Elastic and electronic properties of strontium vanadate: An *ab initio* study.

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Abstract

We have investigated elastic and thermodynamic properties of strontium vanadate ($SrVO_3$), by calculating their elastic constants within the density functional theory scheme. We present calculations of the elastic constants performed accurate *ab initio* total energy calculations using the full-potential linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA) for the exchange-correlation potential.

From the elastic strain tensor we estimate the bulk moduli, Young's moduli, Poisson's ratios and sound velocities of polycrystalline samples. In addition, using the Debye–Grüneisen theory we obtain estimates for the Debye temperatures, specific heats and linear thermal expansion coefficients. Theoretical and experimental values are in reasonable agreement where experimental data are available. Overall, our results show that density-functional calculations can indeed substitute for explicit measurements of monocrystalline materials.

Keywords: First-principles calculation; Elastic constants; Thermodynamic properties

1. Introduction

The perovskite-type oxides have the potential to be attractive functional materials because they have various unique properties. They attracted attention in the last decade as prospective components of solid oxide fuel cell (SOFC) [1, 2, 3, 4, 5, 6]. $SrVO_3$ has a cubic perovskite structure and exhibits Pauli paramagnetic metallic behavior [7, 8].

Elastic properties of a solid are important because they are closely related to various fundamental solid state phenomena and linked to whit thermodynamic properties such as specific heat, thermal expansion, Debye temperature and Grüneisen parameter. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid, for instance, load deflection, thermoelastic stress, internal stain, sound velocities, and fracture toughness. The strontium vanadate has an ideal cubic perovskite structure [1, 7, 9], its simple structure allows it to be a starting point to understand the properties of more complex systems [10, 11]. Khan et al [12] and Atahar P. et al [13] calculated the elastic and thermodynamic properties using empirical models. Also, Shein et al [14] employed the FLAPW-GGA method calculated the elastic constants.

In the present work, we focus on the perovskite-type strontium vanadate, $SrVO_3$. The mechanical and thermodynamic properties, such as bulk modulos, elastic moduli, anisotropy elastic, Debye temperature, heat capacity, and thermal expansion α of $SrVO_3$ were calculated.

2. Methods

2.1. FP-LAPW method

The first-principles calculations were performed based on the density functional theory (DFT). The Kohn-Sham total energies were calculated self-consistently using the linearized augmented plane wave method (FP-LAPW) with local orbital extensions [15], as implemented in the WIEN2k [16, 17] code, where the core states are treated fully relativistically and the semicore and valence states are computed in a scalar relativistic approximation. The exchange-correlation terms were considered in the Perdew-Burke-Ernzerhof form of the generalized gradient approximation (GGA) [18]. We have chosen the muffin-tin radii (R_{MT}) of 2.44, 1.83 and 1.62 a.u. for the Sr, V and O atoms respectively. The self-consistent calculations were done with an LAPW basis set defined by the cutoff $R_{MT}K_{MAX}=9.0$. Inside the atomic spheres, the potential and charge densities were expanded in crystal harmonics up to $L = 10$. Convergence was assumed when the energy difference between the input and output charge densities was less than 1×10^{-5} Ry. The calculations were carried out with a sufficiently large number of k points in the first Brillouin zone (BZ). Was used a $16\times16\times16$ k-point mesh, yielding a different number of k points in the irreducible wedge of the BZ depending on the structure: 165 for the cubic structure with space group Pm-3m(221), 360 for tetragonal deformation 123(P4/mmm) and 584 for orthorhombic deformation 65(Cmmm).

2.2. Elastic properties

The calculate total energy as a function of volume was fitted to the Birch–Murnaghan equation of state [19], from this

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process the equilibrium lattice constant (a) and bulk modulos (B) were obtained. All crystals in cubic structure have only three independent elastic constants, namely C_{11}, C_{12}, and C_{44}. One can apply a small strain and calculate the change of energy or stress to obtain elastic constants C_{ij}. In the crystal structures analyzed in this work an external strain δ from -0.07 to $+0.07$ was applied in the directions as explained by Güemez et al. [20], associated with deformations: isotropic, tetragonal and orthorhombic by

$$\epsilon_{iso} = \begin{pmatrix} (1+\delta)^{1/3} & 0 & 0 \\ 0 & (1+\delta)^{1/3} & 0 \\ 0 & 0 & (1+\delta)^{1/3} \end{pmatrix},$$

$$\epsilon_{tet} = \begin{pmatrix} (1+\delta)^{-\frac{1}{3}} & 0 & 0 \\ 0 & (1+\delta)^{-\frac{1}{3}} & 0 \\ 0 & 0 & (1+\delta)^{\frac{2}{3}} \end{pmatrix}, \quad (1)$$

$$\epsilon_{ort} = \begin{pmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & 1+\delta^2 \end{pmatrix},$$

to distort the lattice vectors, $R' = (1 + \epsilon)R$. The resulting changes of energy are associated with elastic constants,

$$\Delta E_{iso} = \frac{V_0}{2}(C_{11} + 2C_{12})\delta^2$$

$$\Delta E_{tet} = \frac{V_0}{3}(C_{11} - C_{12})\delta^2 \quad \text{and} \quad (2)$$

$$\Delta E_{ort} = 2V_0 C_{44}\delta^2.$$

2.3. VRHG approximation for cubic structure

VRHG (Voigt, Reuss, Hill and Gilvarry) approximation is a scheme for averaging the elastic constants and sound velocities, Voigth [21] assuming homogeneous strain on the compound, the bulk (B) and shear (G) moduli are written as

$$B_V = \frac{1}{3}(C_{11} + 2C_{12}), \qquad G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}). \quad (3)$$

on the other hand, assuming homogeneous stress, Reuss [22] proposes

$$1/B_R = 3S_{11} + 6S_{12}, \qquad 15/G_R = 4S_{11} - 4S_{12} + 3S_{44}, \quad (4)$$

where S_{ij} are the elastic compliance constants. Later, Hill [23] proved that the Voigt and Reuss equation represents upper and lower limits of the true polycrystalline constants. A practical estimate of the polycrystalline moduli is the arithmetic means of the extremes,

$$B_H = 1/2(B_v + B_R), \qquad G_H = 1/2(G_V + G_R). \quad (5)$$

The shear and longitudinal sound velocities v_s and v_l are obtained from equation [21]

$$v_s = \sqrt{\frac{G_H}{\rho}}, \qquad v_l = \sqrt{\frac{B_H + (4/3)G_H}{\rho}}. \quad (6)$$

The average sound velocity is obtained from[24]

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_s^3} + \frac{1}{v_l^3}\right)\right]^{-1/3}. \quad (7)$$

where v_s and v_l are the shear and longitudinal velocities respectively.

Finally, the Young's modulus E and the Zener anisotropy factor A, are calculated in terms of the computed data using following relations

$$E = \frac{9BG}{3B + G}, \quad (8)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}}. \quad (9)$$

2.4. Thermodynamic properties

To calculate the linear thermal expansion coefficient

$$\alpha_L = \frac{1}{3}\gamma_G \frac{C_V}{BV_0} \quad (10)$$

was needed an expression for the specific heat capacity (C_V) and the Grüneisen constant γ_G. Then two approximations of Grüneisen constant were used, defined as[25],

$$\gamma_G^{\text{SL}} = \frac{-V_0}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V} - \frac{2}{3} \quad (11)$$

and,

$$\gamma_G^{\text{DM}} = \frac{-V_0}{2}\frac{\partial^2 P/\partial V^2}{\partial P/\partial V} - \frac{1}{3} \quad (12)$$

where γ_G^{SL} and γ_G^{DM} are Slater and Dugdale-MacDonald approximations, respectively.

From Birch–Murnaghan equation of state [19] one gets

$$\gamma_G^{\text{SL}} = -\frac{1}{6} + \frac{1}{2}B' \quad \text{and} \quad \gamma_G^{\text{DM}} = \frac{1}{6} + \frac{1}{2}B'$$

where B' is dB/dP.

Using elastic constant data, was calculated the Debye temperature (θ_D) by means of the equation[24]

$$\theta_D = \frac{h}{k_B}\left[\frac{3q}{4\pi}\frac{N_A\rho}{M}\right]^{1/3} v_m \quad (13)$$

where h is the Planck's constants, k_B is the Boltzmann's constant, N_A is the Avogadro's number, q is the number of atoms per formula unit, M is the molecular mass per formula unit, ρ is the density and v_m is the average sound velocity Eq. 7.

The specific heat at constant volume (C_V) can be calculated by using the expression

$$C_V = 9qN_Ak_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}dx \quad (14)$$

where q, N_A, k_B, θ_D are the same as defined above and T is temperature.

3. Results and discussion

The equilibrium lattice constants (*a*) and elastic properties calculated for perovskite $SrVO_3$, as obtained within the framework of the FLAPW-GGA calculations, are presented in Table 1. The predicted *a* differs from experimental value by ~ 0.6%, as is expected for first-principles methods employing GGA.

Table 1: The lattice constant a(Å), elastic constants (C_{11}, C_{12} and C_{44}), bulk modulus (*B*) on GPa, Zener anisotropy factor *A* and Poisson'n ratio σ for $SrVO_3$.

	Experiment	This work	Others	DFT[d]
a	3.8424[a],3.84[b] 3.8425[f], 3.841[g] 3.8498[h],3.8451[i]	3.8654	3.84[c]	3.8662
B		179	201[e]	181
C_{11}		323	464[c], 240[e]	270
C_{12}		108	187[c], 182[e]	137
C_{44}		116	140[e]	114
A		1.06	4.5[e]	1.7
σ		0.239	0.350[e]	0.2157

[a]Ref. [7] [f]Ref. [26]
[b]Ref. [8] [g]Ref. [9]
[c]Ref. [12] [h]Ref. [27]
[e]Ref. [13] [i]Ref. [1]
[d]Ref. [14]

The values of elastic constants (C_{ij}) for cubic $SrVO_3$ are presented in Table1. These three independent constants in a cubic symmetry are estimated by calculating the change of total energy on single crystals applying strains to an equilibrium structure (Eqs.1 and 2).

For the elastic constants, at present there are no experimental data to compare with our results but they seem to be in discrepancy with other available theoretical data using empirical[12, 13] methods. On *ab-initio* methods the discrepancy is observed for C_{11} and C_{12} (±20%) where the obtained values disagree with those of Ref [14]; this unexpected agreement comes probably from the stress tensors used (Eq 1). The Zener anisotropy factor *A* is a measure of the degree of elastic anisotropy in solids. *A* will take the value of 1 for a completely isotropic material. A value of *A* smaller or greater than unity shows the degree of elastic anisotropy, our results indicate that $SrVO_3$ is isotropic material, however, using data from Parveen *et. al.* [13] and Shein *et al* [14] $SrVO_3$ is an elastically highly anisotropic compound.

The volume thermal expansion is computed using the Eq. 10 and, as Fig.1 shows, it displays a non-linear behavior, similar to the one observed for transition metal-based perovskites, such as e.g. cobaltites and ferrites [28, 29]. The average thermal expansion coefficient (TEC) of $SrVO_3$ at 300–1223K was calculated to be equal to $1.33 \times 10^{-6} K^{-1}$ and $1.54 \times 10^{-6} K^{-1}$ using γ_G^{SL} and γ_G^{DM}, respectively. The obtained TEC values are in good agreement with the experimental data reported previously (Table 2).
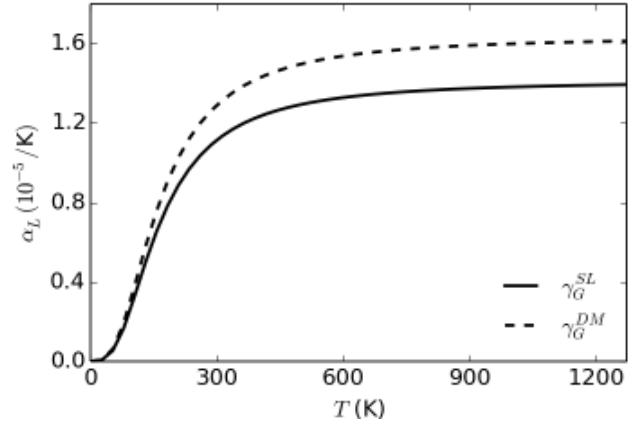

Figure 1: Temperature dependence of thermal expansion coefficient of $SrVO_3$ in wide temperature range (0-1273 K).

Table 2: Average linear thermal expansion coefficient.

$\overline{\alpha}_L \times 10^5 (K^{-1})$	$T(K)$	Ref.
1.80	300-1023	[27]
1.62	300-1273	[1]
1.45	300-1073	[9]
	This work 300-1273	
1.33		γ_G^{SL}
1.54		γ_G^{DM}

Table 3: VRHG approximation and experimental elastic and thermodynamic properties for $SrVO_3$.

	This work	Exp.[9]	Teo.[13]
$v_l(m/s)$	7843	7169	3217
$v_s(m/s)$	4587	4162	650
G(GPa)	113	90	67
E(GPa)	280	224	181
B/G	1.58		
θ_D(K)	670	612	538

The table 3 presents the results of our VRHG approximation calculations. The ratio of the bulk modulus to shear modulus of crystalline phases can predict the brittle and ductile behavior of materials. A high *B/G* ratio is associated with ductility, whereas a low value corresponds to brittle nature. The critical value which separates ductile and brittle materials is around 1.75. When *B/G* ratio is higher than 1.75, the material behaves in a ductile manner; otherwise, the material behaves in a brittle manner. In the present work, the value is lower than 1.75. Which means that $SrVO_2$ is brittle.

The Debye temperature of materials plays an important role in physical quantity. It is basically a measure of the vibrational response of the material. The values of Debye temperature have been obtained from the knowledge of the elastic constants and the sound velocities (including longitudinal, shear and average wave velocities). The values thus obtained are listed in Table 3
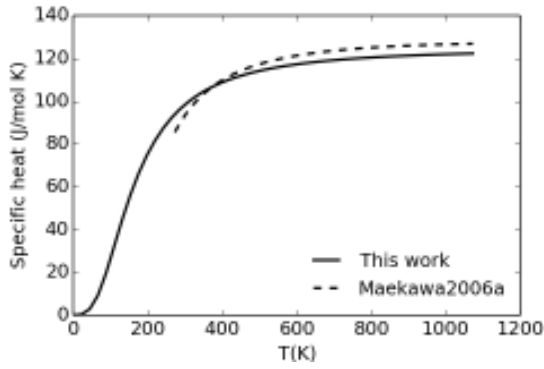
Figure 2: Calculated heat capacity of $SrVO_3$ and its comparison with the experimental work of Maekawa et al.[9]

Figure 3: 3D directional dependence of the Young's modulos.

along with other theoretical [13] and experimental results [9] for the comparison. The predicted velocities and Debye temperature 3 differs from experimental value by $\sim 10\%$, while for Young' s and shear moduli differs by $\sim 25\%$.

The specific heat in the normal state of the material is usually approximated by the contribution of the lattice specific heat. Fig. 2 shows (solid line) the computed results on heat capacity for SrVO3 and the dashed line represents the fitting result of the experimental data[9]. Our results on specific heat have quite good match with the experimental work of Maekawa et al. [9].

In order to better visualize the isotropy of these compounds, is shown a three-dimensional (3D) representation of Young's modulus. For cubic crystals, the directional dependence of Young's modulus in 3D representation can be given by

$$\frac{1}{E} = S_{11} - 2(S_{11} - S_{12} - \frac{1}{4}S_{44})(l_1^2 l_2^2 + l_2^2 l_3^2 + l_3^2 l_1^2) \qquad (15)$$

where S_{ij} represents the elastic compliance constants, and l_1, l_2 and l_3 stand for the directional cosines to the $x-$, $y-$ and $z-$axes, respectively. The Three-dimensional representation of Young's modulus, shown in Figure 3, depicts the elastic isotropy. It can be seen that the elastic isotropy.

To analyze the isotropy on elastic wave velocities, he equation below was used [30]

$$\det |C_{ijkl}n_j n_l - \rho v^2 \delta_{ik}| = 0, \qquad (16)$$

where C_{ijkl} is the single crystal elastic constant tensor, $\vec{n}$ is the propagation direction, ρ is the density, and δ_{ij} is the Kronecker delta function. The eigenvalues of the 3×3 matrix yield the three unique elastic wave velocities (one longitudinal v_l and two shear v_s waves) for a given propagation direction and the eigenvectors correspond the polarization directions. Figure 4 shows the angular variations of the velocities in the zy plane and thus, the high isotropy.

Figure 4: Angular variation of v_l and v_s velocities in the zy plane.

elastic parameters and thermodynamic properties of the polycrystalline $SrVO_3$ ceramics were performed. This work would provide a complete basis for the theoretical description of the elastic and thermal properties of vanadate compounds. Also, it was interesting to compare the results presented here with available experimental data and the match was satisfactory.

4. Conclusions

In summary, were performed FLAPW-GGA calculations for $SrVO_3$–perovskite phase to calculate the elastic constants. Using these results, for the first time, the numerical estimates of
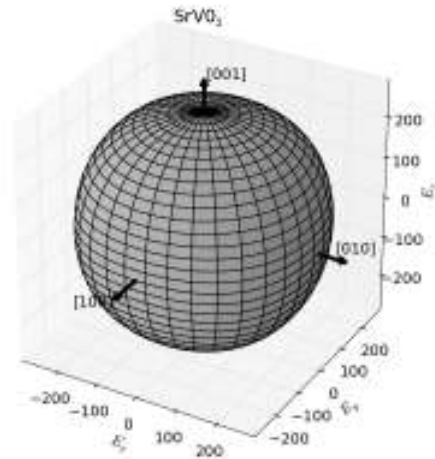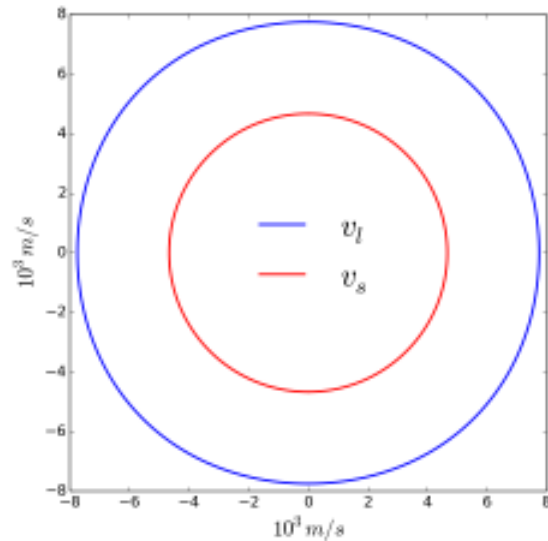
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