the low-temperature dielectric permittivity decreases.

Furthermore, T_a can also be drastically affected by isovalent substitution [18]. Recently, it has been shown that T_a variation is dependent on the Goldschmidt tolerance factor, t [19]. It has been revealed that an increase in t leads to a decrease in T_a and vice versa.

Unlike isovalent substitution, heterovalent doping of STO has been neither fully understood nor systematically studied so far. Moreover, to the best of our knowledge, there is no reference in the literature to STO single crystals with heterovalent dopants at the A site. Only the $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$ ceramic has attracted attention due to the fact that a polar state is detected in this system [13–16]. The origin of such “polar peculiarity” has been related to off-centre displacements of small Bi^{3+} ions on large Sr sites. However, it is not clear why the lattice parameter of $\text{Sr}_{1-1.5x}\text{Bi}_x\text{TiO}_3$ system increases with bismuth content as opposed to other $\text{Sr}_{1-1.5x}\text{M}_x\text{TiO}_3$ systems [13], whereas the radius of Bi^{3+} , like all trivalent ions, is smaller than that of Sr^{2+} [20]. Thus, it is necessary to identify what the main issues are regarding the heterovalent substitution of Sr^{2+} in the STO lattice.

It is important to note that, along with the substitution of Sr^{2+} by trivalent ions, strontium vacancies are formed in order to maintain charge neutrality. Whenever substitution occurs, three Sr^{2+} ions are randomly removed and replaced by two trivalent ions and one strontium vacancy. Whilst the radii of the trivalent ions are already known, or can be accessed from the data available in the literature [20], the strontium vacancy size has never been determined.

The present work aimed to study both the effect of heterovalent substitution of STO in cubic–tetragonal phase transition and polar properties at low temperatures using Raman spectroscopy. For this purpose, trivalent ions ($\text{M} = \text{La}$, Gd and Y) were selected. Though their radii are actually smaller than that of the Sr^{2+} ion, they are nevertheless relatively similar [20], and thus yield a sufficient solubility to process different single-phase compositions. The fact that their radii are similar assures a certain degree of “continuity”, which is needed to thoroughly understand the effect of the ionic radius on STO behaviour. The strontium vacancy size is estimated from Raman data, by assuming a common linear dependence of T_a upon the tolerance factor, regardless of the type of dopant used in this work. This model is also applied to data available from the literature on Bi-doped STO.

2. Experimental

2.1. Sample preparation

$\text{Sr}_{1-1.5x}\text{M}_x\text{TiO}_3$ ceramics, with $\text{M} = \text{La}^{3+}$ ($x = 0.013$, 0.053), Gd^{3+} ($x = 0.01$, 0.02) and Y^{3+} ($x = 0.005$, 0.01),

were prepared by the solid-state reaction of weighed batches of SrCO_3 , TiO_2 and Y_2O_3 or Gd_2O_3 or La_2O_3 . After ball milling in alcohol for 5 h, using Teflon pots and zirconia balls in a planetary mill, the powders were dried and then calcined at 1150°C for 2 h. The calcined powders were milled again for 5 h to obtain powders with a particle size of less than $5\ \mu\text{m}$. Pellets 10 mm in diameter were uniaxially pressed at 100 MPa and then isostatically pressed at 200 MPa. In order to get dense ceramics, the sintering was performed in air at 1500°C for 5 h, with heating and cooling rates of $5^\circ\text{C}\ \text{min}^{-1}$. No secondary phase was observed in the obtained ceramics by both X-ray diffraction and energy-dispersive spectroscopy. From the absence of a secondary phase, the processing method used and the light colour of the obtained ceramics, no reduction in titanium ions was expected. Thus, the charge compensation should be reached mainly via formation of strontium vacancies, as has been generally accepted for donor ion substitution at the A-site [19]. The possibility of B-site substitution by the selected dopants looks highly improbable due to the dopant ionic size being 1.49–1.71 times larger than that of the host Ti^{4+} [20] and the high packing density of ions in SrTiO_3 , reflected in the tolerance factor being very close to 1.

2.2. The Raman technique

Unpolarized Raman spectra were recorded in the spectral range of $10\text{--}1000\ \text{cm}^{-1}$, using a Spectra Physics argon laser operating at $\lambda = 514.5\ \text{nm}$ in a pseudo-backscattering geometry. The scattered radiation was analysed using a Jobin–Yvon T64000 spectrometer equipped with a CCD and a photon-counting detector. The spectral slit width was about $1.5\ \text{cm}^{-1}$. The spectra were registered with a step of 5 K in the temperature range $10\text{--}300\ \text{K}$ at constant temperature, after a waiting time of about 15 min.

A model of independently damped harmonic oscillators, according to the general formula [21]:

$$I(\omega, T) = (1 + n(\omega, T)) \sum_{j=1}^N A_{oj} \frac{\omega \Omega_{oj}^2 \Gamma_{oj}}{(\Omega_{oj}^2 - \omega^2) + \omega^2 \Gamma_{oj}^2} \quad (1)$$

was used for fitting first-order Raman modes, after extracting the corresponding background from each spectrum. Here $n(\omega, T)$ is the Bose–Einstein factor; A_{oj} , Ω_{oj} and Γ_{oj} are the strength, wavenumber and damping coefficient of the j th oscillator, respectively.

3. Results

3.1. Undoped STO ceramics

The unpolarized Raman spectra of SrTiO_3 ceramics at different fixed temperatures are shown in Fig. 1a. Second-order features dominate the spectra at all temperatures. With decreasing temperature, however, the spectra present extra Raman-forbidden infrared-active modes that stem

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