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Vibrational, elastic properties and sound velocities of zinc aluminate spinel

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ABSTRACT

Vibrational and elastic properties and sound velocities of zinc aluminate spinel $ZnAl_2O_4$ are calculated using nine parameter rigid-ion model. We have calculated zone-centre phonon frequencies, elastic constants, bulk modulus, compressibility coefficient, shear modulus, Youngs modulus, Poisson's ratio, Anisotropy factor. The Debye temperature and sound velocities are also calculated for zinc aluminate spinel $ZnAl_2O_4$. A detailed comparison with available experimental and previously calculated data is presented. We find an overall good agreement with the experimental and calculated results available in the literature.

1. Introduction

The spinel family is a model material for the ternary oxides spinel type oxides form an important range of ceramic compounds with great interesting electrical, mechanical, magnetic and optical properties. Spinel structure oxides with general formula AB_2O_4 are the most common non-silicate oxides. It is found in Earth's crust and upper mantle of earth. Spinels have cubic symmetry (space group $Fd3m$), and have an essentially cubic close-packed array of oxygen. The main characteristic feature of spinel structure is the ability to host a wide range of divalent, trivalent, and tetravalent cations. In these types of compounds wide band gaps are found and hence it has attractive photoelectronic and optical applications [1]. These compounds have many unique properties such as high melting temperature, high strength, and high resistance to chemical attack [2].

Zinc aluminate is very interesting compound from computational point of view. It was discovered by a Swedish chemist Gahn [3] in 1807 and $ZnAl_2O_4$ is also known as gahnite based on its discoverer's name Gahn. Gahnite crystal crystallizes in octahedral, dodecahedral and in cubic shape and have a blackish, greenish appearance. Gahnite is mainly found in granitic pegmatites, but also in contact altered limestone and metasomatic replacement veins and ores. The major localities of gahnite are the replacement ores in Franklin, NJ, USA and Falun and in the metasomatic deposit in Western Australia [4].

Zinc aluminate spinel has many uses such as a catalyst for the dehydration of saturated alcohols to olefins [5], methanol and higher alcohol synthesis [6,7], preparation of polymethylbenzenes [8], synthesis of styrenes from acetophenons [9] and double bond isomerisation of alkenes [10]. Zinc aluminate spinel has a high thermal stability, low acidity and a hydrophobic behaviour and hence it can be used as a catalyst support. Moreover, it has a strong metal-support interaction preventing e.g. platinum and platinum/tin to sinter [11]. It can also be used as a second phase in glaze layers of white ceramic tiles to improve wear resistance and mechanical properties and to preserve whiteness [12].

Vibrational properties of zinc aluminate spinel can be studied from semi-empirical method as well as with the *ab initio simulation* technique. As for semi-empirical models, only the few input parameters were sufficient, well examined and they are computationally inexpensive and they are generally run faster than *ab initio simulation* technique and provide reliable calculated results.

The vibrational properties of $ZnAl_2O_4$ are studied by many workers using Raman and infrared spectroscopy [13–19]. Sinha et al. [20,21] have calculated the zone-centre phonon frequencies, for $ZnAl_2O_4$ using three parameter short-range force constant model. They have also calculated the zone-centre phonon frequencies for $ZnAl_2O_4$ using the force constants of $MgAl_2O_4$ for better understanding of mass effect on the vibrational modes. Fang et al. [22] have calculated the zone-centre phonon frequencies, elastic constants and the bulk modulus of $ZnAl_2O_4$ using first principles molecular dynamics computer code VASP [23–25]. In this program they have first calculated the electronic structure from first principles and then the interatomic forces via the Hellmann–Feynman theorem. Lopez et al. [26] have calculated the zone-centre phonon frequencies within the framework of the density function theory and the projector-augmented wave [27,28] method using the VASP

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code [23–25]. The exchange and correlation energy was described within the local density approximation [29].

Elastic constants of solids provide the information about the stability and stiffness of the crystals. It is also important to find the mechanical properties of the solids the knowledge of which is important for many practical applications. Pandey et al. [30] have calculated the elastic constants, bulk modulus for $ZnAl_2O_4$ using two-body interatomic pair potential method in the framework of the shell model. Recently, Khenata et al. [31] have calculated the elastic constants and bulk modulus of $ZnAl_2O_4$ using full-potential linear augmented plane-wave method [32] based on density functional theory [33]. Bouhemadou and Khenata [34] have calculated the elastic properties of $ZnAl_2O_4$ using pseudo-potential plane-wave approach based on density functional theory [35,36] and implemented in the CASTEP code [37]. Zerarga et al. [38] have performed the calculations for elastic properties for $ZnAl_2O_4$ by using the full-potential augmented plane wave plus local orbitals (FP − (L)APW + lo) approach [39–41], based on density functional theory [42] and implemented in the most recent version of the WIEN2K package [43]. Exchange and correlation functional is given by the local density approximation of Perdew and Wang [44].

$ZnAl_2O_4$ is a wide band-gap semiconductor and hence it has attracted much interest as possible transparent conducting oxide materials. Recently Karazhanov and Ravindran [45] have studied the structural properties, electronic structure and optical spectra and Dixit et al. [46] have studied the electronic structure and band gap of $ZnAl_2O_4$ within the frame work of density function theory.

In the present paper, we have studied the vibrational, elastic and thermodynamic properties of $ZnAl_2O_4$ using a proposed theoretical model. In this model we have used three bond-stretching, three-bond bending and three effective dynamical charges of the ions.

Zinc aluminate ($ZnAl_2O_4$) having the spinel structure and it has the same crystallographic structure as the natural occurring mineral spinel ($MgAl_2O_4$) having the space group $Fd3m$. It has a cubic structure made out of eight molecular units ($ZnAl_2O_4$), where the 32 oxygen atoms form an fcc-lattice with eight zinc cations located in the tetrahedral holes and 16 aluminium cations located in the octahedral holes. Zinc aluminate spinel $ZnAl_2O_4$ crystallizes with two formula units in the primitive rhombohedral unit cell. Group theoretical analysis [47–49] shows that three acoustic modes and 39 optic modes are distributed at the zone-centre as

$$\Gamma = A_{1g} + E_g + 2E_u + 2A_{2u} + T_{1g} + 3T_{2g} + 4T_{1u} + 2T_{2u} \quad (1)$$

where A_{1g}, E_g and T_{2g} are Raman-active modes and T_{1u} modes are infrared-active modes while the remaining modes are silent modes.

2. Potential model

The lattice dynamical method is carried out by using the rigid-ion model proposed by Kushwaha [50]. In this model the potential energy of the spinel structure compounds are split into two parts (i) the short range non-Coulombic part and (ii) the long-range Coulombic part, written as

$$\Phi = \phi^N + \phi^C \quad (2)$$

For the short-range non-Coulombic interaction, the potential energy of the spinel structure ϕ^N using Taylor's series can be expressed as,

$$\phi^N = \sum_{lmn}\left[\frac{1}{r}\left(\frac{d\phi^N}{dr}\right)_{|r|=|r_k|}\left\{r^o_{lmn}(S_{lmn}-S_o)+\frac{1}{2}|S_{lmn}-S_o|^2\right\} + \frac{1}{2}\left\{\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi^N}{dr}\right)\right\}_{|r|=|r_k|}\{r^o_{lmn}\cdot(S_{lmn}-S_o)\}^2\right] \quad (3)$$

where S_0 and S_{lmn} are the displacements of the central ion and its first neighbour ions from their normal positions, r_{lmn} represents the position coordinates of neighbouring ions in equilibrium. l, m, n, represent the direction cosines of the line joining the central ion and a nearest neighbour. $|\mathbf{r_k}|$ is the nearest neighbour distance.

In our work we have considered the non-Coulombic interaction between central ion and its three nearest neighbours. Let A_k be the bond-stretching force constant defined by the second derivative of the potential energy ϕ^N:

$$\frac{e^2}{V}A_k = \left.\frac{d^2\phi^N}{dr^2}\right|_{|r|=|r_k|} \quad (4)$$

The bond-bending force constant B_k is expressed as the first derivative of the potential energy ϕ^N:

$$\frac{e^2}{V}B_k = \left.\frac{1}{r}\frac{d\phi^N}{dr}\right|_{|r|=|r_k|} \quad (5)$$

Here $k = 1, 2, 3$ for first, second and third neighbours.

For the long-range interaction, i.e., for ϕ^C, the contributions of long-range Coulombic interaction have been calculated by the Ewald's method [51].

3. Elastic and related properties

Elastic constants of zinc aluminate spinel $ZnAl_2O_4$ are calculated from the dynamical matrix $D_{\alpha\beta}(\mathbf{q}kk')$ by expanding it as a function of q in the neighbourhood of $\mathbf{q} = 0$ [52], the relation between the elastic constants and the coupling coefficients can be established. The calculated elastic constants C_{11}, C_{12} and C_{44} are listed in Table 3. Once the elastic constants is derived then bulk modulus B, compressibility coefficient K, shear modulus G, Youngs modulus Y, Poisson's ratio σ, Anisotropy factor A are calculated with the given relations [53,54]:

$$B = \frac{C_{11}+2C_{12}}{3}$$

$$K = \frac{1}{B}$$

$$G = \frac{G_V+G_R}{2}$$

where

$$G_V = \frac{C_{11}-C_{12}+3C_{44}}{5}$$

$$\frac{5}{G_R} = \frac{4}{C_{11}-C_{12}} + \frac{3}{C_{44}}$$

$$Y = \frac{(C_{11}+2C_{12})(C_{11}-C_{12})}{C_{11}+C_{12}}$$

$$\sigma = \frac{C_{12}}{C_{11}+C_{12}}$$

$$A = \frac{2C_{44}}{C_{11}-C_{12}}$$

are the most interesting elastic properties for applications are also calculated in terms of computed data.

Debye temperature is an important fundamental parameter related to many other physical properties such as elastic constants, specific heat and melting temperature. The Debye temperature Θ_D can be calculated as [55]: