

Optical properties of orthovanadates, and periodates studied from first principles theory



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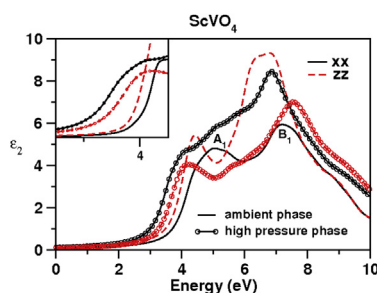
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HIGHLIGHTS

- Orthovanadates, periodates are insulators.
- Band gap decreases with decrease in the cation size, and also moving to high pressure phase.
- Orthovanadates are better host scintillators than periodates.
- Orthovanadates can be better used as host scintillators in the high pressure phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Detailed ab-initio studies on electronic structure and optical properties have been carried out for orthovanadates, and periodate compounds, ScVO_4 , YVO_4 , LuVO_4 , and NaIO_4 , KIO_4 , RbIO_4 , CsIO_4 based on the Full potential linearized augmented plane wave method within the frame work of Density Functional Theory using Tran and Blaha modified Becke–Johnson potential (TB-mBJ). We have compared the optical properties of orthovanadates with periodates, and also with its high pressure phase. The main difference observed in moving from orthovanadates to periodates is the increase in band gap, and bands turn out to be less dispersive. By considering all these facts, we predict orthovanadates to be better scintillators than periodates, which is well explained from the band structure, and optical properties calculations. In addition, we also compared the optical properties of orthovanadates at ambient, and high pressure and we observed a decrease in the band gap of orthovanadates, increase in valence band width at high pressure when compared to ambient phase. Tuning the band gap, which is an important criteria for scintillators, can be observed in orthovanadates by decreasing the cation size, and also by moving to the high pressure scheelite phase. High pressure phase of orthovanadates might be more favourable as the zircon to scheelite transition is irreversible, and the transition pressure is also less around 8 GPa.

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1. Introduction

ABO_4 type ternary oxide compounds are important because of their wide range of applications as laser host compounds, catalyst,

polarizer, phosphors, scintillators, field emission display, nuclear-waste storage medium, optical isolators, circulators, beam displacers, oxidizers etc. [1]. The main goal of this paper is to explore these ABO_4 type scintillator host compounds, which mainly focusses on orthovanadates, and periodates. Most of the orthovanadates crystallize in tetragonal zircon-type structure consisting of isolated VO_4 tetrahedra surrounding the A atom forming AO_8

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dodecahedra [2]. With the increase in the radius of the cation, these compounds crystallize in monazite structure rather than zircon. The zircon type structure is preferred over monazite structure because of the increased radiative transitions. These are good host compounds which emit colours with the addition of suitable dopant's. Among them, YVO_4 is one of the widely used optical material as it possess small radii and can emit variety of colours with doping [3]. Zuocai et al. [4] synthesised, studied the structural, elastic, lattice dynamical properties of both the phases of YVO_4 [5,6], and reported the dynamical stability of these two phases, where scheelite is more optically isotropic than zircon structure. At high pressure, these orthovanadates undergo phase transition from scheelite to further low symmetric monoclinic phase. Spectroscopic properties of LuVO_4 under high pressure have been studied and phase transitions are reported from zircon \rightarrow scheelite \rightarrow monoclinic structures at 8 GPa, 16 GPa respectively [7]. The electronic structure of zircon-type orthovanadates under pressure was investigated and it was reported that cation substitution influence the electronic states [8]. Red shift of the vanadate band gap observed with the cation substitution, further results in decrease of the band gap as observed with the Bi doping in these orthovanadates [9,10]. Errandonea et al. [2] studied the transition pressure of ABO_4 orthovanadates, and found it to be in the range of 7–8 GPa independent of cation size, and also observed two transitions i) zircon \rightarrow scheelite ii) scheelite \rightarrow monazite but in the case of ScVO_4 only first transition is observed, whereas in the case of EuVO_4 , LuVO_4 , both the transitions are observed. First transition i.e. from zircon to scheelite is an irreversible process, while the second (scheelite to monazite) one is reversible. Irreversible transition from zircon to scheelite is also observed by other groups [11,6]. It is well known that across the phase transition, electronic structure and optical properties changes quite significantly as seen for example in TbVO_4 , DyVO_4 , where the transmission changes from colourless to yellow, and also absorption edge decreases [12]. Similarly in YVO_4 absorption edge shift from 3.87 to 2.77 eV at 7.5 GPa indicating the importance of these properties [13].

In addition, we have also studied XIO_4 compounds ($X = \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$), which are good oxidizing agents. Perchlorates are used in pyrotechnics, but they are targeted for elimination because of environmental and health issues, and these can be replaced by the periodates which are less toxic. Periodates can also be used in explosives, which contain a mixer of fuels and oxidizer's. Secondary explosives generally have oxygen deficiency, which restrict the heat release. Addition of oxidizing agents in proper proportions to these explosives increases the combustion of explosives, resulting in large amount of energy release. These compounds decompose at high temperature and produce oxygen making them to act as good oxidizing agents. Periodates replaces perchlorates with less toxicity, and more thermodynamic stability [14,15]. These can also be used as nano energetic gas detectors, for gas generation, as conduction salts [16], and also find illumination application. RbIO_4 show pressure induced phase transition at 5.3 GPa, 7.2 GPa, where the former is the transition from scheelite to pseudoscheelite, while latter denotes the transition from pseudoscheelite to wolframite. At 7.2 GPa, it will change the colour to brownish black. Transition pressure from pseudoscheelite to wolframite phase increases with increasing ionic radius. At still higher pressure around 18.3 GPa, it further transform to still dense complex structure [17]. KIO_4 also undergo a phase transition at 6.5 GPa which is completed at 9.8 GPa [18]. Pressure induced phase transitions were observed in CsIO_4 at 1.5, 4.5, and 6.2 GPa. Transition at 1.5 GPa involve tilting of IO_4 tetrahedral unit, while at 4.5 GPa, 6.5 GPa transitions take place from pseudoscheelite to wolframite, and wolframite to lower symmetric complex denser structure respectively. Temperature

induced phase transition is also observed in CsIO_4 at around 423 K, where it transforms from orthorhombic to tetragonal scheelite phase [19]. These composites are very sensitive to the external impact or friction.

There are numerous experimental and theoretical studies available on the structural phase transition under pressure on these compounds [2,3,5,7,11,17–23], but there are only very few studies available regarding the optical properties. The optical properties calculations are important for scintillators in order to optimize their performance and also to develop new scintillating materials. Here we are interested in studying, and comparing the optical properties of orthovanadates with periodates and also with its high pressure phase based on the electronic structure. In the case of periodates, calculations were performed only at ambient phase due to lack of structural information regarding the high pressure phase. To the best of our knowledge, no experimental or theoretical studies are available on the electronic structure and optical properties of periodates.

2. Computational details

All electron Density Functional Theory calculations have been performed in order to study the electronic structure and optical properties of orthovanadates, periodates using the Full potential linearized augmented plane wave method (FP-LAPW) implemented in wien2K code [24,25]. FP-LAPW is an accurate method to calculate the optical properties. In this method, each atom is surrounded by the muffin tin sphere, and the unit cell of the crystal is partitioned into atomic sphere region, and interstitial region. Atomic sphere region is expanded in terms of spherical harmonics up to $l_{max} = 10$, as atomic like wave function, while the interstitial region can be expanded through the plane wave basis with wave vector cut-off of K_{max} . We have used the $R_{MT} K_{max}$ value to be 9, where R_{MT} is the smallest muffin tin radii, K_{max} is the plane wave cut-off. All the calculations were carried out at the corresponding experimental lattice constant with relaxed internal atomic positions by using the Perdew-Burke-Ernzerhof generalized gradient approximation [26] for exchange-correlation functional at ambient as well as at high pressures. Tetrahedron method is used to integrate the Brillouine zone. We have checked for the k-point convergence and $13 \times 13 \times 5$ k-mesh with 147 k-points in Irreducible Brillouin zone (IBZ) is used for CsIO_4 , $10 \times 10 \times 10$ k-mesh with 102 k-points, 144 k-points in the IBZ for zircon and scheelite structure respectively. It is well known that band gap values calculated using the standard exchange-correlation functionals is usually underestimated compared with that of experimental band gap. So in the present calculations, we have used Tran and Blaha modified Becke–Johnson potential (TB-mBJ) [27,28], which is computationally less expensive compared to GW calculations and give comparable experimental band gap values. The calculated optical spectra depends strongly on the BZ sampling, so we increased the k-mesh for the optical properties calculations to $17 \times 16 \times 6$ with 324 k-points in the IBZ for CsIO_4 , $17 \times 17 \times 17$ k-mesh with 405 k-points, 657 k-points in IBZ for zircon and scheelite phases of all the compounds respectively.

3. Results and discussions

3.1. Crystal structure

Orthovanadates crystallize in zircon-type tetragonal structure at ambient phase with space group $I4_1/amd$, and at high pressure, distortions lead to scheelite type tetragonal structures with space group $I4_1/a$. Lattice parameters of these compounds increases with increase in the cation size in the following sequence

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