

Exploring the Structural, Electronic and Optical Properties of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ Double Perovskite: A DFT Investigation

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Abstract

This work provides a complete first-principles study of the structural, electronic and optical properties of the double perovskite $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ with the doping amount $x=0.25, 0.50, 0.75$ and 1.0 . Structural optimization shows that the compositions all exhibit cubic symmetry with $\text{Fm}\bar{3}\text{m}$ space group, and are both geometrically and dynamically stable, based on tolerance factor calculations and phonon dispersion analysis. The electronic structure calculations show that as Nb is replaced by V, the band gap decreases dramatically, resulting in 1.473, 1.046, 0.785 and 0.565 eV values, and changes the transition from direct to an indirect band gap character with higher concentration of V. These electronic changes are mainly due to the increased level of hybridization between the V-3d/Rh-4d states and the O-2p orbitals. The optical response studied using the complex dielectric function, absorption coefficient, extinction coefficient, reflectivity, optical conductivity and energy-loss spectrum, shows significant strengthening in the visible and near-infrared range as V content increases. For the full substituted compound Ba_2VRhO_6 , a distinct redshift at the absorption edge and enhanced plasmon resonance at high energies is seen. In conclusion, the tunable band-gap property and enhanced optical characteristics of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ perovskites suggest that they may be useful candidates for high-efficiency solar cells, broadband photodetectors, and multifunctional optoelectronic devices.

Keywords: Double Perovskites, $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$, Doping effect, Band gap engineering, Optoelectronic properties.

تأثير استبدال الفاناديوم على الخصائص البنيوية والإلكترونية والبصرية للبيروفسكايت المزدوج $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$: دراسة باستخدام نظرية الكثافة الوظيفية (DFT).

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الخلاصة

يقدم هذا العمل دراسة شاملة من المبادئ الأولى للخصائص البنيوية والإلكترونية والبصرية للبيروفسكايت $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ المزدوج، مع نسب تشويب 0.25، 0.5، 0.75 و 1.0. يُظهر التحسين الهندسي أن جميع التركيبات تتمتع بتناظر مكعب مع المجموعة الفراغية $\text{Fm}\bar{3}\text{m}$ ، وأنها مستقرة هندسيًا وديناميكيًا، استنادًا إلى حسابات عامل التسامح وتحليل تشتت الفونون. تُظهر حسابات البنية الإلكترونية أنه مع استبدال النيوبيوم بالفاناديوم، تنخفض فجوة النطاق بشكل كبير، لتصل إلى 1.473، 1.046، 0.785 و 0.565 إلكترون فولت، ويتغير الانتقال من فجوة نطاق مباشرة إلى فجوة نطاق غير مباشرة مع زيادة تركيز الفاناديوم. تُعزى هذه التغيرات الإلكترونية بشكل أساسي إلى زيادة مستوى التهجين بين حالات V-3d/Rh-4d ومدارات O-2p. أظهرت الاستجابة البصرية المدروسة باستخدام دالة العزل الكهربائي المعقدة، ومعامل الامتصاص، ومعامل الخمود، والانعكاسية، والتوصيلية البصرية، وطيف فقد الطاقة، تحسنًا ملحوظًا في نطاق الضوء المرئي والأشعة تحت الحمراء القريبة مع زيادة محتوى الفاناديوم. بالنسبة للمركب Ba_2VRhO_6 المُستبدل بالكامل، لوحظ انزياح واضح نحو الأحمر عند حافة الامتصاص، بالإضافة إلى تعزيز رنين البلازمون عند الطاقات العالية. في الختام، تشير خاصية فجوة النطاق القابلة للضبط والخصائص البصرية المحسنة للبيروفسكايت $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ إلى أنها قد تكون مرشحة واعدة للخلايا الشمسية عالية الكفاءة، وكواشف الضوء واسعة النطاق، والأجهزة الإلكترونية الضوئية متعددة الوظائف.

1. Introduction

The multifunctional materials research is now active, owing to the natural structural flexibility, chemical flexibility and strong electron-lattice coupling of double perovskite oxides of the general formula $A_2BB'O_6$, which can be exploited for optoelectronics, thermoelectrics, spintronics and energy conversion technologies [1-4]. The ordered population of the B and B' sites with two different transition-metal cations leads to a rich physicochemical behavior in these systems, and can be engineered to have both band structures, magnetic interactions, optical responses, and phonon transport on-demand by replacing cations [5-7]. In recent years, the rational design and modelling of such compounds have gained remarkable speed, particularly using the density functional theory (DFT) as a reliable theoretical framework to understand all aspects of their electronic, optical, structural, and stability performance [8-11].

Barium based Double Perovskites are of particular interest because the ionic radius of the Ba^{2+} ions is large, which leads to a stable cubic structure and good metal-oxygen hybridization [12, 13]. The Ba_2NbRhO_6 system has potential, but it is a promising frontier to be able to manipulate its properties by doping. The incorporation of Vanadium (V) at the B site as a substitute for Nb is a promising way to tune the properties of conduction band, carrier mobility, structural stability and optical response, crucial for the optimization of optoelectronic performance [14-16]. Although the Ba_2NbRhO_6 compound is important, there is no systematic study on the effect of Vanadium doping to the properties of the compound, so far, which is known as the $Ba_2Nb_{1-x}V_xRhO_6$ series. The current study is motivated by the lack of knowledge to systematically study the structural stability, electronic and optical properties of $Ba_2Nb_{1-x}V_xRhO_6$ for different compositions ($x = 0.25, 0.50, 0.75$ and 1.0) using first-principles DFT calculations. The optimized crystal structure, tolerance factor, phonon stability, band structure, density of states, and different optical properties such as dielectric function, absorption, and reflectivity are analyzed, providing a complete description of the effect of Vanadium doping on the structure and the improvement of the optical response in the visible spectrum. It provides fresh perspectives on the promise of these materials to be used in next-generation photovoltaics and optoelectronics.

2. Computational Method

The Structural, stability, electronic and optical properties of $Ba_2Nb_{1-x}V_xRhO_6$ ($x = 0.25, 0.50, 0.75$, and 1.0) will be investigated by DFT method by using LCAO Quantum ATK software [17]. All properties were modeled with the GGA-PBE exchange and correlation functional and obtained with FHI pseudopotentials, while the computed electronic properties were obtained using the MGGA functional and SG15 pseudopotentials [18]. All the calculations were carried out with the cutoff of the kinetic energy of 150 Hartree, energy convergence of 10^{-6} eV/atom and Monkhorst-Pack with a spacing in k-point grid of $12 \times 12 \times 12$, so that all the calculated values were fully converged [4]. Finally, the combined computational approach proves to be a good compromise between the numerical accuracy and the computational speed, and a multifunctional character of this series of compounds, $Ba_2Nb_{1-x}V_xRhO_6$ ($x = 0.25, 0.50, 0.75$, and 1.0), can be strongly characterized. The magnetic ground state was also checked by performing spin polarized calculations. However, no significant energy lowering was achieved in comparison with the calculations for the non-spin-polarized compounds which indicates that compound is non-magnetic.

3. Results and Discussions

3-1 Structural properties and stability

Figure 1 (a-e) shows the cubic structures of the 2x2x2 supercells of $\text{Ba}_2\text{NbRhO}_6$ and $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ for different concentrations of V ($x = 0.25, 0.50, 0.75$, and 1.0). It was found that all compounds crystallize in a cubic structure with the space group $\text{Fm}\bar{3}\text{m}$, and the optimized structures were taken as the initial templates for all subsequent computational analyses. In this structure, the atoms are distributed over the Wyckoff positions as follows: Ba atoms occupy the 8c sites ($1/4, 1/4, 1/4$), while Nb/V and Rh atoms are located at the 4a ($0, 0, 0$) and 4b ($1/2, 1/2, 1/2$) positions, respectively, whereas O atoms occupy the 24e sites. This structural arrangement generates a periodic substitution of (Nb/V) O_6 and RhO_6 octahedra along the crystallographic axes, which mainly supports the stability of the cubic phase, indicating its structural stability throughout the entire doping range.

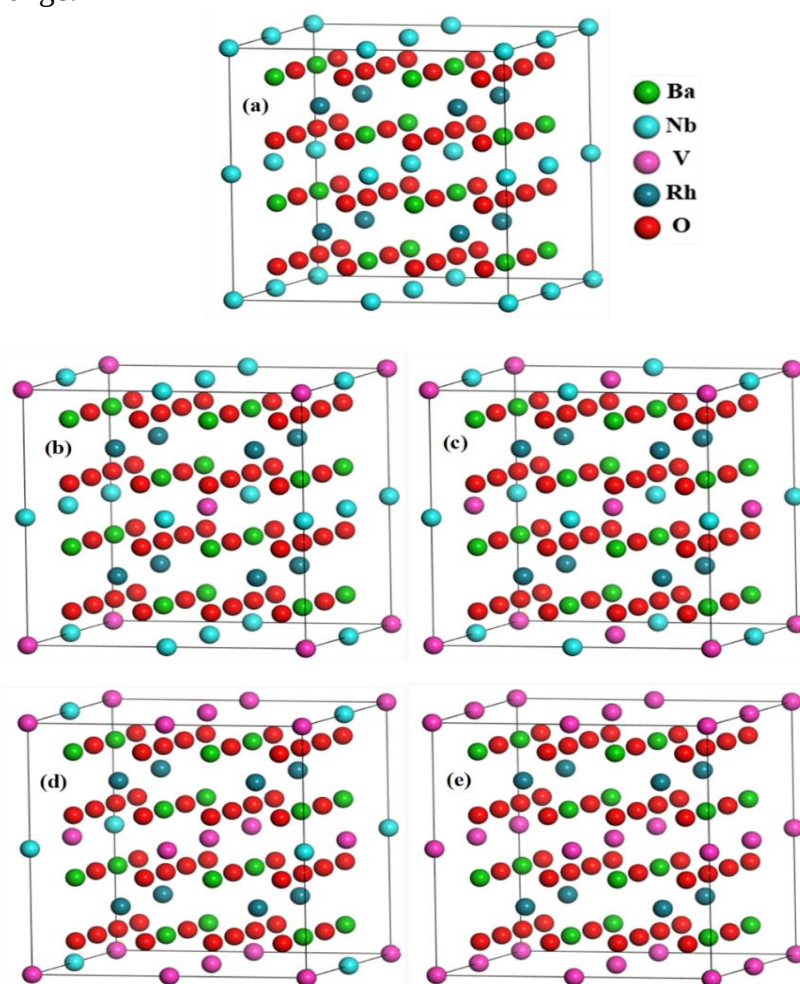


Figure -1 Crystal structures of the 2x2x2 supercells of $\text{Ba}_2\text{NbRhO}_6$ and $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ for different concentrations of V ($x = 0.25, 0.5, 0.75$, and 1.0).

The total energy of the unit cell was calculated over a sequence of different volumes to obtain the ground-state structural parameters with high accuracy. The obtained energy-volume (E-V) data were fitted using the third-order Birch-Murnaghan equation of state [5], where the total energy E and the unit-cell volume V are related according to the following equation [6, 7]:

$$E(V) = E_0(V) + \left[\frac{B_0 V}{B_0 (\bar{B}_0 - 1)} \right] \times \left[B_0 \left(1 - \frac{V_0}{V} \right) + \left(\frac{V_0}{V} \right)^{\bar{B}_0} - 1 \right] \quad (1)$$

In which E is the total energy at the equilibrium volume (V_0), which is the bulk modulus B_0 at zero pressure, and B'_0 is the pressure derivative. The influence of vanadium substitution on the energy stability of the cubic phase is confirmed by the smooth and well-defined parabolic shape of the calculated E - V curves, as shown in Figure 2(a-e). For the doped compounds $\text{Ba}_2\text{Nb}_{0.75}\text{V}_{0.25}\text{RhO}_6$, $\text{Ba}_2\text{Nb}_{0.5}\text{V}_{0.5}\text{RhO}_6$, $\text{Ba}_2\text{Nb}_{0.25}\text{V}_{0.75}\text{RhO}_6$, and Ba_2VRhO_6 , the equilibrium volumes are found to be 906.683, 895.123, 883.629, and 872.275 (a.u.)³, respectively, corresponding to lattice constants of 8.1303 Å, 8.0956 Å, 8.0608 Å, and 8.0261 Å. A clear decreasing trend in both lattice constant and equilibrium volume is observed with increasing vanadium concentration. This reduction is mainly attributed to the smaller ionic radius of V^{5+} (0.54 Å) compared to Nb^{5+} (0.6377 Å), leading to lattice contraction, which is consistent with the general behavior of perovskite systems, which are in line with known trends in perovskite tolerance factors.

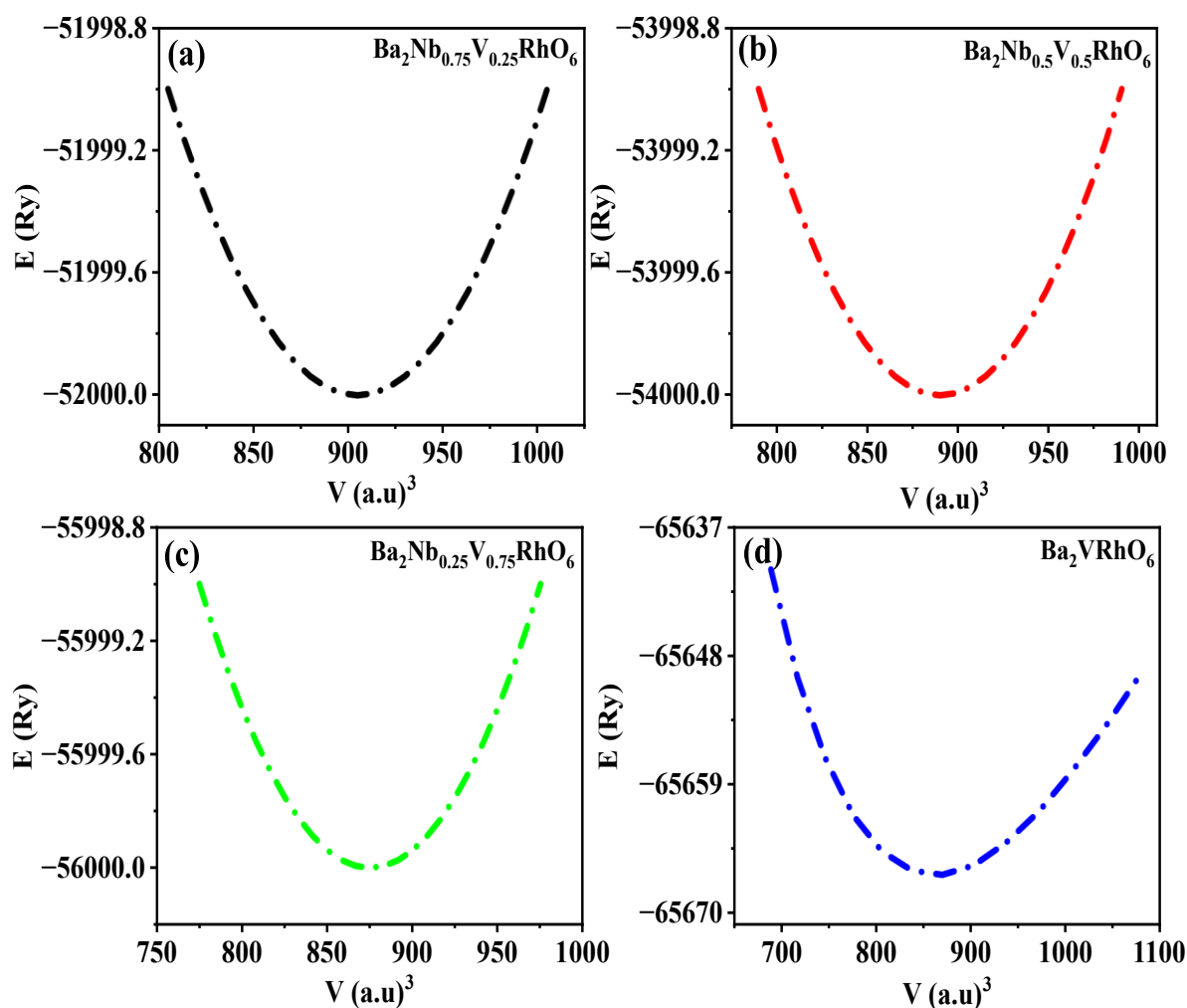


Figure -2 Energy-volume curves of the ground-state parameters of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x = 0.25, 0.5, 0.75$, and 1.0) double perovskite.

The geometric stability of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ compounds was further evaluated by calculating the Goldschmidt tolerance factor (t), octahedral factor (μ), and new tolerance factor (T) using Shannon ionic radii ($\text{Ba} = 1.61 \text{ \AA}$, $\text{Nb} = 0.6377 \text{ \AA}$, $\text{V} = 0.54 \text{ \AA}$, $\text{Rh} = 0.665 \text{ \AA}$, $\text{O} = 1.4 \text{ \AA}$). These stability indices were calculated through the following relations [8-10]:

$$t = \frac{r_{\text{Ba}} + r_{\text{O}}}{\sqrt{2}(r_{\text{B}} + r_{\text{O}})} \quad (2)$$

$$\mu = \frac{r_{\text{B}}}{r_{\text{O}}} \quad (3)$$

$$T = \frac{r_{\text{O}}}{r_{\text{B}}} - n_{\text{Ba}} \left(n_{\text{Ba}} - \frac{r_{\text{Ba}}/r_{\text{B}}}{\ln(r_{\text{Ba}}/r_{\text{B}})} \right) \quad (4)$$

where r_{Ba} , r_{B} , r_{O} , and n_{Ba} signify, respectively, the ionic radii of Ba, the average ionic radii of the B-site cations (Nb/V and Rh), O and the oxidation state of Ba. The results in Table 1. show that the traditional tolerance factor is between 1.044 and 1.063 which is within the universally accepted stability range in cubic perovskites ($0.81 < t < 1.11$) [11]. The calculated octahedral factors are 0.4566, 0.431. While the value of 0.4566 lies within the commonly accepted stability range ($0.44 < \mu < 0.90$) [12], the value of 0.439 and 0.431 are only slightly below the lower limit. Since the octahedral factor is an empirical guideline rather than a strict stability criterion, this minor deviation does not necessarily indicate structural instability. Further, the changed values of new tolerance factors of 3.644 to 3.761 are not over the critical limit of 4.18, thus further supporting the idea of geometric stability.

Table 1: Calculated lattice constant (a), equilibrium volume (V_0), and geometric stability indices t, μ , and T for $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ compounds.

Parameters	$\text{Ba}_2\text{NbRhO}_6$	$\text{Ba}_2\text{Nb}_{0.75}\text{V}_{0.25}\text{RhO}_6$	$\text{Ba}_2\text{Nb}_{0.5}\text{V}_{0.5}\text{RhO}_6$	$\text{Ba}_2\text{Nb}_{0.25}\text{V}_{0.75}\text{RhO}_6$	Ba_2VRhO_6
$a \text{ (\AA)}$	8.165 [19]	8.1303	8.0956	8.0608	8.0261
$V \text{ (a.u.)}^3$	918.343 [19]	906.683	895.123	883.629	872.275
Tolerance factor (t)	0.99 [19]	1.044	1.050	1.056	1.063
New Tolerance factor (T)		3.644	3.679	3.718	3.761
Octahedral factor (μ)	0.69 [19]	0.4566	0.448	0.439	0.431

The dynamical stability was analyzed using phonon dispersion calculations, as shown in Figure 3 (a–d). All phonon branches possess positive frequencies throughout the Brillouin zone without any imaginary modes, indicating that the studied $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ compounds are dynamically stable in the cubic phase. In addition, the phonon spectra remain generally similar with increasing vanadium concentration, suggesting that the crystal structure preserves its stability after doping.

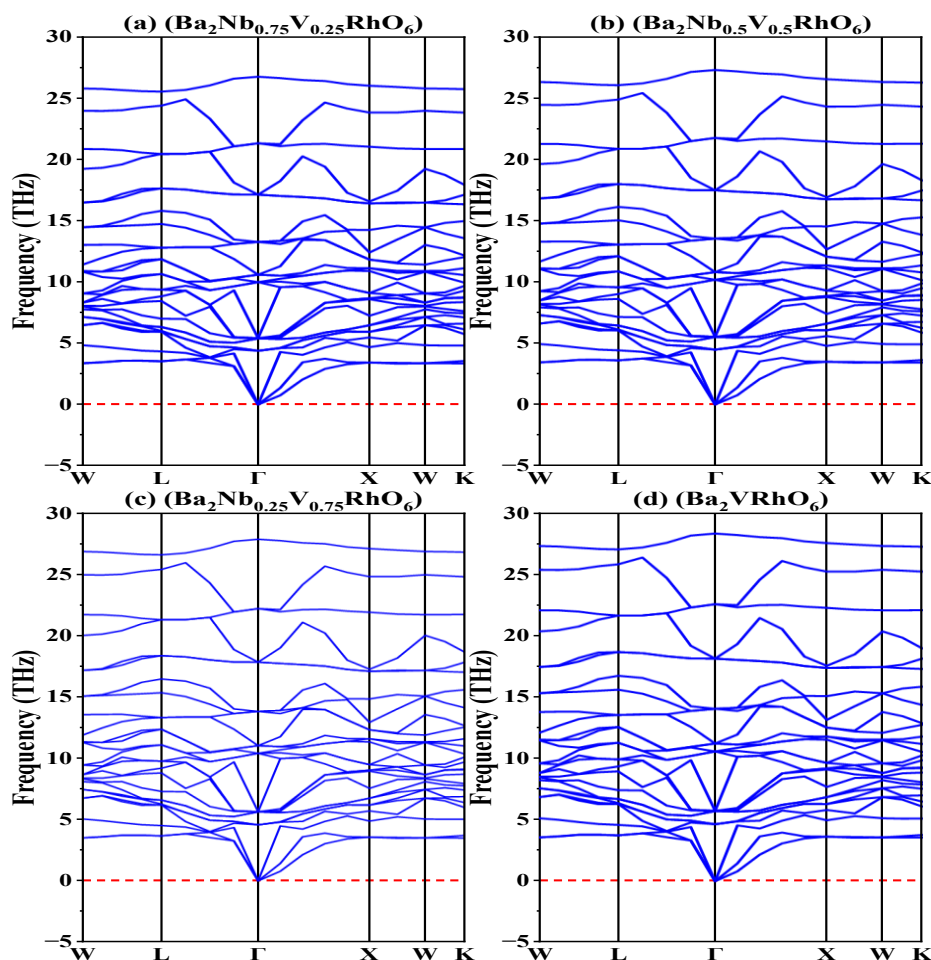


Figure -3 Phonon Dispersion Curves of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x = 0.25, 0.5, 0.75$, and 1.0) double perovskite.

3-2 Electronic Properties

The electronic analysis of the double perovskite compounds is an important in understanding the electronic properties and evaluating their possible applications [20]. The pure structure demonstrates a direct band gap of around 1.831 eV [19] whereas the calculated band structures and total density of states (TDOS) in figure 4 when the compound is doped with Vanadium (V) at the Niobium (Nb) site ($x = 0.25, 0.50, 0.75, 1.00$), a change in the nature of the band gap from direct to indirect is observed as compared to $\text{Ba}_2\text{NbRhO}_6$ [19]. The shift of the VBM position to X point and the CBM shift to the Gamma position for all doping ratios is due to a change in the electronic transition mechanism in the crystal structure. In addition, the bandgap is recorded to systematically and gradually decrease with the increase in doping concentration, up to 1.473 eV, 1.046 eV, 0.785 eV, and finally to 0.565 eV at the maximum V concentration. This development is clearly indicative of the effect of doping on the energy gap that can be exploited in thermoelectric and infrared optoelectronics devices [21].

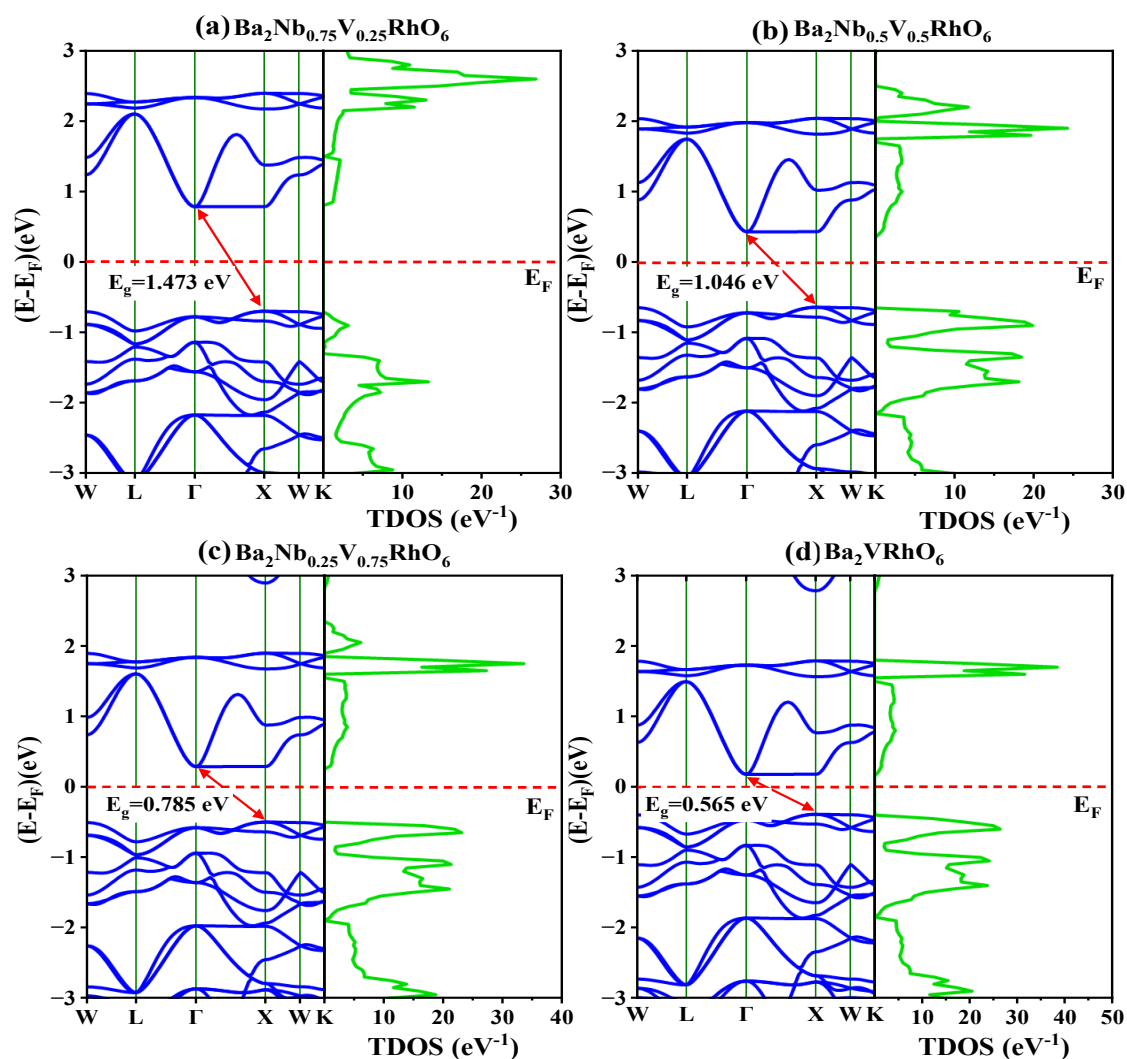


Figure -4 Band structure and total density of state of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x = 0.25, 0.5, 0.75$, and 1.0) double perovskite.

However, the TDOS curves show a clear discontinuity in the density of states near the Fermi level, as expected for semiconductors. Greater Vanadium content also leads to an increase in the density of states near the band edges, suggesting a redistribution of electronic states and a convergence of the valence and conduction bands. This behavior shows the influence of the changes of the electronic structure of the compound without causing a metallic transition, the bandgap remains finite and, despite the decrease, the infrared optical absorption is increased and the electrical conductivity is improved, hence, potentially, the transport of charge carriers in thermoelectric and infrared optoelectronics applications is improved [12, 22].

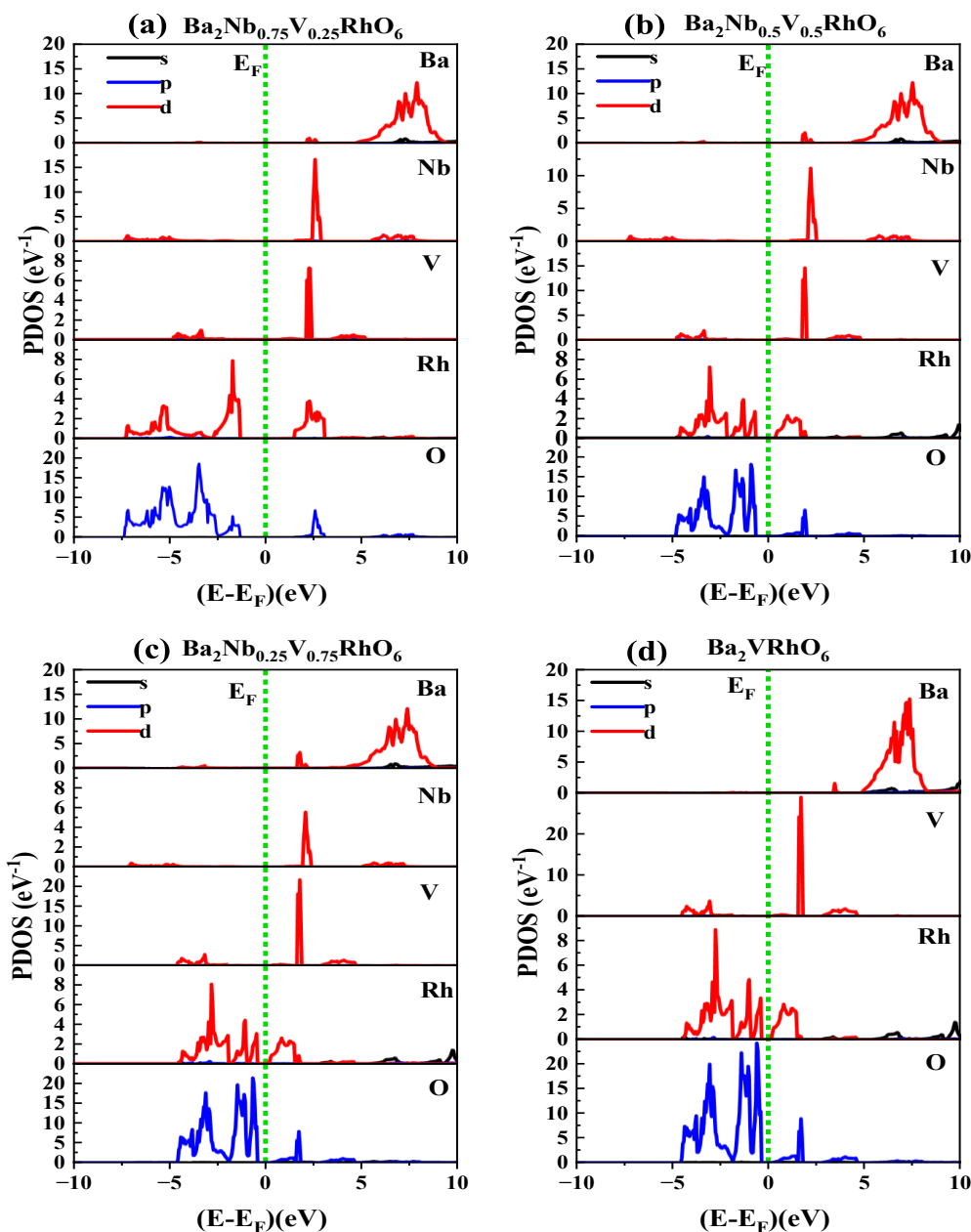


Figure -5 PDOS evolution in $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x = 0.25, 0.5, 0.75$, and 1.0); analysis of Orbital Contributions for Ba, Nb, Rh, O, and V.

To explain the origin of this behavior in terms of orbitals, the Partial Density of States (PDOS) analysis offers accurate information about the changing electronic structure caused by the doping. In the pure compound $\text{Ba}_2\text{NbRhO}_6$ [19], the valence band lies below the Fermi level with the main character of the valence band orbitals being O-2p hybridized with Rh-4d states. On the other hand, the lower edge of the conduction band consists predominantly of Nb-4d orbitals at relatively higher energies explaining the large energy gap. In the presence of Vanadium (doping level $x = 0.25, 0.50, 0.75, 1.0$), the valence band still has the same characters, with O-2p and Rh-4d orbitals being dominant (as shown in Fig. 5 (a-d)), with the band gap also remaining unchanged. A gradual change takes place, however, in the conduction band, with a progressive appearance of V-3d bands

at lower energies than the Nb-4d bands, so that the 3d band takes over the contribution to the conduction band minimum. As the doping level increases, the energy gap decreases as these states gradually move closer to the Fermi level. In addition, it is observed that there is an improvement in V3d-O2p hybridization towards the band edges. This observation has confirmed the effect of doping on the electronic structure and improvement of the electronic and optical properties of the compound while maintaining its basic semiconducting properties, which can be applied in the electronics/optoelectronics field [23].

3-3 Optical Properties

Systematic investigation of the optical properties of the $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x = 0.25, 0.50, 0.75, 1.0$) perovskites were performed in terms of the frequency-dependent complex dielectric function.

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (5)$$

and the optical parameters associated with them the refractive index $n(\omega)$, the extinction coefficient $k(\omega)$, the absorption coefficient $\alpha(\omega)$, the reflectivity $R(\omega)$, the optical conductivity $\sigma(\omega)$, and the energy-loss function $L(\omega)$. These quantities give a detailed picture of the electromagnetic radiation-electronic structure interaction and are needed to judge the suitability of these materials for optoelectronic and photovoltaic applications [24, 25]. Using the Kramers-Kronig relations [19, 26, 27] the optical parameters were calculated:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (6)$$

$$\varepsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega' \quad (7)$$

$$n(\omega) = \frac{1}{2} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{1/2} \quad (8)$$

$$k(\omega) = \frac{1}{2} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2} \quad (9)$$

$$\alpha(\omega) = \frac{2\omega}{c} k(\omega) \quad (10)$$

$$R(\omega) = \left| \frac{n(\omega) - 1 + ik(\omega)}{n(\omega) + 1 + ik(\omega)} \right|^2 \quad (11)$$

$$\sigma(\omega) = \text{Re} \left[-i \frac{\omega}{4\pi} \{ \varepsilon(\omega) - 1 \} \right] \quad (12)$$

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \quad (13)$$

The real part exhibits high values in the low-energy region of the pure compound has an initial (static) value in the range of ≈ 4.9 [19], where it is observed that this value increases significantly with increasing vanadium doping to reach about ≈ 12.85 , as shown in figure.6 (a), at full V substitution ($x = 1.00$), indicating an increase in polarizability due to the introduction of V-3d states. The pure compound have a clear peak at an energy of about 3.25 eV [19], but with the onset of doping, a continuous shift of these peaks toward the low-energy region occurs, where the peak gradually approaches the Fermi level to appear at an energy of about 1.5 eV in the fully doped case ($x = 1.0$), and it is the highest and sharpest peak in this range. This is followed by a gradual decrease with increasing energy, where $\varepsilon_1(\omega)$ crosses zero at energies ranging between 3–4 eV and reaches negative values, indicating the occurrence of plasmon resonance associated with the collective oscillations of electrons and a change in the nature of the optical response of the material to become metal-like in that energy region [28, 29]. The imaginary component of the dielectric function, figure 6(b), that corresponds to interband electronic transitions, has several sharp peaks in

the visible and UV regions. The doped compounds show wider and stronger peaks in comparison with the pristine system [19], indicating that the probability of optical transitions between the occupied and unoccupied electronic states is increased by V substitution. Most of these transitions come from O-2p to V-3d/Nb-4d and O-2p to Rh-4d excitations [30, 31]. Moreover, the anisotropic response along different crystallographic directions shows the crystal lattice has strong directional dependence of its optical response [32]. As seen in Fig. 6(c), the refractive index $n(\omega)$ of the material decreases drastically following the V substitution, especially in the low-energy range, suggesting that the interaction between the incident photon and the electron cloud of the material is stronger. Increased refractive response is directly related with the increased dielectric polarization caused by V derived electronic states [30]. At the same time, the extinction coefficient $k(\omega)$, figure 6(d), also rapidly rises with increasing V concentration, which signifies an enhanced attenuation of electromagnetic radiation in the material. The larger $k(\omega)$ value is found as a result of the additional electronic states created close to the conduction band edge [29, 32]. The absorption coefficient $\alpha(\omega)$ demonstrates the comparatively low absorption in the low energy range and a sudden rise in visible and UV energy ranges as seen in figure 6(e). In all the V-doped compounds the absorption intensity is considerably higher than in the pristine compound $\text{Ba}_2\text{NbRhO}_6$ [19] in a wider window of the photon energy. This enhancement has been mainly attributed to the emergence of V-3d states, which enable further interband electronic transitions and decrease the optical band gap [31, 33]. Additionally, as the V concentration increases, the absorption edge of the doped systems moves towards lower photon energies, thus verifying the red-shift behavior and the enhanced visible light collection property of the doped systems [31]. This type of operation is highly desirable for optoelectronic and photovoltaic applications [34]. In figure 6(f), the optical conductivity spectra $\sigma(\omega)$ show several strong peaks related to the electronic excitations induced by the photons. The magnitude of the conductivity increases gradually as V concentration increases, showing the increase in mobility of the carriers and the increase in the photoinduced charge transport. The enhancement can be correlated with the higher density of electronic states near the Fermi level caused by the V substitution [29, 35]. Thus, the doped compounds have better electronic transport characteristics than the undoped compound and can be used for photoresponsive and optoelectronic applications [34]. The reflectivity spectra show moderate reflectivity at low photon energy and oscillatory reflectivity at higher photon energy, figure 6(g). The reflectivity intensity after substitution V shows an increase of reflectivity for certain energy ranges, which suggests a stronger interaction between the incident photons and the free carriers. The increased reflectivity also indicates the onset of partial metallic features as a result of the extra d-electron contribution of the vanadium [32, 35]. Besides, the optical isotropy of the analysed compounds is also confirmed by the directional variation of the reflectivity spectra [33]. Pronounced plasmonic resonance peaks are seen in the energy-loss function $L(\omega)$ (figure 6(h)) corresponding to collective oscillations of the conduction electrons. The peaks get sharper and more intense after V substitution, suggesting that the plasmonic excitations and carrier-screening effect are intensified. With the rise of V concentration, the loss peaks appear to shift, which is an indication that the electronic structure and the carrier concentration of the material is greatly modified by vanadium [29, 31].

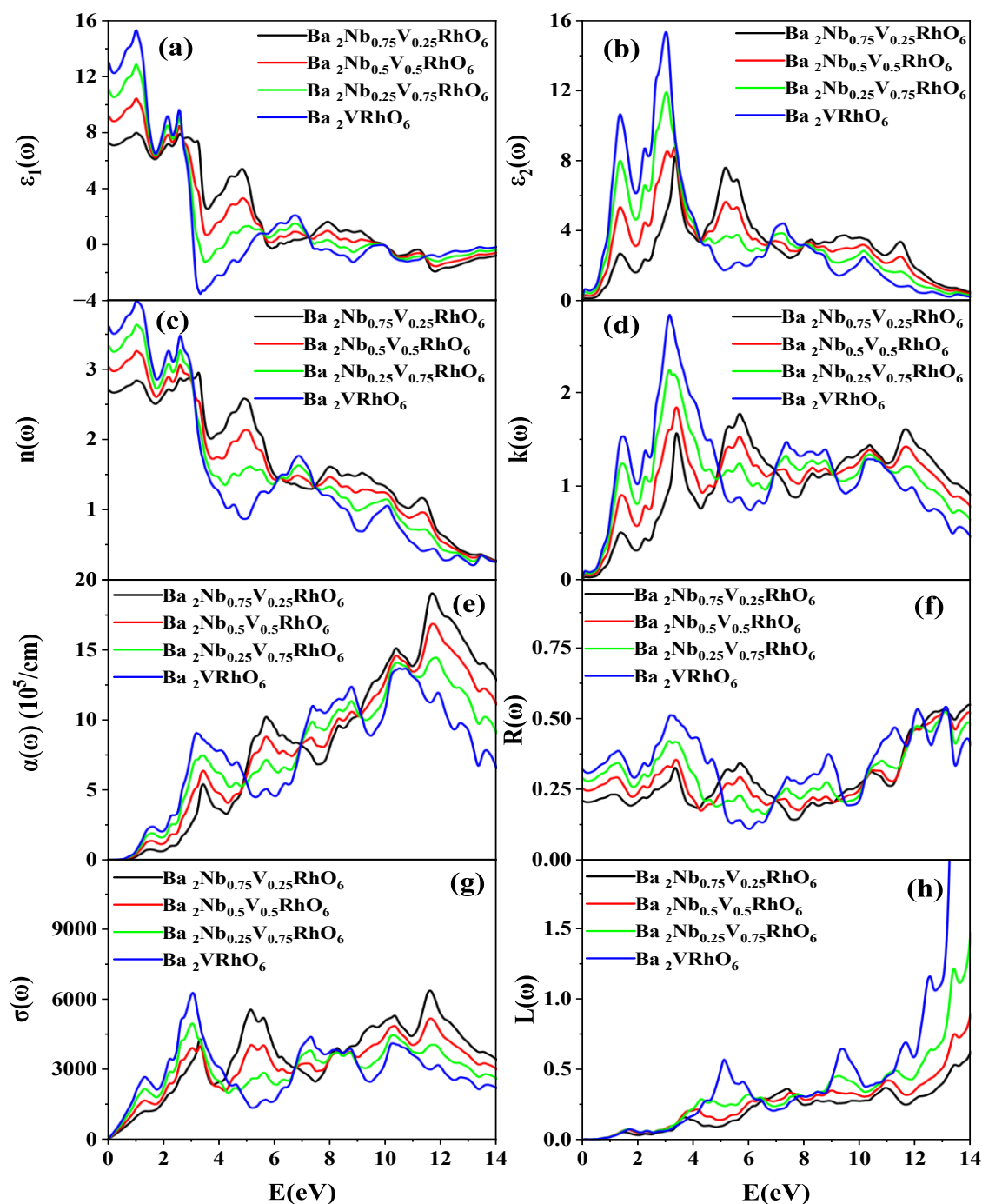


Figure -6 Optical properties of $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x=0.25, 0.50, 0.75$, and 1.0) double perovskite.

The results we have obtained indicate that the V substitution can successfully tune the optical response of $\text{Ba}_2\text{NbRhO}_6$ by increasing the orbital hybridization, dielectric polarization, interband electronic transitions, and the concentration of carriers. The enhanced optical conductivity, improved absorption capability, increased dielectric response and high degree of optical isotropy indicate that the V-doped compounds are promising materials for use in advanced optoelectronic, photovoltaic and ultraviolet photodetection applications [28, 33].

4. Conclusions

Using first-principles computations, the multifunctional properties of the double perovskite series $\text{Ba}_2\text{Nb}_{1-x}\text{V}_x\text{RhO}_6$ ($x = 0.25, 0.50, 0.75$ and 1.0) were systematically investigated. Based on the tolerance factor estimates and phonon dispersion analysis, all compositions are dynamically stable and structurally optimized, which confirms the stabilization in the cubic $\text{Fm}\bar{3}\text{m}$ phase. The overall lattice contraction manifests itself in the energy-volume (E-V) curves, which show a systematic contraction with increasing V-content on the Nb-site resulting from the lattice contraction of V^{5+} compared to Nb^{5+} . The strong hybridization between V-3d, Rh-4d and O-2p orbitals leads to the formation of a direct band gap (Electronic analysis) of 1.831 eV in the pristine compound $\text{Ba}_2\text{NbRhO}_6$, which transforms into an indirect band gap with increasing x values down to 0.565 eV at $x = 1.00$. Optical measurements show a distinct red shift and simultaneously an increase in both the absorption and the optical conductivity in the visible and near-infrared regions with increasing vanadium content. Among the investigated compositions, Ba_2VRhO_6 ($x = 1.00$) demonstrates the most favorable combination of electronic and optical properties, making it the most promising candidate for optoelectronic and photovoltaic applications. These findings provide useful theoretical guidance for the design and development of new double-perovskite materials with tunable multifunctional properties.

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