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Investigation of structural, elastic, electronic, optical and vibrational properties of silver chromate spinels: Normal ($CrAg_2O_4$) and inverse (Ag_2CrO_4)

A.K. Kushwaha [a, *], Ş. Uğur [b], S. Akbudak [c], G. Uğur [b]

[a] Department of Physics, K.N. Govt. P.G. College, Gyanpur, Bhadohi, 221304, India
[b] Department of Physics, Faculty of Science, Gazi University, 06500, Ankara, Turkey
[c] Department of Physics, Faculty of Arts and Sciences, Adiyaman University, 02100, Adiyaman, Turkey

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ABSTRACT

Structural and elastic properties of silver chromate in normal ($CrAg_2O_4$) and inverse (Ag_2CrO_4) spinel structure have been studied using density functional theory (DFT) together with Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional implemented in VASP package. It is observed that studied compound satisfy the well-known requirements of mechanical stability for cubic crystals. So we can infer that studied compound is stable both in normal ($CrAg_2O_4$) and inverse (Ag_2CrO_4) spinel structure. Electronic, optical and vibrational properties of Ag_2CrO_4 at 0 and 11 GPa have also been studied. Zone-centre phonon frequencies and the phonon dispersion relations along high symmetry directions of the silver chromate have been calculated using phonon software with the forces calculated with VASP. Our calculated lattice constant values, Raman spectrum modes and fundamental bandgap values are in good agreement with recent studies which can motivate further experimental and theoretical attention.

1. Introduction

The spinel structure compounds AB_2O_4 having space group (Fd-3m), is cubic and consist of a slightly distorted cubic close-packed arrangement of O-ions and it is also classified as normal and the inverse spinels. In the case of normal spinel, A type of cations occupy 1/8 of the tetrahedral sites and B type of cation occupy 1/2 of the octahedral sites while in the case of, inverse spinel, one half of the B-cations occupy the tetrahedral sites and the other half of B-cations and the A-cations occupy the octahedral sites. In the present paper, for clarity in the presentation, the normal spinel structures are written as AB_2O_4 while inverse spinel structures are written as B_2AO_4.

Silver chromate which is a good candidate of semiconductor photocatalysis have attracted much attention due to its high capacity of visible light absorption [1–3]. TiO2 one of the most popular photocatalyst could only absorb 4% of solar energy due to its high bind gap of 3.2 eV [4,5]. However Ag_2CrO_4 having a narrow band gap of 1.75 eV and showing activity in visible region up to 570 nm [6] is a novel photocatalyst in visible-light region and correlates the crystal structures and electronic properties of Ag-based chromates. Apart from photocatalysis [7], another field that silver chromate plays an important role is reducing environmental pollution [8]. In conventional catalysis, after the process hazardous gases like CO2 are given to the environment which increases pollution. However compounds such as silver chromate which are used in semiconducting photocatalysis decompose organic pollutants into non-hazardous compounds [9]. Research in literature showed that silver chromate can be obtained via different methods such as hydrothermal [10], sonochemical [11], precipitation [12] and reversed micellar [13]. Due to its practical applications silver chromate has been extensively studied both experimentally [14–32] and theoretically [33]. There are also some papers that include a combination of experimental and theoretical studies [34–36]. Compared to many experimental studies there is only one pure theoretical study in literature [37]. And this theoretical study is based on first-principles calculations as it was the same for theoretical part of the studies including a combination of experimental and theoretical studies. To mention some of these studies; very recently, Perez et al. [34] have studied the Ag_2CrO_4 compound

* Corresponding author.
E-mail address: akkphys_bu@yahoo.com (A.K. Kushwaha).

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at ambient conditions and found that Ag_2CrO_4 compound crystallizes in orthorhombic phase (space group *Pnma*). Gabriel S. Silva et al. [35] presented an experimental and theoretical study to analyze the effects of different preparation conditions on the electronic structure, morphology, and photoluminescence properties of Ag_2CrO_4, Maria. T. Fabbro et al. [36] carried out a combination of experimental and theoretical study devoted to rationalize early events associated with the formation of Ag nanoparticles on Ag_2CrO_4. J. Zhang et al. theoretically investigated silver chromate using density functional theory together plane-wave pseudopotential method [37].

The objective of the present paper is to study the structural, elastic and electronic properties of silver chromate with spinel structure at 0 and 11 GPa and it is found that the studied compound is stable in normal ($CrAg_2O_4$) as well inverse (Ag_2CrO_4) spinel structure. We have also studied the optical and vibrational properties of Ag_2CrO_4 at 0 and 11 GPa.

2. Computational method

Density functional theory (DFT) calculations were performed using the medeA-VASP software package [38,39]. We have used projector augmented wave (PAW) potentials constructed within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) form [40]. The plane-wave basis set was restricted by a cutoff energy of 644 eV. The first Brillouin zone integrations are performed using Monkhorst-Pack scheme with $8 \times 8 \times 8$ **k** -point meshes [41]. All the structures are fully relaxed with a force tolerance of 0.01 eV $Å^{-1}$. The **k** space integration was performed using the linear tetrahedron method [42]. The elastic constants are obtained by the strain-stress relationship [43].

3. Results and discussion

3.1. Structural properties

Silver chromate spinel is a close packed face-centered-cubic structure with space group Fd-3m and its unit cell contains eight formula units. In the present paper, we have studied the Silver chromate spinel compound in normal ($CrAg_2O_4$) as well as inverse (Ag_2CrO_4) class of spinel with the fractional coordinates given in Table 1. The calculated lattice parameters for normal ($CrAg_2O_4$) as well as inverse (Ag_2CrO_4) spinel is shown in Table 1. and it is found that our calculated lattice value ($a = 8, 79$) at 11 GPa is very close to the experimental lattice constant ($a = 8, 75$) of Perez et al. [34] at 11 GPa. From Table 1, we conclude that with increasing pressure the lattice parameter decreases for normal ($CrAg_2O_4$) as well as inverse (Ag_2CrO_4) spinel. We have calculated the bond distances Cr−O and Ag−O for $CrAg_2O_4$ at 0 and 11 GPa 1.68 Å and 2.46 Å, 1.67 Å and 2.35 Å, respectively.

Table 2
Calculated bulk modulus (*B*, in GPa), elastic constants (C_{11}, C_{12}, C_{44}, in GPa) Shear modulus (*G*, in GPa), Young's modulus (*E*, in GPa), and *B/G*.

	$CrAg_2O_4$		Ag_2CrO_4	
	0 GPa	11 GPa	0 GPa	11 GPa
B	72.45	139.66	72.30	133.64
C_{11}	92.50	184.12	90.89	175.62
C_{12}	62.42	117.43	63.00	112.66
C_{44}	29.38	29.10	27.90	29.07
G	23.65	30.80	22.31	30.03
E	63.97	86.06	60.70	83.82
B/G	3.06	4.53	3.24	4.45

3.2. Elastic properties

Knowing the derivative of the energy as a function of lattice strain we have also calculated the three elastic constants C_{11}, C_{12} and C_{44} for Ag_2CrO_4 normal and inverse spinel and listed them in Table 2. Our calculated elastic constants of normal spinel are smaller than some known spinels [44]. Table 2 shows that the computed elastic constants (C_{11}, C_{12} and C_{44}) of the two (normal and inverse) spinel satisfy the well known requirements of mechanical stability for cubic crystals [45] given by

$$(C_{11} - C_{12}) > 0, C_{12} < B < C_{11}, (C_{11} + 2C_{12}) > 0, C_{44} > 0 \quad (1)$$

This indicates that the investigated normal ($CrAg_2O_4$) and inverse (Ag_2CrO_4) spinels are mechanically stable. The bulk modulus, *B*, for a cubic system can be calculated using $B = (C_{11} + 2C_{12})/3$. Shear modulus (G) is derived using the following relation: $G = (C_{11} - C_{12} + 3\ C_{44})/5$. Young's modulus, *E*, are given by the standard formula of elasticity $E = 9B/(1+(3B/G))$.

Our calculated values of elastic properties (*B, G, E,* and *B/G*) for normal ($CrAg_2O_4$) and inverse (Ag_2CrO_4) spinels are given in Table 2. Our calculated bulk modulus values at 0 GPa for $CrAg_2O_4$ and Ag_2CrO_4 are 72.45 and 72.30 GPa, respectively. And these values overestimates the value (52 GPa) obtained by Santamaria et al. [34]. Our bulk modulus are bigger than that $SrCrO_4$ which is reported by Gleissner et al. [46].

As a matter of fact that one of the most widely used empirical criterion to distinguish between ductile and brittle behavior of a material is the Pugh's ratio *B/G* [47]. According to this empirical criterion, if the ratio *B/G* is higher than 1.75, the ductile behavior is predicted, otherwise the material behaves in a brittle manner. In

Table 1
Calculated lattice parameter (*a*, in Å), fractional coordinates for the spinel phase at 0 GPa and 11 GPa.

		a	Atom	x	y	z
$CrAg_2O_4$	0 GPa	9.139928	Ag	0.5	0.5	0.5
			Cr	0.125	0.125	0.125
			O	0.2312	0.2312	0.2312
	11 GPa	8.826001	Ag	0.5	0.5	0.5
			Cr	0.125	0.125	0.125
			O	0.2343	0.2343	0.2343
Ag_2CrO_4	0 GPa	9.103666	Ag	0.0	0.0	0.0
			Cr	0.375	0.375	0.375
			O	0.2687	0.2687	0.2687
	11 GPa	8.797225	Ag	0.0	0.0	0.0
			Cr	0.375	0.375	0.375
			O	0.2657	0.2657	0.2657
	[32]	8.759		0.26508	0.26508	0.26508