

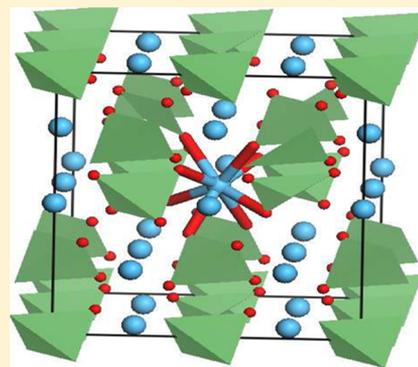
High-Pressure Structural Stability and Optical Properties of Scheelite-type ZrGeO_4 and HfGeO_4 X-ray Phosphor Hosts

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ABSTRACT: Ab initio calculations were performed on the scheelite-type MGeO_4 ($\text{M} = \text{Hf}$ and Zr) compounds, which find a wide range of applications such as in X-ray imaging. We have studied the high-pressure structural stability, elastic constants, electronic structure, and optical properties of these compounds through density functional theory calculations. Two different density functional approaches, plane wave pseudopotential method (PW-PP) and full potential linearized augmented plane wave method (FP-LAPW), were used for the present study. The ground-state structural and vibrational properties are calculated and found to be in good agreement with experimental data. The compressibility of Zr and Hf germanates is found to be anisotropic as the a -axis is less compressible over the c -axis due to the presence of Ge–O bonds along the a -axis, which is further confirmed from the ordering of the elastic constants that follows $C_{11} > C_{33}$. The electronic structure of the compounds has been calculated through recently developed Tran Blaha-modified Becke Johnson potential. The calculated electronic structure shows that the compounds are insulators with a gap of 5.39 eV for ZrGeO_4 and 6.25 eV for HfGeO_4 , respectively. Optical anisotropy of these compounds is revealed from the computed optical properties such as complex dielectric function, refractive index, and absorption coefficient. In addition, it is observed that Ti-doped ZrGeO_4 and HfGeO_4 turn out to be good phosphors as the pristine compounds have an energy gap greater than the visible range; upon Ti doping, the band gap reduces, and, as a result, emission spectra occur in the visible region and are well explained in the present study.



INTRODUCTION

Phosphors have a wide range of applications in X-ray imaging, detection, fluoroscopy, etc. Phosphors are used in the medical field particularly in X-ray imaging. The role of these phosphors is to reduce the exposure to X-rays while ensuring the sharpness of the image. To increase the sharpness of the image, we need higher density phosphor with sufficient conversion efficiency. A good X-ray phosphor must be a good absorber of X-ray, with high density and high luminescence efficiency.^{1–3} Over the past few decades, several X-ray phosphors such as BaFCl , $\text{Gd}_2\text{O}_2\text{S}$, Ln_2O_3 , Sr_2CeO_4 , AB_2O_4 ($\text{A} = \text{Sr}$, Zn , and Ca ; $\text{B} = \text{Ga}$, In , Y , and Al), $\text{LuTaO}_4\text{:Nb}$, $\text{Hf}_3\text{SnO}_8\text{:Nb}$, BaHfO_3 , and $\text{HfO}_2\text{:Ti}$ were developed.^{1,2} It is well-known that scheelite-type ABO_4 compounds can serve as good X-ray phosphors. Among the ABO_4 compounds, germanates of Zr and Hf possess high density and high conversion efficiency, which enables them to be used as X-ray phosphors. When doped with an impurity atom such as Ti, both ZrGeO_4 and HfGeO_4 are found to act as high density X-ray phosphors.^{2,4} These germanates have also been used as solid-state scintillators,⁵ heterogeneous catalysts,⁶ and laser-host materials.⁷

The scientific research on the scheelite-type compounds is mainly focused on the structural stability of the compounds under high pressure.^{8–12} These studies concluded that the

scheelite-structured compounds transform to monoclinic structure under high pressure. In contrast to these oxides, germanates of Zirconium and Hafnium have been relatively less studied both from theory and from experiment. Panchal et al. experimentally reported the equation of state (EOS) of ZrGeO_4 and HfGeO_4 up to the pressure of 20 GPa.¹³ The study reveals that both of the compounds do not undergo any phase transition up to the pressure of 20 GPa, in contrast to that of ThGeO_4 ,¹⁴ which undergoes phase transition from scheelite structure to monoclinic fergusonite structure. This strongly suggests that there is a clear need to understand the high-pressure structural stability of germanates of zirconium and hafnium from a theoretical point of view to address the peculiar high-pressure characteristics.

Theoretical study based on density functional theory calculations is an effective way to understand the properties of solid materials at ambient as well as high pressures. In this present work, we aim to understand the high-pressure structural stability of ZrGeO_4 and HfGeO_4 and also shed light on the optical properties with the help of electronic structure by

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performing the first principles density functional calculations. In addition, the main goal of the present work lies in highlighting the effect of Ti doping in ZrGeO_4 and HfGeO_4 as they are claimed to be good phosphors. The rest of this Article is organized as follows: Section 2 deals with the computational details, results and discussion are given in section 3, and we end this Article with the conclusions in section 4.

COMPUTATIONAL DETAILS

The crystal structure, elastic, and vibrational properties were calculated using the Cambridge Sequential Total Energy package.^{15–17} We have used Vanderbilt-type ultrasoft pseudopotentials¹⁸ with a planewave expansion of the wave functions. The electronic wave functions were obtained using the density mixing scheme,¹⁹ and the structures were relaxed using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method.²⁰ The exchange–correlation potential of Ceperley and Alder²¹ parametrized by Perdew and Zunger²² in the local density approximation (LDA) and also the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) parametrization²³ was used to describe the exchange–correlation potential. The pseudo atomic calculations were performed for Zr $4d^25s^2$, Hf $5d^26s^2$, Ge $4s^24p^2$, and O $2s^22p^4$. The Monkhorst–Pack scheme of k -point sampling was used for integration over the Brillouin zone.²⁴ The convergence criteria for structure optimization and energy calculation were set to ultra fine quality. We have a cutoff energy of 420 eV and $4 \times 4 \times 4$ k -points grid for all of the calculations. In the geometry relaxation, the self-consistent convergence threshold on the total energy is 5×10^{-7} eV/atom, and the maximum force on the atom is 10^{-4} eV/Å. The elastic constants are calculated for the optimized crystal structure at ambient conditions by using the volume-conserving strain technique²⁵ as implemented in CASTEP code. We have relaxed the internal coordinates of the strained unit cell to arrive at the elastic constants.

The electronic structure and optical properties have been calculated by using the full-potential linearized augmented planewave method as implemented in WIEN2k code^{26,27} by using the origin choice of 2. For the calculation of electronic structure, we have used a $10 \times 10 \times 10$ k -grid with 144 k -points in the irreducible Brillouin zone (IBZ) and $18 \times 18 \times 18$ k -grid with 780 k -points in IBZ for the calculation of optical properties for the k -space integration. We have used the convergence parameter $R_{\text{MT}}K_{\text{max}} = 9$, where K_{max} is the planewave cutoff and R_{MT} is the smallest of all atomic sphere radii, and the muffin-tin radius was assumed to be 2.13, 1.80, and 1.54 au for Zr, Ge, and O elements, respectively, in the case of ZrGeO_4 compound, and 2.12, 1.87, and 1.47 au for Hf, Ge, and O, respectively, for the compound HfGeO_4 . Electronic structure calculations were performed using the Perdew–Burke–Ernzerhof (PBE),²³ Engel–Vosko,²⁸ and Tran and Blaha modified Becke–Johnson potential (TB-mBJ).^{29,30} To study the effect of Ti doping in ZrGeO_4 and HfGeO_4 , a supercell of size $2 \times 1 \times 1$ has been constructed where Zr and Hf were replaced by Ti (0.25) atom (muffin-tin radii of Ti 2.13 au in the case of ZrGeO_4 and 2.12 au in the case of HfGeO_4 compound). With this supercell structure, we have calculated the electronic and optical properties to find the effect of doping on these properties with the TB-mBJ functional.

RESULTS AND DISCUSSION

Crystal Structure at Ambient Pressure. The compounds ZrGeO_4 , HfGeO_4 crystallize in tetragonal crystal structure with spacegroup $I4_1/a$ (88) with 4(b) Wyckoff positions for M (Zr, Hf) atom and 4(a) and 16(f) for Ge, O atoms, respectively. The structure consists of an isolated GeO_4 tetrahedron linked by 8-fold coordinated metal cation polyhedra.^{31,32} The scheelite crystal structure of HfGeO_4 is shown in Figure 1. As a first step,

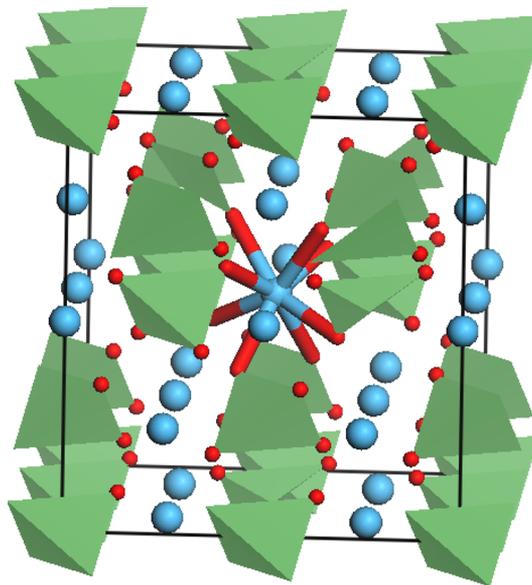


Figure 1. The scheelite crystal structure of HfGeO_4 . Here, the blue ball indicates the Hf atom, the red ball indicates the O atom, and the Ge atom is within the tetrahedra.

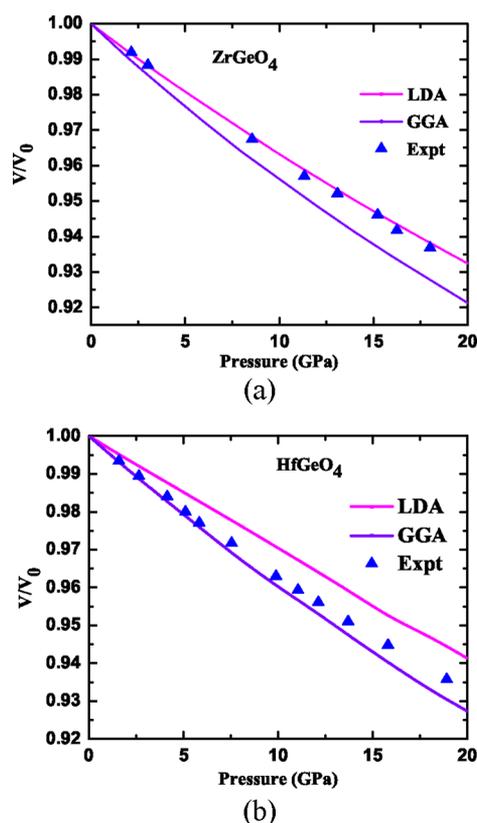
we have optimized the experimental crystal structure of both compounds ZrGeO_4 and HfGeO_4 by using LDA and GGA. The calculated equilibrium lattice parameters of both compounds using LDA and GGA exchange–correlation functionals are presented in Table 1 along with the experimental data. The difference between the computed and experimental volume is less within LDA as compared to GGA. The calculated volume at the LDA level is underestimated by 3.8%, 2.5%, whereas the GGA overestimated the volume by 3.2%, 8.3% for ZrGeO_4 and HfGeO_4 respectively. Therefore, for the ground-state structural properties of Zr- and Hf-based scheelite compounds, the agreement between the theoretical and experimental values is good with LDA over GGA. This is in good accord with the earlier theoretical reports on the scheelite structured compounds where LDA works well in the description of crystal structure.¹⁴

Structural Properties under Pressure. To study the effect of hydrostatic pressure on the crystal structure of ZrGeO_4 and HfGeO_4 , we have used the variable cell optimization technique as implemented in CASTEP code. We applied hydrostatic pressure up to 20 GPa. The external pressure was gradually increased by an increment of 2 GPa in each time. Under a given pressure, the internal coordinates and unit cell parameters of the germanate crystal were determined by minimizing the Hellmann–Feynman force on the atoms and the stress on the unit cell simultaneously. The computed pressure-normalized volume diagrams by using LDA and GGA along with experimental data are plotted in Figure 2a and b, respectively. Up to the studied pressure range of 20 GPa, the

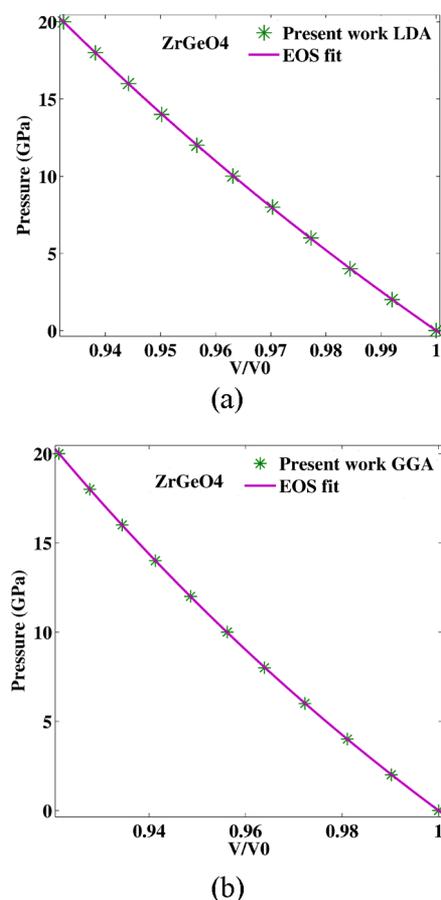
Table 1. Calculated Ground-State Properties of Tetragonal ZrGeO₄ and HfGeO₄ at Ambient Pressure

lattice parameter	LDA	GGA	expt
ZrGeO ₄			
<i>a</i> (Å)	4.804	4.910	4.866 ^a
<i>b</i> (Å)	4.804	4.910	4.866 ^a
<i>c</i> (Å)	10.406	10.694	10.550 ^a
<i>V</i> (Å ³)	240.2	257.8	249.8
Zr	(0, 0, 0.5)	(0, 0, 0.5)	(0, 0, 0.5) ^a
Ge	(0, 0, 0)	(0, 0, 0)	(0, 0, 0) ^a
O	(0.2541, 0.1613, 0.0634)	(0.2568, 0.8143, 0.0575)	(0.2664, 0.1726, 0.0822) ^a
HfGeO ₄			
<i>a</i> (Å)	4.805	4.982	4.862 ^b
<i>b</i> (Å)	4.805	4.982	4.862 ^b
<i>c</i> (Å)	10.472	10.83	10.497 ^b
<i>V</i> (Å ³)	241.8	268.9	248.1 ^b
Hf	(0, 0, 0.5)	(0, 0, 0.5)	(0, 0, 0.5) ^b
Ge	(0, 0, 0)	(0, 0, 0)	(0, 0, 0) ^b
O	(0.2607, 0.1656, 0.0830)	(0.2514, 0.1645, 0.0681)	(0.2678, 0.1739, 0.0831) ^b

^aReference 31. ^bReference 32.

**Figure 2.** Pressure versus V/V_0 of (a) ZrGeO₄ and (b) HfGeO₄.

volume reduction V/V_0 is approximately 7% in LDA and 8% in GGA for both of the compounds. It should be noted that for both of the compounds, LDA works well at ambient conditions, and as pressure increases, GGA values are found to be in close agreement with experiments for HfGeO₄. The computed pressure volume–data have been fitted to the Murnaghan equation of state (EOS). The corresponding figures are shown in Figure 3a,b within LDA and GGA, respectively, for ZrGeO₄,

**Figure 3.** Pressure versus V/V_0 of ZrGeO₄: (a) LDA and (b) GGA fitted with Murnaghan equation of state.

and in Figure 4a and b, we have shown them for HfGeO₄. The bulk modulus B and its pressure derivative B_0' are found to be $B_0 = 247.7$ GPa, $B_0' = 3.985$ in LDA and $B_0 = 200.1$ GPa, $B_0' = 4.692$ in GGA for ZrGeO₄, whereas $B_0 = 265.7$ GPa, $B_0' = 4.473$ in LDA and $B_0 = 226.5$ GPa, $B_0' = 4.044$ in GGA for HfGeO₄, respectively. The high bulk modulus of the compound results in low compressibility. The bulk modulus values of these compounds are found to be greater than those of other scheelite-type compounds CaWO₄ (74 GPa),¹¹ SrWO₄ (63 GPa),¹¹ PbWO₄ (66 GPa),¹¹ and ThGeO₄ (183 GPa).¹⁴ Therefore, both of these compounds are hard and less compressible than the above-mentioned scheelite compounds.

The variation of lattice parameters a and c with pressure are given in Figure 5a for ZrGeO₄ and in Figure 5b for HfGeO₄, respectively, along with the experimental data. Clearly, the compression of Zr and Hf germanates is anisotropic as the lattice parameters have different compression behavior with pressure. For both of the compounds, the c -axis is 1.4% more compressible than the a -axis in LDA, whereas it is 1.6% in GGA. The compressibility of the lattice axis through LDA calculations is in good agreement with the experimental result, that is, 1.3% more compression of c -axis over a -axis. This anisotropy in the axial compressibility of scheelite (Zr and Hf) GeO₄ compounds is also observed in the other scheelite compounds such as ThGeO₄ and also for zircon, ZrSiO₄. This may also be due to the fact that in both of the compounds Ge–O bonds are aligned along the a -axis. The Mulliken bond populations of Ge–O and M(Zr, Hf)–O are found to be 0.58,

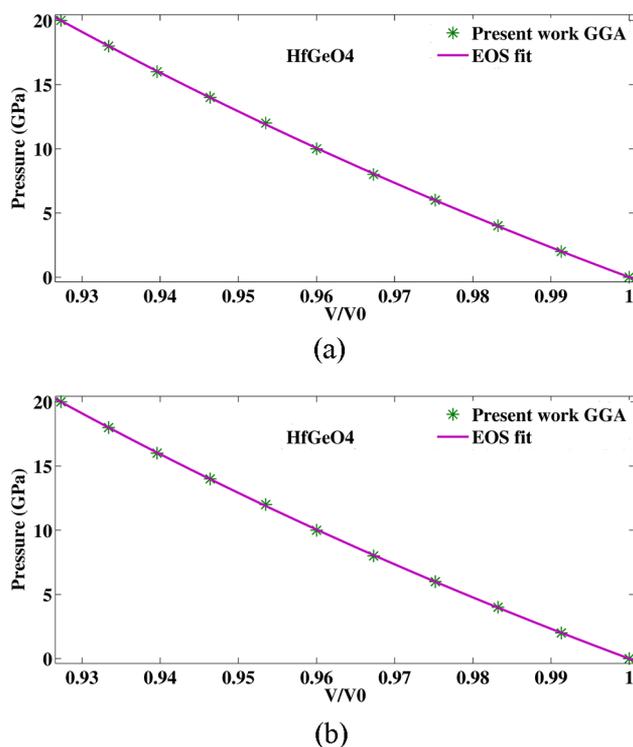


Figure 4. Pressure versus V/V_0 of HfGeO_4 : (a) LDA and (b) GGA fitted with Murnaghan's equation of state.

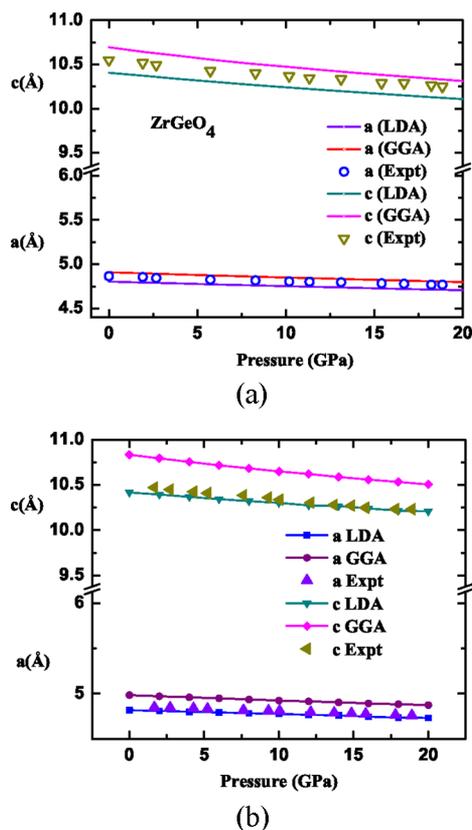


Figure 5. Variation of lattice parameters of (a) ZrGeO_4 and (b) HfGeO_4 with pressure.

0.34 for ZrGeO_4 and 0.56, 0.40 for HfGeO_4 , respectively. This clearly shows that both of the materials are covalent in nature.

Bulk Modulus and Elastic Constants. The elastic constants have been calculated to assess the mechanical stability of the studied compounds. Because the compounds have tetragonal crystal symmetry, there are six independent elastic constants, C_{11} , C_{12} , C_{13} , C_{33} , C_{44} , and C_{66} . The calculated elastic constants are presented in Table 2. To the best of our knowledge, there are no experimental data available to compare with the present values. The mechanical stability of the tetragonal crystal requires the whole set of elastic constants satisfying the Born–Huang criterion³³ given by $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, and $[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0$. Clearly, the calculated elastic constants satisfy all of the stability criteria indicating the scheelite-type structured Zr and Hf germanates to be mechanically stable systems. The bulk modulus of the compounds is calculated by using the elastic constants data, and the value is given in Table 2. The calculated bulk modulus of both of the compounds is in fair agreement with the experimental values. The calculated bulk moduli from the elastic constants agree well with those directly obtained from the fitting of the pressure–volume data to the Murnaghan EOS. It should be noted that the computed bulk modulus value of ZrGeO_4 ($B = 245.2$ GPa) is higher than that of zircon ZrSiO_4 ($B = 225.2$ GPa) but lower when compared to HfGeO_4 ($B = 266.6$ GPa).

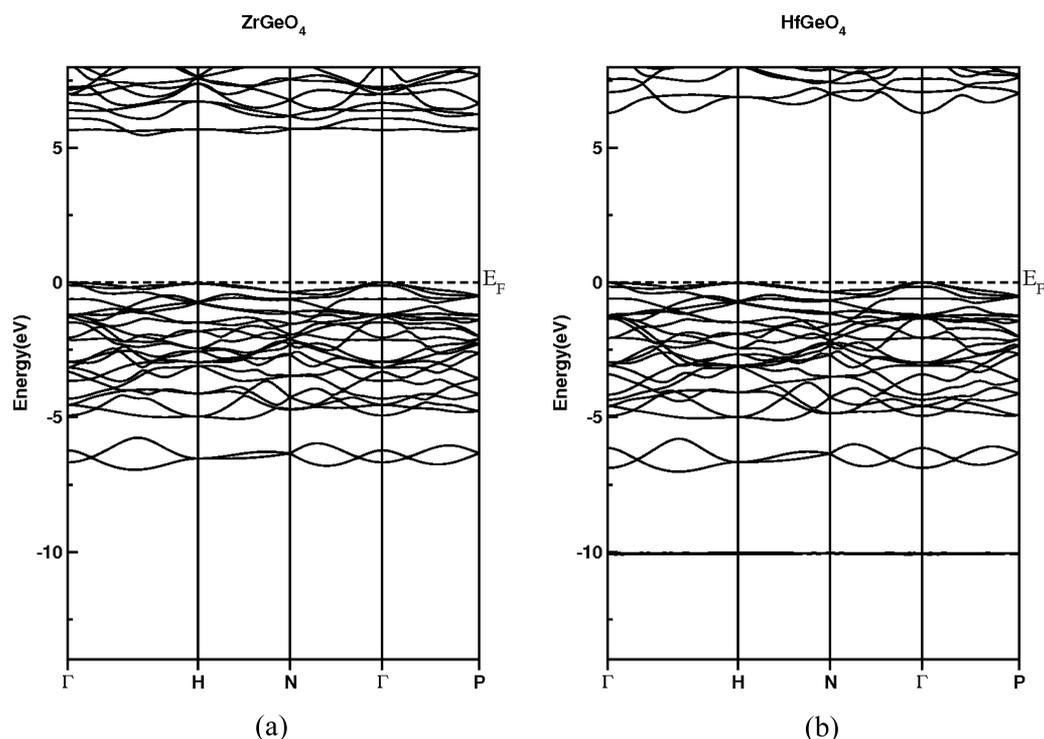
Electronic Properties. It is well-known that the scheelite structured ABO_4 compounds are wide band gap semiconductors.⁸ To the best of our knowledge, there are no studies available on electronic structure and optical properties of the scheelite structured germanates ZrGeO_4 and HfGeO_4 . The electronic band structures of the ZrGeO_4 and HfGeO_4 have been calculated using three different exchange–correlation functionals, GGA-PBE, EV-GGA, and TB-mBJ as implemented in WIEN2k code. Among these functionals, the TB-mBJ functional results in improving the energy gaps when compared to experiment. Koller et al. calculated the electronic band gaps of semiconducting transition metal oxides using the TB-mBJ functional, which are in very good agreement with experiments.³⁰ Recently, Dixit et al. calculated electronic band structures of binary and ternary oxides using the TB-mBJ potential along with GW calculations. Their study concludes that the calculated band gaps compare well with those obtained from GW calculations and also with experiment.³⁴ Camargo-Martinez et al. calculated the electronic band gaps of different types of semiconductors and insulators using the TB-mBJ functional, which are consistent with experimental results.³⁵ Therefore, in this study, we have used the TB-mBJ functional to determine the exact band gap values of ZrGeO_4 and HfGeO_4 compounds besides the usual PBE and EV functionals. The calculated electronic band structures of the germanates along high symmetry directions are shown in Figure 6a and b, respectively. The computed band structures clearly show that ZrGeO_4 has the band gap of 5.39 eV, whereas HfGeO_4 has the band gap of 6.25 eV, respectively. One should notice that the valence band maxima (VBM) and conduction band minima (CBM) are located at Γ point for HfGeO_4 leaving the compound as a direct band gap insulator, whereas ZrGeO_4 is an indirect gap material as VBM and CBM occur along Γ and H , respectively. The band gaps calculated using the three exchange correlational functionals GGA-PBE, EV-GGA, and TB-mBJ are presented in Table 3.

The calculated densities of states (DOS) for the investigated compounds are shown in Figure 7a and b, respectively, which

Table 2. Single-Crystal Elastic Constants (C_{ij} in GPa) and Bulk Modulus B (GPa) of $ZrGeO_4$ and $HfGeO_4$ Calculated at the Theoretical Equilibrium Volume within LDA

compound	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B
$ZrGeO_4$	444.9	190.9	151.5	365.8	82.9	113.3	245.2 [229.4] ^a (238) ^b
$HfGeO_4$	447.5	209.6	177.5	397.5	95.9	128.1	266.6 [235.7] ^a (242) ^b

^aThe bulk modulus value calculated within GGA. ^bReference 13.

**Figure 6.** Calculated band structure of $MGeO_4$ ($M = Zr, Hf$) along the high symmetry directions using the TB-mBJ functional at the experimental lattice constants.**Table 3.** Calculated Band Gap, in eV, of $MGeO_4$ ($M = Zr, Hf$) Compounds Using GGA, EV, and TB-mBJ Functionals at the Experimental Lattice Constants

method	$ZrGeO_4$	$HfGeO_4$
GGA	4.03	4.29
EV	4.28	4.66
TB-mBJ	5.39	6.25

are helpful in identifying the character of band states at different energy levels. The DOS plots show two upper and middle valence bands in the case of $ZrGeO_4$ compound and three bands, upper valence band, middle valence band, and lower valence band, in the case of $HfGeO_4$. For both of the compounds, the upper valence band is formed due to hybridization of O-p states, Ge-p, and M (Hf, and Zr)-d states around the energy range -5 to 0 eV, the middle valence band is mostly from Ge-s and O-p states situated around the energy range of -7.0 to -5.7 eV, and an extra lower valence band is present in the case of $HfGeO_4$ when compared to $ZrGeO_4$ due to the presence of extra f-electrons in Hf around the energy range from -10 to -9.4 eV. We found strong hybridization of Ge-p, O-p states, which reveal the covalent bond between the Ge and O atoms. In both cases, the conduction band is formed due to the d-states of Zr and Hf metal atoms.

To know the effect of Ti doping on the electronic structure properties, we have calculated the partial density of states with

Ti-doped $ZrGeO_4$ and $HfGeO_4$, and the corresponding figures are shown in Figure 7c and d, respectively. We observed the additional Ti-d states are present in the energy gap of the host compound around the energy range 3.2 – 4.9 eV for $ZrGeO_4$ compound and 3.3 – 4.5 eV for $HfGeO_4$ compound, thereby reducing the original band gap of these compounds to 3.2 and 3.3 eV for $ZrGeO_4$, $HfGeO_4$ compounds, respectively.

Optical Properties. Optical properties of $ZrGeO_4$ and $HfGeO_4$ have been studied by using the TB-mBJ potential. To calculate the optical properties, we have used a denser k -point grid of $18 \times 18 \times 18$ to arrive at the accurate optical properties. The complex dielectric function ($\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$), which gives the response of the material to external photon perturbation, consists of real and imaginary parts. The real part of the dielectric function ϵ_1 can be calculated from the imaginary part by using the Kramers–Kronig relations, and the knowledge of both the real and the imaginary parts of the dielectric function allows the calculation of important optical properties such as refractive index, reflectivity, and absorption coefficients. The calculated absorptive part $\epsilon_2(\omega)$ and the dispersive part $\epsilon_1(\omega)$ of the complex dielectric function as a function of photon energy are shown in Figure 8a and b, respectively. In the imaginary part of the dielectric function, the threshold energy increases from Zr to Hf because of the increase in the band gap values from Zr to Hf. The maximum value of the imaginary part of dielectric function is found to be

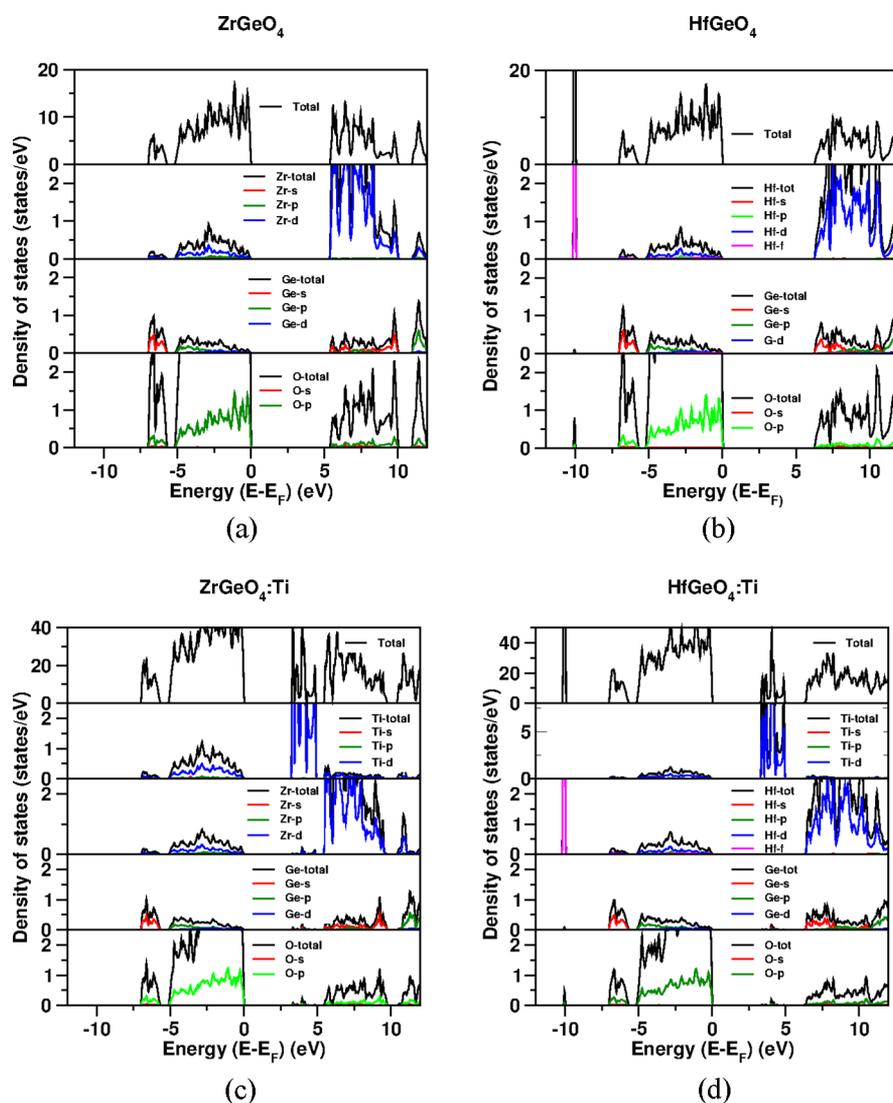


Figure 7. Total and partial density of states of (a) ZrGeO_4 , (b) HfGeO_4 , and Ti-doped (c) ZrGeO_4 and (d) HfGeO_4 compounds calculated using the TB-mBJ functional.

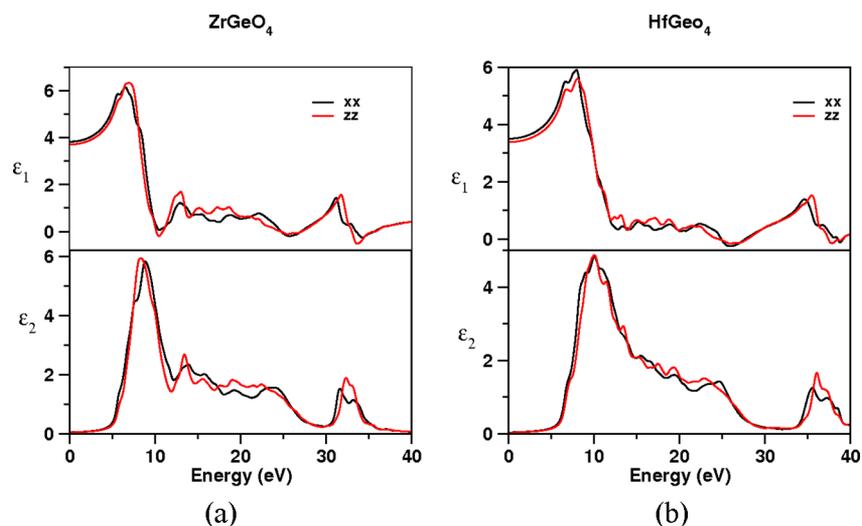


Figure 8. Calculated dielectric function of (a) ZrGeO_4 , (b) HfGeO_4 using TB-mBJ functional.

5.93 at energy of 8.34 eV in the case ZrGeO_4 , while in the case of HfGeO_4 the maximum value of 4.84 is reached at energy of

10 eV. It is known that the absorptive part of the dielectric function $\varepsilon_2(\omega)$ can be related to the band structure by means of

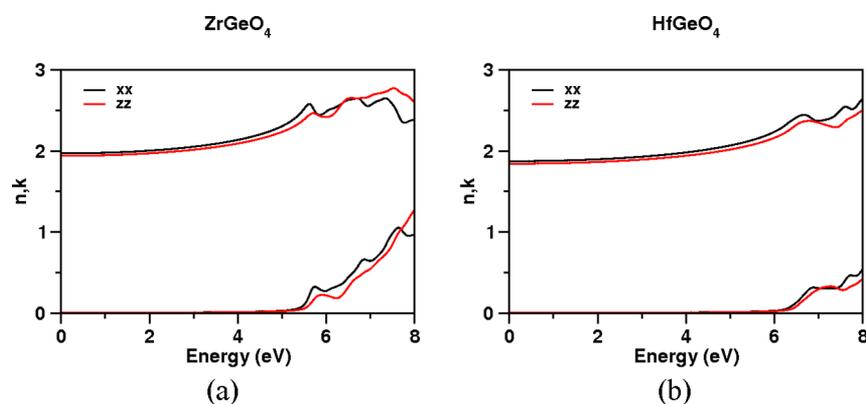


Figure 9. Calculated refractive index of (a) ZrGeO_4 , (b) HfGeO_4 using the TB-mBJ functional.

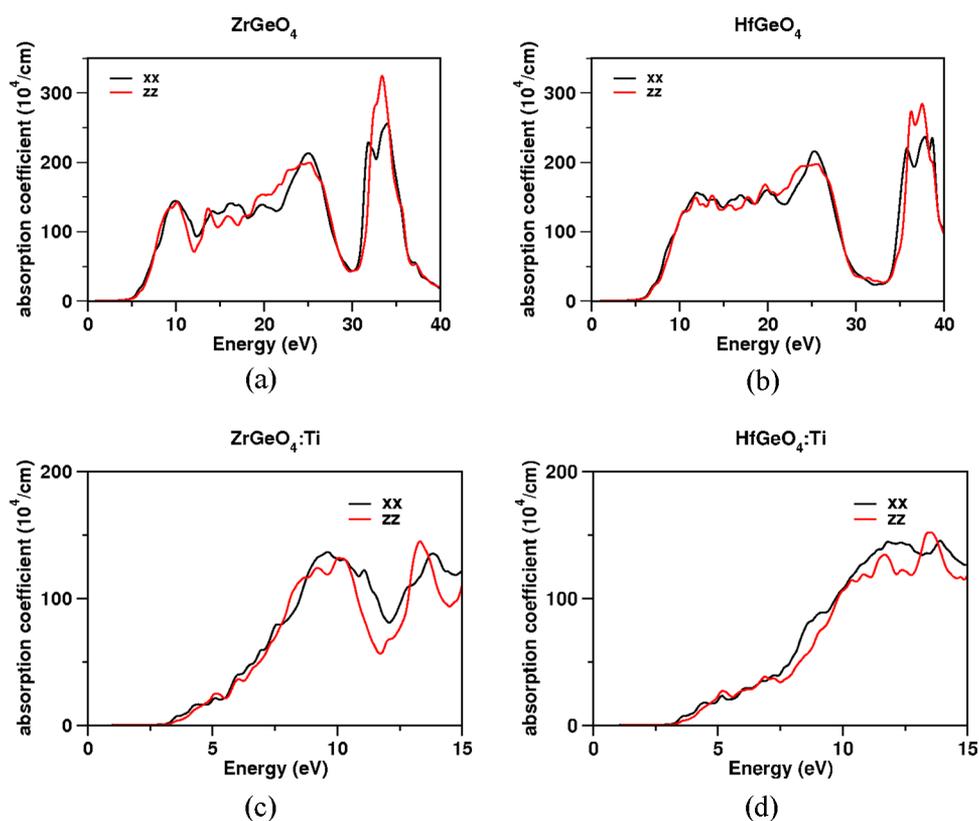


Figure 10. Absorption spectra of (a) ZrGeO_4 , (b) HfGeO_4 , (c) $\text{ZrGeO}_4:\text{Ti}$, and (d) $\text{HfGeO}_4:\text{Ti}$ compounds using the TB-mBJ functional.

interband transitions. The calculated $\epsilon_2(\omega)$ spectra of both of the germanates have different peaks at different photon energies, which are entirely due to the optical transitions from the occupied states (valence band) to unoccupied states (conduction band). The sharp peak observed at 8.34 eV in ZrGeO_4 and at 10 eV in HfGeO_4 may be due to the transition from the “p” states of O to the “d” states of Zr. The calculated dispersive part of dielectric function $\epsilon_1(\omega)$ clearly shows that both of the germanates are optically anisotropic materials and the static values of $\epsilon_1(\omega)$ are given by 3.82 and 3.70 for the compound ZrGeO_4 along the x , z directions and 3.49, 3.38 for the compound HfGeO_4 , respectively. The calculated $\epsilon_1(\omega)$ is found to increase with photon energy and reaches a maximum value and then decreases with increase in the photon energy. We also calculated the refractive index “ n ” and extinction coefficient “ κ ” of the germanates as a function of incident photon energy, which are shown in Figure 9a and b,

respectively. The refractive index follows the opposite trend to that of the band gap. The static refractive index values of the compounds are 1.94, 1.855 for the ZrGeO_4 , HfGeO_4 compounds, respectively, which is opposite to that of the band gap; that is, band gap values increase from Zr to Hf. The calculated frequency-dependent absorption coefficient is shown in Figure 10a and b, which is directly proportional to the imaginary part of dielectric function. From Figure 10a and b, it is clearly seen that the absorption edge moves to higher energies as we move from Zr to Hf because of the increase in the band gap values from ZrGeO_4 to HfGeO_4 . For both of the compounds, we observed the absorption spectra mostly in the region 6–40 eV, that is, in the ultraviolet region.

It is reported that $\text{MGeO}_4:\text{Ti}$ ($\text{M} = \text{Zr}$ and Hf) are good phosphors.^{2,4} To study the effect of Ti addition on these compounds, we have calculated the electronic and optical properties of ZrGeO_4 and HfGeO_4 with Ti doping. We

observed the doped Ti states near the conduction band as shown in Figure 7c and d. Similar results are also obtained in the first principles study of $\text{HfO}_2\text{:Ti}^{36}$ where the impurity states formed are near the bottom of the conduction band leading to the reduction in the band gap; moreover, it is also found that $\text{HfO}_2\text{:Ti}$ is a good phosphor. In our present study, we also observed the band gap to reduce with the addition of Ti. We have also calculated the absorption spectra of Ti-doped ZrGeO_4 and HfGeO_4 compound as shown in Figure 10c and d and found the spectra shift to a lower energy region as compared to the host compound. As a result, we may expect the emission spectra to be in the visible region, which might be a reason for these compounds to be a good phosphor with the addition of Ti.

Vibrational Properties. Vibrational properties are obtained by the use of linear response method within the density functional perturbation theory (DFPT).^{37,38} In this method, the force constants matrix can be obtained by differentiating the Hellmann–Feynman forces on atoms with respect to the ionic coordinates. This means that the force constant matrix depends on the ground-state electron charge density and on its linear response to a displacement of the atoms. By variational principle, the second-order change in energy depends on the first-order change in the electron density, and this can be obtained by minimizing the second-order perturbation in energy, which gives the first-order changes in the density, wave functions, and potential. In the present study, elements of the dynamical matrix are calculated on the $4 \times 4 \times 4$ grid of k -points using the linear response approach. The primitive cell of the germanates contains 2 formula units, and hence there are 36 vibration modes. Out of these 36 modes, three are acoustic modes and the remaining 33 are optical modes. The following shows the details of group theory symmetry decomposition of the modes: acoustic modes, $A_u + 2E_u$, and optical modes, $8E_u + 4A_u + 3B_u + 10E_g + 5B_g + 3A_g$. In these modes, E_u and A_u are infrared active, whereas E_g , B_g , and A_g modes are Raman active and B_u modes are silent. The calculated vibrational frequencies are presented in Table 4 along with the experimental Raman frequencies values of ZrGeO_4 . In the case of the present germanates, there are in total 13 Raman active phonon modes $3A_g + 5B_g + 5E_g$. Out of these 13 modes, seven are internal modes of GeO_4 tetrahedra. The modes with frequencies 811.3 cm^{-1} (A_g), 790.4 cm^{-1} (E_g), and the mode at 732.4 cm^{-1} (B_g) in ZrGeO_4 and the modes with frequencies 830.1 cm^{-1} (A_g), 826.1 cm^{-1} (E_g), and the mode with frequency 766.3 cm^{-1} (B_g) in HfGeO_4 are due to the stretching of Ge–O bonds, respectively. The bending modes are situated at 414.8 cm^{-1} (A_g), 425.6 cm^{-1} (B_g), 610.7 cm^{-1} (B_g), and 538.7 cm^{-1} (E_g) in ZrGeO_4 and 383.2 cm^{-1} (A_g), 401.1 cm^{-1} (B_g), 564.4 cm^{-1} (B_g), and 497.6 cm^{-1} (E_g) in HfGeO_4 , respectively. The remaining six modes are rotational (A_g and E_g) and translational modes ($2B_g$ and $2E_g$).

CONCLUSION

We have studied the high-pressure structural stability, elastic constants, and vibrational properties of scheelite-type MGeO_4 ($M = \text{Zr, Hf}$) compounds, which are good X-ray phosphors by using planewave pseudopotential method and electronic and optical properties using full potential linearized augmented plane wave method. We found that there is no structural phase transition until the studied pressure range of 20 GPa, which is in good agreement with the experiment. We also noticed that both of the compounds are highly incompressible, and it is

Table 4. Vibrational Frequencies of ZrGeO_4 and HfGeO_4 Calculated at Theoretical Equilibrium Volume within LDA. Here RA refers to Raman Active and IA refers to Infrared Active

mode	ZrGeO_4 (ref 4)	mode	HfGeO_4
B_g	167.3 (171) (RA)	E_g	153.0 (RA)
E_g	180.5 (182) (RA)	B_g	157.1 (RA)
A_u	194.1 (IA)	A_u	174.9 (IA)
E_u	196.9 (IA)	E_u	204.6 (IA)
E_g	252.7 (255) (RA)	E_g	246.3 (RA)
A_g	288.6 (294) (RA)	E_u	269.6 (IA)
A_u	292.4 (IA)	B_g	269.9 (RA)
E_u	299.7 (IA)	A_u	294.3 (IA)
B_g	317.8 (306) (RA)	A_g	306.2 (RA)
B_u	340.2	B_u	366.1
A_g	383.2 (378) (RA)	E_g	398.3 (RA)
E_g	384.4 (368) (RA)	A_g	414.8 (RA)
B_g	404.1 (406) (RA)	B_g	425.6 (RA)
E_u	439.3 (IA)	E_u	479.4 (IA)
E_g	497.6 (495) (RA)	E_g	538.7 (RA)
A_u	527.9 (IA)	A_u	553.3 (IA)
B_g	564.4 (565) (RA)	B_g	610.7 (RA)
B_u	630.6	B_u	676.0
E_u	712.4 (IA)	E_u	724.4 (IA)
A_u	716.1 (IA)	A_u	741.2 (IA)
B_g	732.4 (729) (RA)	B_g	766.3 (RA)
B_u	781.7	B_u	793.7
E_g	790.4 (782) (RA)	E_g	826.1 (RA)
A_g	811.3 (802) (RA)	A_g	830.1 (RA)

found to be more compressible along the c -axis than along the a -axis, which might be due to the presence of a strong covalent Ge–O bond along a -axis. This fact is also confirmed from the calculated elastic constants, which follow the order $C_{11} > C_{33}$. In addition, we have also calculated the vibrational properties and discussed the Raman and IR frequencies of the germanates, which are in reasonable agreement with the experiment. The investigated germanate compounds are found to be insulators, and the band gap is more for HfGeO_4 than for ZrGeO_4 . The optical properties were calculated and analyzed through the computed band structures. We also studied the doping effect of Ti on electronic structure, and we found this doped state to be near the conduction band edge. As a result, the band gap of these compounds decreases, and we also observed the absorption spectra to shift to lower energy regions, leading to the expectation that the emission spectra may be in the visible range, which might be a reason for these compounds to be good X-ray phosphors when doped with Ti.

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Notes

The authors declare no competing financial interest.

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