

Specific Heat of Cubic Phase of Protonic Conductor SrZrO₃

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Strontium zirconate belongs to ABO₃ perovskite oxides family and based on their potential applications, this material is attracting interest because of its chemical and mechanical stability at high temperatures as well as their high protonic conductivity. The perovskites SrZrO₃ have also been studied extensively as they are end-members of the grey phase that is observed as a precipitate in spent nuclear uranium oxide fuel. It is therefore knowledge of the thermal properties of the end member compounds of this grey phase is thus of importance. Since most of the applications of SrZrO₃ are taking place at high temperature at which strontium zirconate exist in cubic phase. Hence in the present study we have studied phonon density of states and specific heat of SrZrO₃ in its high temperature cubic phase by applying lattice dynamical theoretical model. The calculated results are interpreted with existing experimental results.

Key Words: Lattice dynamics, specific heat, proton conductor, SrZrO₃

INTRODUCTION

In recent years, many experimental and theoretical investigations were devoted to the study of perovskite-type oxides: typically ABO₃ (A: large cation with different valence and B: transition metal). Strontium zirconate belongs to ABO₃ perovskite oxides family and has many characteristics which are suitable for high-voltage and high-reliability capacitor applications. This class of materials has great potential for a variety of device applications due to their simple crystal structures and unique ferroelectric and dielectric properties. Among the perovskite oxides studied most intensively are zirconates of alkaline earth metals, particularly BaZrO₃ and SrZrO₃. Indeed, they are currently gaining considerable importance in the field of electrical ceramics, refractories and heterogeneous catalysis. Additionally, they have received great attention as high temperature proton conductors with the possibility of applications in fuel cells or hydrogen sensors^{1,2}. In the recent decade, lots of computational works have been carried out to study structures, energetic and dynamics of protonic conduction in AZrO₃ (A=Ca, Sr, Ba). Molecular dynamics (MD) simulations indicated that two types of paths exist for proton transfer; one is the diffusion around an O ion while

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retaining the O–H bond and the other is the diffusion between two neighboring O ions while switching the O–H bond between them³. Quantum MD simulations⁴ and quantum mechanical techniques based on density functional theory (DFT)⁵ have been carried out to calculate the diffusion coefficients and the activation energies for the proton diffusion in the oxides. These calculations greatly deepened our understanding of the mechanism of proton transport in acceptor-doped perovskite-type oxides, and also provided a possible method to design new oxides with high protonic conductivity. However, there is a lack of fundamental understanding at the microscopic level on most of the structural ceramics including BaZrO₃ and SrZrO₃. This could be partially explained by difficulties in using computer modeling to reproduce the unusual physical properties of the ceramic materials. In order to understand the fundamental spectroscopic and thermo dynamical properties of SrZrO₃, it is imperative that the thermal properties of these materials can be thoroughly understood. In the present work the specific heat of SrZrO₃ in cubic phase at constant volume has been calculated from the vibrational spectra at various temperatures by adopting Blackman's sampling techniques⁶. Concerning the structural aspect, the SrZrO₃ compound shows a cubic perovskite-type crystal structure. The space group (Pm3m:221) contains 48 symmetry operations including inversion. The Wyckoff positions of the atoms are Sr 1a (0.0, 0.0, 0.0), Zr 1b (0.5, 0.5, 0.5) and O 3c (0.0,0.5, 0.5). SrZrO₃ is reported to undergo at least three phase transitions as follows⁷⁻¹⁰. Orthorhombic (*Pnma*)→ orthorhombic (*Cmcm*) → tetragonal (*I4/mcm*) → cubic (*Pm3m*) at 970 K, 1100 K, and 1440 K, respectively. SrZrO₃ has a rather high melting temperature of about 2647°C and consequently it is cubic in a wide range of temperature where most of its applications take place. Therefore, in this work, we are studying thermal properties of SrZrO₃ in its cubic phase. From the point of view of lattice dynamics, the unit cell contains five atoms give rise to 15 phonons (three acoustics and 12 optic). The symmetry of these phonons at the Γ point (in terms of the O_h representation) is

$$\Gamma (\text{O}_h) = 4\text{T}_{1u} + \text{T}_{2u}$$

where T_{1u} and T_{2u} represent the normal modes with triple degeneracy. One T_{1u} mode is acoustic and the rest are optical modes. The T_{2u} mode is inactive, while T_{1u} modes are only IR active. The compound in cubic phase has no Raman mode.

METHODOLOGY

In the present investigation a de Launey angular force (DAF) constant model¹¹ has been used to study the phonons in the SrZrO₃. In DAF model, the relative displacement of the reference atom and one of the neighbors is considered. The restoring force on the reference atom is taken to be proportional to the component of the relative displacement perpendicular to the line joining the two atoms at their equilibrium positions. The forces due to all neighbors are calculated separately and summed up together. Different force constants are used

for the various categories of neighbors and the net force on the reference atom is obtained by summing over the contribution from all the neighbors. The present calculation involves four central force constants $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ and four angular force constants $\alpha_1', \alpha_2', \alpha_3'$ and α_4' between Zr-O, Sr-O, Sr-Zr and O-O atoms respectively up to third nearest neighbor. Recently Vali¹² has studied lattice dynamics of cubic phase of SrZrO₃ within density functional theory. In the present calculation the interatomic force constants are obtained by fitting the calculated results of Vali¹² at the ZC for transverse infrared active Phonon frequencies. The force constants thus calculated are listed in table 1.

Taking these force constants as input parameters, the dynamical matrix is solved at the zone center (ZC) as well as along three symmetric directions [q00], [qq0] and [qqq]. The ZC phonons and phonon dispersion curves in three symmetric directions are plotted and discussed in our earlier paper¹³.

Table 1: Values of force constants (10^3 dyne cm^{-1})

Force constant	SrZrO ₃
α_1 (Zr-O)	123.0
α_1' (Zr-O)	6.0
α_2 (Sr-O)	-11.3
α_2' (Sr-O)	9.8
α_3 (Sr-Zr)	18.0
α_3' (Sr-Zr)	4.5
α_4 (O-O)	4.2
α_4' (O-O)	1.0

The frequency distribution function $g(\nu)$ of the normal modes of vibration of a solid is a key property from which specific heat of SrZrO₃ has been calculated. We have calculated the phonon density of states (PDOS) of this compound by applying a sampling method⁶. In the sampling method, one solves for the eigenvalue of the dynamical matrix at the maximum possible number of points that form a mesh in the irreducible section of the first BZ of the reciprocal lattice. A sorting of different frequencies, with proper weighing factors, leads to the evaluation of $g(\nu)$. The specific heat at constant volume has been calculated from the vibrational spectra at various temperatures by adopting Blackman's sampling techniques⁶. According to Blackman, the specific heat C_v is given by

$$C_v = k \int_0^{\infty} x^2 e^x g(\nu) d\nu / (e^x - 1)^2 \quad \text{---- (1)}$$

here $x = h\nu/kT$, h being the Planck's constant and k is Boltzmann's constant. Knowing the frequency spectrum the value of C_v can be calculated. In the present work the frequency spectrum is obtained in terms of 30 different frequency intervals and therefore the above equation (1) reduces to

$$C_v = \sum_1^{30} C_v(\nu) g(\nu) / 15000 \quad \text{---- (2)}$$

Here $C_v(\nu)$ is specific heat for the system assuming all the atoms vibrate with constant frequency ν . The value of C_v corresponding to each $(h\nu/kT)$ is presently determined by applying Einstein's quantum theory of specific heat. According to Einstein, the average energy of an oscillator vibrating with frequency ν is given by

$h\nu / (e^x - 1)$. Accordingly the energy of a gram atom of the solid consisting of N atoms is $U = 3N h\nu / (e^x - 1)$

We have then,

$$C_v(\nu) = dU/dT = 3R \frac{x^2 e^x}{(e^x - 1)^2} \quad \text{---- (3)}$$

Using expression (3) the value of $C_v(\nu)$ for various x values are calculated. Having obtained the values of $C_v(\nu)$ for various $h\nu/kT$, the average specific heat of C_v of SrZrO_3 is calculated using equation (2). The specific heat is calculated for various temperatures ranging from 10K to 300K and is shown in figure 1.

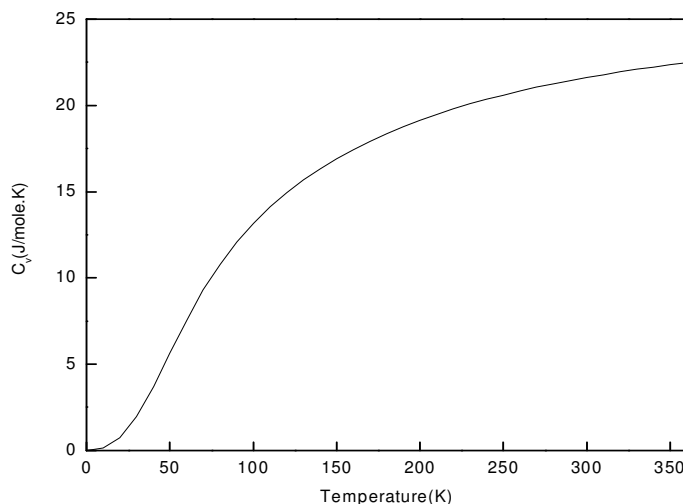


Fig.1 Specific heat curve of SrZrO_3 in cubic phase

RESULTS AND DISCUSSION

It is clear from table 1 that the calculated force constant α_1 between Zr-O is strongest among all other interatomic interactions and is followed by α_3 (Sr-Zr) and is in agreement with finding of Wakamura¹⁴. This suggests that the covalent bonding between (Zr-O) is strongest than that between (Sr-Zr), (O-O) and (Sr-O).

The larger force constant corresponds to stronger bond give rise to larger value of frequency. One of the central force constant α_2 between Sr-O is negative. The negative force constant corresponds to motion along modes that lead to energy lowering. From figure 1 it is clear that the nature of graph satisfies the well known relation $C_v=3R$ at higher temperature. The nature of specific heat curve in this work is found to be similar to other available results. Kurosaki *et al.*¹⁵ have measured the heat capacities of SrZrO₃ in orthorhombic phase and found the negligible difference in heat capacities in two phase of SrZrO₃. The present work thus contributes new theoretical data sets for further study of thermo dynamical properties of SrZrO₃ in cubic phase.

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