



# Temperature dependence of the damping constant and the relaxation time close to the tetragonal-cubic phase transition in SrZrO<sub>3</sub>



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## ABSTRACT

The damping constant  $\Gamma_{sp}$  due to the pseudospin-phonon coupling is calculated as a function of temperature using the pseudospin-phonon coupled model and the energy fluctuation model close to the tetragonal-cubic transition ( $T_C = 1443$  K) in SrZrO<sub>3</sub>. Using the observed Raman frequencies and the linewidth (FWHM) of the soft modes ( $E_g$  and  $A_{1g}$ ) from the literature, predictions of both models studied, are examined for the tetragonal-cubic transition in this crystalline system. Values of the activation energy  $U$  are extracted and also the inverse relaxation time is predicted as a function of temperature close to the phase transition studied in SrZrO<sub>3</sub>.

Divergence behaviour of the damping constant (FWHM) of the soft modes is predicted from both models as also observed experimentally when  $T_C$  is approached from the tetragonal to the cubic phase in SrZrO<sub>3</sub>. The relaxation time also diverges close to the  $T_C$  in this crystal. It is indicated that the tetragonal-cubic transition is of a second order as predicted from both models studied here, as also observed experimentally in SrZrO<sub>3</sub>.

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## 1. Introduction

Perovskite-type oxide structures which have the general formula of ABO<sub>3</sub> where A = Ca, P for Ba and B = Ti or Zr, have been investigated extensively since 1940s [1]. Among those materials, SrZrO<sub>3</sub> has also been studied extensively due to its high-temperature applications such as fuel cells, electrolysis and hydrogen gas sensors [2–4].

SrZrO<sub>3</sub> undergoes a series of phase transitions. It is orthorhombic (space group Pbnm) at room temperature and changes to the orthorhombic Cmcm at 973 K. As the temperature increases to 1103 K, its crystal structure changes to the tetragonal (I4/mcm) and then to cubic Pm $\bar{3}$ m transition at 1443 K [5–12]. This perovskite material has a high melting temperature of about 2920 K [13] so that it has a cubic structure in a wide range of temperature, which is favorable from the point of view of technological applications as also pointed out previously [4]. Structural changes in SrZrO<sub>3</sub> have been studied experimentally by thermal analysis and X-ray neutron diffraction [5,6] and by the measurements of high-temperature heat capacity and thermal expansion [7,8], elastic anomalies in

the SrZrO<sub>3</sub>-SrTiO<sub>3</sub> solid solution [15]. Recently, structural phase transitions in SrZrO<sub>3</sub> have been investigated with the differential scanning calorimetry (DSC), high temperature X-ray diffraction and dilatometry as anomalies of thermal expansion coefficients [16]. The phase transitions in this material have been obtained as second order, first order and second order at 1042, 1119 and 1375 K, respectively and the variation of heat capacity ( $\Delta C_p$ ) at the second order phase transition has been calculated [16]. Photoluminescence emission in SrZrO<sub>3</sub> and SrTiO<sub>3</sub> perovskites [3,17] and phase transition in SrZrO<sub>3</sub> by Raman spectroscopy [11,12] have also been studied experimentally. First-principles density functional calculations have been performed to study the electronic properties of SrZrO<sub>3</sub> [4]. Using density functional perturbation theory, the optical dielectric constant, Born effective charges and phonon dispersion curves of cubic SrZrO<sub>3</sub> have been evaluated [18]. Using this theory, the electronic band structure, the electronic and lattice contribution to the dielectric constant of orthorhombic SrZrO<sub>3</sub> have been investigated [19]. Also, the electronic band structure of orthorhombic Pbnm SrZrO<sub>3</sub> has been calculated using a density functional theory with local spin-density approximation method [20]. The optical properties of cubic SrZrO<sub>3</sub> have been calculated and it has been pointed out that there are no experimental data for optical properties of the paraelectric cubic phase of this compound [21].

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More recently, using first-principles calculations the electronic, structural and vibrational properties of SrZrO<sub>3</sub> have been investigated [22].

It has been shown that a phase transition in SrZrO<sub>3</sub> is due to the consideration of a soft mode of vibration associated with the relations of the oxygen octohedron in the cubic phase [6], in particular, the phase transition between cubic and tetragonal phases ( $T_C = 1443$  K) is due to the collapse of the R<sub>25</sub> mode at the R point of the cubic Brillouin zone [11]. The lattice dynamics of cubic SrZrO<sub>3</sub> has shown that the experimentally observed I4/mcm and Imma low-symmetry phases can be regarded as results of soft mode condensation at R and M points, respectively [18]. Due to the fact that the two lowest-frequency Raman-active E<sub>g</sub> and A<sub>1g</sub> modes in the tetragonal (I4/mcm) phase originate from the soft R<sub>25</sub> (F<sub>2u</sub>) mode in the cubic phase of SrZrO<sub>3</sub>, their Raman frequencies soften as T → T<sub>C</sub> toward the tetragonal (I4/mcm) phase (below T<sub>C</sub>) and the temperature dependence of both soft modes (E<sub>g</sub> and A<sub>1g</sub>) obeys the Curie law, also those soft modes remain underdamped and their damping constant (linewidth) increases with temperature [23], as pointed out previously [11]. Experimentally, those two optical modes (E<sub>g</sub> and A<sub>1g</sub>) showed remarkable softening approached together and their peak intensities continuously decreased with increasing temperature, as pointed out previously [18]. In particular, between the orthorhombic (Pbnm) and orthorhombic (Cmcm) phases, the Raman mode A<sub>g</sub> (at 500 cm<sup>-1</sup>) as an optical mode shows considerable softening up to 973 K and hardening above 1023 K, as observed experimentally [12]. In a phase transition involving Raman active modes, the order parameter is a rotation (internal strain) of the ZrO<sub>6</sub> octohedra associated with a soft  $q \approx 0$  acoustical phonon (the ferroelastic mode) [12] as the ferroelastic transition of the optical type [24]. Thus, it has been indicated that the phenomenon of softening and hardening at around T<sub>C</sub> can be interpreted as originating at the phase transition temperature, which satisfies the universal scaling of the internal strain coordinate that is associated with the optical A<sub>g</sub> mode as an order parameter [12].

As shown by various ferroelectric materials such as KDP (potassium dihydrogen phosphate), TGS (triglycine sulfate), BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> (PZT-x) etc., the dynamic properties of SrZrO<sub>3</sub> can change near the tetragonal-cubic transition (T<sub>C</sub> = 1443 K). As in the ferroelectric compounds stated above, the tetragonal-cubic transition in SrZrO<sub>3</sub> is associated with the soft modes, mainly the E<sub>g</sub> and A<sub>1g</sub> modes with the Raman frequencies decreasing abruptly as the T<sub>C</sub> is approached from the tetragonal to the cubic phase with increasing temperature. Not only the Raman frequencies of those soft modes but also their linewidths (FWHM) and the relaxation time as expected, exhibit anomalous behaviour near T<sub>C</sub> in SrZrO<sub>3</sub>. The anomalous behaviour of those physical quantities considered near T<sub>C</sub> as observed experimentally, can be described by the theoretical models. In particular, the temperature dependence of the Raman frequencies, linewidths and the relaxation time of the soft modes (E<sub>g</sub> and A<sub>1g</sub>) in SrZrO<sub>3</sub>, which are associated with the phase transition between the tetragonal and the cubic phases in this compound can be investigated near T<sub>C</sub>. Thus, by analyzing the experimental data for the dynamic quantities on the basis of the predictions of the theoretical models, a first order and second order (or weakly first order and nearly second order) nature of the transition between the tetragonal and cubic phases, can be explained in SrZrO<sub>3</sub>. This is the motivation of our study given here.

In this study, by considering the temperature dependence of the Raman frequencies of the soft modes (E<sub>g</sub> and A<sub>1g</sub>) as an order parameter in SrZrO<sub>3</sub>, we calculate the damping constant (linewidth) of those modes for the tetragonal-cubic transition (T<sub>C</sub> = 1443 K) in this material. For this calculation, pseudospin-phonon coupled model and the energy fluctuation model are

used, which have been applied to the KDP type ferroelectrics [25,26]. We have used previously those two models to calculate the temperature dependence of the damping constant of different phonon modes for BaTiO<sub>3</sub>[27,28], PbTiO<sub>3</sub>[29] and PbZr<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> (x = 0.45) [30]. In the present work, by using the experimental data for the Raman frequencies of the E<sub>g</sub> and A<sub>1g</sub> phonon modes in SrZrO<sub>3</sub>[11], the damping constants due to both models are fitted to the observed linewidths (FWHM) near the tetragonal-cubic phase transition. Activation energy is deduced from the temperature dependence of the damping constant of the soft modes (E<sub>g</sub> and A<sub>1g</sub>) and the inverse relaxation time is predicted as a function of temperature in SrZrO<sub>3</sub>. Below, in Section 2 we give our calculations and results. In Sections 3 and 4, discussion and conclusions are given.

## 2. Calculation and results

The temperature dependence of the damping constant for the soft modes (E<sub>g</sub> and A<sub>1g</sub> modes) in SrZrO<sub>3</sub> was calculated using two models, namely, pseudospin-phonon coupled model and the energy fluctuation model. In those two models, the damping constant  $\Gamma_{sp}$  is calculated from the temperature dependence of the order parameter  $P$  due to the pseudospin-phonon interaction according to the relation

$$\Gamma_{sp} \propto (1 - P^2) \langle \tau_q^2 / \tau \rangle \quad (1)$$

where  $\tau_q$  is the relaxation time of the order parameter with wave vector  $q$  and  $\tau$  is the flipping time of the pseudospins. This ratio of  $\langle \tau_q^2 / \tau \rangle$  can be considered as the effective correlation time of the order parameter  $P$ [25] with the non-interacting parameter  $\tau$ . The temperature dependence of the damping constant  $\Gamma_{sp}$  for the pseudospin-phonon coupled model has been obtained [31] in the form of [25,26].

$$\Gamma_{sp} \approx A(1 - P^2) \ln \left[ \frac{T_C}{T - T_C(1 - P^2)} \right] \quad (2)$$

which we express as

$$\Gamma_{sp} = I'_0 + A'(1 - P^2) \ln \left[ \frac{T_C}{T - T_C(1 - P^2)} \right] \quad (3)$$

where  $I'_0$  is the background damping constant (linewidth),  $A'$  is a constant and  $T_C$  denotes the transition temperature.

The pseudospin-phonon coupling which causes the phonon frequencies shifted, has also been studied [32] since the shift in the phonon frequency is proportional to the order parameter so that the critical broadening occurs due to the energy fluctuation of the phonon mode [25]. This gives rise to the energy-fluctuation model with the damping constant

$$\Gamma_{SP} = I_0 + A \left[ \frac{T(1 - P^2)}{T - T_C(1 - P^2)} \right]^{\frac{1}{2}} \quad (4)$$

where  $I_0$  is the background damping constant and  $A$  is also a constant, as before. Including the soft mode-hard mode interaction, the damping constant strongly depends on the temperature [33] and with the anharmonic interactions for a soft mode frequency in the form

$$\omega_s = \omega_0(T_C - T)^{\frac{1}{2}} \quad (5)$$

the damping constant can be expressed [25] as

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