# First principles insight into magnetic and optoelectronic properties of Ni doped KNbO<sub>3</sub> perovskite

F. Rafique<sup>a</sup>, M. Ishfaq<sup>a</sup>, S. A. Aldaghfag<sup>b</sup>, M. Yaseen<sup>a,\*</sup>, M. Zahid<sup>c</sup>, M. K. Butt<sup>a</sup> *Spin-Optoelectronics and Ferro-Thermoelectric (SOFT) Materials and Devices Laboratory, Department of Physics, University of Agriculture, Faisalabad 38040, Pakistan* 

<sup>b</sup>Department of Physics, College of Sciences, Princess Nourah bint Abdulrahman University, P. O. Box 84428, Riyadh 11671, Saudi Arabia <sup>c</sup>Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan

The future technologies belong to the spin-based electronics (called spintronics) which is considered as highly efficient and quick response device with advanced functionalities. In order to develop a functional spintronic device, it is pertinent to control the spin currents and readout of their magnetic states which exemplify the importance of presented study. Herein, physical properties of KNbO<sub>3</sub> are engineered via concentration dependent Ni doping with dopant's concentration of 12.5%, 25%, 50%, and 75%. Ferromagnetic character is obtained along with spin polarized bands and DOS structures. Further analysis of projected DOS reveals the Ni-d based metallic character in spin down channel along with semiconductive nature in spin up version, translating the considered doped systems into half metallic ferromagnetic (HMFM) materials. The computed HM direct gaps are 0.956, 0.957, 1.040 and 0.876 eV for K<sub>0.875</sub>Ni<sub>0.125</sub>NbO<sub>3</sub>, K<sub>0.75</sub>Ni<sub>0.25</sub>NbO<sub>3</sub>, K<sub>0.5</sub>Ni<sub>0.5</sub>NbO<sub>3</sub>, and K<sub>0.25</sub>Ni<sub>0.75</sub>NbO<sub>3</sub>, respectively. The magnetic moment values obtained for K<sub>0.875</sub>Ni<sub>0.125</sub>NbO<sub>3</sub>, K<sub>0.75</sub>Ni<sub>0.25</sub>NbO<sub>3</sub>, K<sub>0.5</sub>Ni<sub>0.5</sub>NbO<sub>3</sub>, and K<sub>0.25</sub>Ni<sub>0.75</sub>NbO<sub>3</sub>, are 1.00153, 1.00003, 1.02449, and 1.04210  $\mu_B$  per formula unit, respectively. The determined magnetic moment values illustrate the ferromagnetism in studied Ni modified KNbO<sub>3</sub>, perovskites, which is originated from Ni and minor contribution of O ions. Further, optical response of Ni doped KNbO<sub>3</sub> is studied which show UV region of light as a strong absorbing region. The presented results predict the suitability of considered material in various optical filters and spintronic devices.

(Received May 19, 2023; Accepted August 13, 2023)

Keywords: Doping, DFT, Spintronics, Half metallic ferromagnets, Optical properties

## **1. Introduction**

Half metallic ferromagnetic (HMFMs) materials have attained remarkable attention as an emerging family of compounds since their discovery by de-Groot et al., back in 1980s [1, 2]. In an ideal HMFM spin-polarized material, one spin channel displays metallic character and the other show insulating or semiconducting nature, which depicts 100% spin polarized electronic states at Fermi level [3]. Recently, perovskites (chemical formula: ABO<sub>3</sub>; A and B are any suitable cation) have attracted a substantial interest of researchers due to their tendency to host various combination of cations providing us a plenty of room to engineer the physical properties via doping. The 3d transition metals (TMs) have been regarded as main source of magnetism in various doped perovskites such as in Fe doped BaTiO<sub>3</sub> [4], Fe doped PbTiO<sub>3</sub> [5], Cr doped SrSnO<sub>3</sub> [6] and N doped BaTiO<sub>3</sub> and SrTiO<sub>3</sub> [7]. Moreover, alkaline niobate perovskites like piezoelectric photocatalytic action, pyroelectric and superior chemical, and mechanical stability [8, 9]. Among

<sup>\*</sup> Corresponding author: myaseen\_taha@yahoo.com https://doi.org/10.15251/JOR.2023.194.453

454

them potassium niobate (KNbO<sub>3</sub>) is appeared as most significant ferroelectric perovskite. It is suitable for photocatalytic assisted water splitting used for hydrogen formation in presence of UV light radiation because of its easy availability, cost effective, environment friendly, and long-term durability [10-15]. Also, most typical ferroelectric oxides possess band gap ( $E_g$ )> 3 eV, that indicate the major light absorption in UV region. So, it is necessary to reduce Eg of ferroelectrics [16]. The engineering of  $E_g$  in ferroelectrics in visible range is an effective research field. It has been explored that chemical doping can be used for effective reduction of Eg of KNbO<sub>3</sub> [17]. Several dopants such as Zn, Ba, and Cu have been used to tune physical characteristics of KNbO<sub>3</sub> [18]. Gonzalez et al. investigated the tuning of Eg of KNbO3 through chemical doping of  $Bi(X,Yb)O_3$  where (X=Mn, Fe). The decrease in the direct  $E_g$  up to 2.2 eV was observed [19]. Shen and Zhou studied the structural and optoelectronic characteristics of Cu-modified KNbO<sub>3</sub> using DFT [20]. Their results predicted the metallic nature as the concentration of Cu is increased. In addition, Liang and Shao determined the impact of TMs' doping on physical features of KNbO<sub>3</sub>. The doping of V, Mn, and Fe reduced the optical band gap of KNbO<sub>3</sub>, signifying the importance of doping as an effective engineering route to obtain desirable properties for specific applications [21].

In this research work, magnetoelectronic, and optical characteristics of the  $K_{1-x}Ni_xNbO_3$  (x=12.5%, 25%, 50% and 75%) are determined by employing the first principles calculations. This study presents a handful insight into the asymmetric spin polarized electronic states. The outcomes recommend the Ni doped KNbO<sub>3</sub> system for its possible usage in the field of spintronics and optoelectronics.

## 2. Method of calculation

The DFT based full potential linearized augmented plane wave (FP-LAPW) approach [22] is utilized to examine magnetic and optoelectronic features of Ni doped KNbO<sub>3</sub> perovskite. Generalized gradient approximation parameterized by Perdew-Burke-Ernzerhof (GGA-PBE) is utilized to figure out the exchange correlation energies of considered doped systems [23]. KNbO<sub>3</sub> exists in stable cubic structure with Pm-3m space group in its paraelectric form [26]. In the cubic structure of KNbO<sub>3</sub>, K atom are presented at (0, 0, 0) positions, Nb atoms lie at (1/2, 1/2, 1/2) positions, while three atoms of oxygen are located at (0,1/2,1/2), (1/2, 0, 1/2) and (1/2, 1/2, 0) positions. The chosen muffin tin radii are 1.60, 2.0 and 1.50 a.u. for K, Nb, and O atoms, correspondingly. The R<sub>MT</sub> x K<sub>max</sub> values are set as 8.0, where R<sub>MT</sub> stands for the smallest value of spherical radii and K<sub>max</sub> represents the highest value of reciprocal lattice vector [24]. A 10×10×10 k-mesh was chosen to ensure the best convergence. The selected valence orbitals were 4s<sup>1</sup>, 4d<sup>4</sup>  $5s^1$  and  $2s^2 2p^4$  for K, Nb, and O atoms, respectively. For the total energy convergence criterion of  $10^{-6}$  eV was set to ensure the self-consistency during calculations.

#### 3. Results and discussions

#### **3.1. Electronic properties**

The spin polarized density of states (DOS) and band structures (BSs) of concentration dependent Ni doped KNbO<sub>3</sub> are computed using PBE-GGA. The BSs, as shown in Fig. 1(a-d), depict the HMFM nature with spin up  $E_g$  lying at  $\Gamma$ - $\Gamma$  symmetry points for all doped systems. With semiconducting nature in spin up channel, the 100% spin polarization is viable due to metallic spin down channel. The formula of spin polarization in ferromagnetic materials is given below.

$$\mathbf{P} = \frac{\rho^{\uparrow}(E_F) - \rho^{\downarrow}(E_F)}{\rho^{\uparrow}(E_f) + \rho^{\downarrow}(E_F)} \tag{1}$$

Here  $\rho \uparrow (E_F)$  and  $\rho \downarrow (E_F)$  are spin-polarized DOS at Fermi level (E<sub>F</sub>) for up and down states, respectively [25]. The computed spin up E<sub>g</sub>s are 0.956, 0.957, 1.040 and 0.876 eV for, K<sub>0.875</sub>Ni<sub>0.125</sub>NbO<sub>3</sub>, K<sub>0.75</sub>Ni<sub>0.25</sub>NbO<sub>3</sub>, K<sub>0.5</sub>Ni<sub>0.5</sub>NbO<sub>3</sub>, and K<sub>0.25</sub>NbO<sub>3</sub>, respectively, while pristine

 $KNbO_3$  has semiconducting feature with  $E_g$  of 2.3 eV [26]. This half metallicity is favorable for various spintronic devices. Also, half metallicity in TM doped perovskites have been reported in various studies indicating the validity of presented outcomes [15].



Fig. 1. The computed spin polarized band gaps for (a)  $K_{0.875}Ni_{0.125}NbO_3$ , (b)  $K_{0.75}Ni_{0.25}NbO_3$ , (c)  $K_{0.5}Ni_{0.5}NbO_3$  and (d)  $K_{0.25}Ni_{0.75}NbO_3$ .

The spin-polarized projected DOS (PDOS) analysis of compound  $K_{1-x}Ni_xNbO_3$  (x=12.5%, 25%, 50% and 75%) is performed to identify the role of each particular orbitals in defining the HM nature of studied doped systems. For  $K_{1-x}Ni_xNbO_3$  (x=12.5%), the upper portion of the VB varies from -3.0 eV to  $E_F$  and is mainly populated by Ni-*d* states with considerable participation of O-*p* in spin up and down states as shown in Fig. 2c. For  $K_{1-x}Ni_xNbO_3$  (x=25%),  $E_g$  of 0.957 eV is observed in majority spin version as shown in Fig. 2d and 2e. In case of PDOS, the top of the VB (-4 eV to  $E_F$ ) is primarily due to the Ni-*d* with involvement of Nb-*d* and O-*p* in both spin channels as illustrated in Fig. 2f. For  $K_{1-x}Ni_xNbO_3$  (x=50%), the  $E_g$  is appeared as 1.040 eV in up spin version and down spin exhibit overlapping character as shown in Fig.3a and 3b. In addition, the major contribution is from Ni-*d* and Nb-*d* states with minor influence of O-*p* states. For  $K_1$ .  $xNi_xNbO_3$  (x=75%), the calculated value of  $E_g$  is 0.876 eV for spin up channel. In addition, the major contribution is from Ni-*d* and Nb-*d* states along with minor influence of O-*p* states for both states. Conclusively, the Ni-*d* orbital is mainly responsible for HMFM nature of  $K_{1-x}Ni_xNbO_3$  at all the mentioned doping concentrations.



Fig. 2. GGA computed spin-polarized (a&b) TDOS (c) PDOS of  $K_{0.875}Ni_{0.125}NbO_3$ , and spin-polarized (d & e) TDOS and (f) PDOS of  $K_{0.75}Ni_{0.25}NbO_3$ .



Fig. 3. The GGA computed spin-polarized (a&b) TDOS (c) PDOS of  $K_{0.5}Ni_{0.5}NbO_3$ , and spin-polarized (d & e) TDOS and (f) PDOS of  $K_{0.25}Ni_{0.75}NbO_3$ .

### 3.2. Optical characteristics

The optical characteristics of  $K_{1-x}Ni_xNbO_3$  (x=12.5%, 25%, 50% and 75%) are evaluated in terms of dielectric function  $\varepsilon(\omega)$ , reflectivity  $R(\omega)$ , optical conductivity  $\sigma(\omega)$ , extinction coefficient  $k(\omega)$ , absorption coefficient  $\alpha(\omega)$ , and refractive index  $n(\omega)$ . These optical parameters describe the interaction among the incident photons with the material's surface. These parameters can be computed by using the dielectric parameters. Hence, at first, dielectric function is computed by using the mathematical relations given below [27-29]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$
 (2)

where,  $\varepsilon_1(\omega)$  stands for real component of dielectric function while  $\varepsilon_2(\omega)$  stands for imaginary component of dielectric function. The  $\varepsilon_1(\omega)$  is related to polarization of incident energy while

 $\varepsilon_2(\omega)$  demonstrate the absorption of energy by the material [34]. The  $\varepsilon_1(\omega)$  can be derived from  $\varepsilon_2(\omega)$  by Kramers-Kroning equation given below [35].

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^\theta \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$
(3)

where  $\varepsilon_2(\omega)$  is computed by following relation:

$$\varepsilon_{2}(\omega) = \frac{e^{2}h}{\pi m^{2}\omega^{2}} \sum_{\nu c} \int |n, n'(k, q)|^{2} \delta \left[ \omega_{n, \acute{n}}(k) - \omega \right] d^{3}k$$
(4)

Where, p in Eq. 3 stands for principal integral, while first term in Eq. 4 is the normalized momentum matrix component, and k and q are wave function of the corresponding CB and VB.

The remaining optical parameters can be computed by given formulae [30-33]:

$$n(\omega) = \frac{1}{\sqrt{2}} \left[ \varepsilon_1(\omega) + \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_1(\omega)^2} \right]^{\frac{1}{2}}$$
(5)

$$\alpha (\omega) = 4\pi k(\omega)/\lambda \tag{6}$$

$$k(\omega) = \frac{1}{\sqrt{2}} \left[ \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_1(\omega)^2} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$
(7)

$$\sigma(\omega) = \frac{\omega}{4\pi} \varepsilon_2(\omega) \tag{8}$$

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$
(9)

The plot of  $\varepsilon_1(\omega)$  is demonstrated in Fig. 4(a). The values of  $\varepsilon_1(\omega)$  linearly varies with the change in energy and attains highest values at 2.46, 2.48, 3.0 and 3.1 eV for  $K_{0.875}Ni_{0.125}NbO_3$ ,  $K_{0.75}Ni_{0.25}NbO_3$ ,  $K_{0.5}Ni_{0.5}NbO_3$ , and  $K_{0.25}Ni_{0.75}NbO_3$ , respectively. With considerable fluctuations, the  $\varepsilon_1(\omega)$  turns negative in 5-5.2 eV energy span. These negative values are linked to the metallic performance of considered doped systems showing highly reflective behavior. Furthermore, the  $E_g$ and  $\varepsilon_1(\omega)$  at zero frequency limit for Ni doped KNbO<sub>3</sub> fulfill the following relation:  $\varepsilon_1(0) \approx 1 + (\hbar\omega_p/E_g)^2$ , which is called as Penn's model [36].



Fig. 4. Computed (a)  $\varepsilon_1(\omega)$ , (b)  $\varepsilon_2(\omega)$  (c)  $\alpha(\omega)$  and (d)  $\sigma(\omega)$  of  $K_{I-x}Ni_xNbO_3$  (x=12.5%, 25%, 50% and 75%) compound.

The imaginary component of dielectric function  $\varepsilon_2(\omega)$  is directly linked with electronic BS of compound and defines absorptive nature of the compound. Apart from the greater cutoff values, the maximum peak of  $\varepsilon_2(\omega)$  occurs in 3.0-4.0 eV energy span for all doped systems,

which illustrate the maximum absorptive behavior of light in UV region (see Fig. 4b). The absorption coefficient  $\alpha(\omega)$  determines the number of photons being absorbed by a material. The  $\alpha(\omega)$  values are given in Fig. 5a. The  $\alpha(\omega)$  values starts from 0 eV and attains the maximum peaks at 8.2, 8.3, 8.35 and 8.5 eV for  $K_{0.875}Ni_{0.125}NbO_3$ ,  $K_{0.75}Ni_{0.25}NbO_3$ ,  $K_{0.5}Ni_{0.5}NbO_3$ , and  $K_{0.25}Ni_{0.75}NbO_3$ , respectively. The  $\sigma(\omega)$  determines the concentration of free electrons created owing to the bond-breaking by electron-photon interactions. The computed optical conductivity  $\sigma(\omega)$  gives highest peak at 2.2 eV with the magnitude values of 4918, 5390, 5884 and 6399  $(\Omega.cm)^{-1}$  for  $K_{0.875}Ni_{0.125}NbO_3$ ,  $K_{0.75}Ni_{0.25}NbO_3$ ,  $K_{0.5}Ni_{0.5}NbO_3$ , and  $K_{0.25}Ni_{0.75}NbO_3$ , correspondingly, as exemplified in Fig. 5b. The  $\sigma(\omega)$  peaks are mainly dependent on  $\alpha(\omega)$  (see Fig. 5a&b).



Fig. 5. Plots of (a)  $\varepsilon_1(\omega)$ , (b)  $\varepsilon_2(\omega)$  (c)  $\alpha(\omega)$  and (d)  $\sigma(\omega)$  of  $K_{1-x}Ni_xNbO_3$  (x=12.5%, 25%, 50% and 75%) compound.



Fig. 6. Plots of (a)  $n(\omega)$  (b)  $k(\omega)$  and (c)  $R(\omega)$  of  $K_{1-x}Ni_xNbO_3(x=12.5\%, 25\%, 50\% and 75\%)$  compound.

The  $n(\omega)$  depicts the transparency of a compound in response to the light incident on the surface. In case of highly transparent materials, its value is very low. In this study, the positive values correspond to the light absorption by the compound. The cut off value of  $n(\omega)$  i.e., n(0) fulfills the following relation  $n^2(0) = \varepsilon_1(\omega)$ , and its maximum value is obtained between 2.3 - 2.6 eV as given in Fig. 6a.

The ability to absorb the incident light is explained by extinction coefficient  $k(\omega)$ . The  $n(\omega)$  and  $k(\omega)$  are linked to  $\varepsilon_2(\omega)$  as well as  $\varepsilon_1(\omega)$  by the following relations  $2nk = \varepsilon_2(\omega)$  and  $n^2 - k^2 = \varepsilon_1(\omega)$ , respectively [37]. The  $k(\omega)$  plots are given in Fig. 6b, which show the similar like trend as of  $\varepsilon_2(\omega)$ . The increase in energy results in lowering the  $k(\omega)$  values. Lastly,  $R(\omega)$  provides the information about the reflective behavior of the considered materials [38]. The  $R(\omega)$  values rise from zero energy limit and approaches to the maximum values at approximately 5.0 eV for all mentioned Ni doped KNbO<sub>3</sub> compounds (see Fig. 6c). The  $R(\omega)$  values are higher in the region in which  $\varepsilon_1(\omega)$  is negative (see Figs. 4a & 6c). The upper mentioned optical parameters describe Ni doping as a useful strategy to engineer the optical properties implying their importance in various optical filter applications.

#### 3.3. Magnetic properties

To better comprehend the ferromagnetic behavior, self-consistent field calculations were performed, and considerable value of magnetic moment was observed for studied doped systems. Asymmetric pattern of spin polarized DOS and BS also confirm the origin of magnetic moment. Total and local magnetic moments of Ni doped KNbO<sub>3</sub> compound is tabulated in Table 2. The computed total magnetic moment values are 1.00153, 1.00003, 1.02449 and 1.04210  $\mu_B$  per formula unit of 12.5%, 25%, 50% and 75% Ni doped KNbO<sub>3</sub> compound, respectively. The dopant Ni cation is reported as major reason for the origin of ferromagnetism in KNbO<sub>3</sub>. The partial magnetic moments of Ni are 1.12164, 1.10810, 1.07471 and 1.12259  $\mu_B$  per formula unit of K<sub>0.875</sub>Ni<sub>0.125</sub>NbO<sub>3</sub>, K<sub>0.75</sub>Ni<sub>0.25</sub>NbO<sub>3</sub>, K<sub>0.5</sub>Ni<sub>0.5</sub>NbO<sub>3</sub>, and K<sub>0.25</sub>Ni<sub>0.75</sub>NbO<sub>3</sub>, respectively. It is to be noted that moment values of interstitial, K and Nb cations are negligible as compared to Ni moments. This trend is in line with asymmetric PDOS of Ni cation (see Fig. 2&3). This study presents a novel and potentially advantageous approach towards inducing ferromagnetism in KNbO<sub>3</sub> implying their importance to use these compounds in various magnetic devices.

Compound	E <sub>g</sub> (eV)	M <sub>int</sub>	M <sub>Ni</sub>	M <sub>k</sub>	M <sub>Nb</sub>	Mo	Total
Pure	2 [26]	-	-	-	-	-	-
K <sub>0.75</sub> Ni <sub>0.25</sub> NbO <sub>3</sub>	0.956	0.07146	1.12164	0.00033	0.01526	0.00619	1.00153
K <sub>0.5</sub> Ni <sub>0.5</sub> NbO <sub>3</sub>	0.957	0.06715	1.10810	0.00049	0.02812	0.01808	1.00003
K <sub>0.5</sub> Ni <sub>0.5</sub> NbO <sub>3</sub>	1.040	0.03992	1.07471	0.00037	0.03186	0.04307	1.02449
K <sub>0.25</sub> Ni <sub>0.75</sub> NbO <sub>3</sub>	0.876	0.13421	1.12259	0.00064	0.05144	0.04432	1.04210

Table 1. Calculated band gap, local, interstitial, and total magnetic moments ( $\mu_B$ ) for  $K_{1-x}Ni_xNbO_3$  (x=12.5, 25, 50 and 75%) compound.

#### 4. Conclusions

The magneto-optoelectronic characteristics of Ni doped KNbO<sub>3</sub> are computed by using first principles method. The magnetic moments of 1.0  $\mu_B$  per formula unit for all doped systems show the induced ferromagnetism. The computed DOS and BS of each doped system show asymmetric spin-polarization with Ni being the most polarized in the vicinity of Fermi level. Further, PDOS were computed which exhibit hybridization between Ni-*d* and O-*p* orbitals in the vicinity of E<sub>F</sub>. The HM nature of studied materials is mainly influenced by Ni-d orbitals that are found to be contributing at the E<sub>F</sub> in the down spin channel. Furthermore, the optical properties are analyzed to investigate the optical response of the doped systems. The apical amount of optical absorption and greater extinction coefficient in UV region of light suggest this material's suitability for optical filters.

## Acknowledgement

The authors express their gratitude to Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2023R81), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

# References

[1] N. Kim, R. Kim, and J. Yu, Journal of magnetism and magnetic materials, 460, 54-60 (2018); https://doi.org/10.1016/j.jmmm.2018.03.034

[2] R.A. de Groot, F.M. Mueller, P.G. van Engen, and K.H.J. Buschow, Phys. Rev. Lett. 50, 2024–2027 (1983); <u>https://doi.org/10.1103/PhysRevLett.50.2024</u>

[3] Q. Mahmood, B.U. Haq, M. Yaseen, A. Shahid, and A. Laref, Solid State

Communications, 299, 113654 (2019); https://doi.org/10.1016/j.ssc.2019.113654

[4] I.N. Apostolova, A.T. Apostolov, S. Golrokh Bahoosh, and J.M. Wesselinowa, Journal of applied physics, 113(20), 203904 (2013); <u>https://doi.org/10.1063/1.4807412</u>

[5] T. Zheng, H. Deng, W. Zhou, X. Zhai, H. Cao, L. Yu, P. Yang, and J. Chu, Ceramics International, 42(5), 6033-6038 (2016); https://doi.org/10.1016/j.ceramint.2015.12.157

[6] M.K. Butt, M. Yaseen, A. Ghaffar, and M. Zahid, Arabian Journal for Science and

Engineering, 45, 4967-4974 (2020); https://doi.org/10.1007/s13369-020-04576-6

[7] K. Yang, Y. Dai, and B. Huang, Applied Physics Letters, 100(6), 062409 (2012); https://doi.org/10.1063/1.3684832

[8] S. Azam, M. Irfan, Z. Abbas, M. Rani, T. Saleem, A. Younus, N. Akhtar, B. Liaqat, M. Shabbir, and A.G. Al-Sehemi, Dig. J. Nanomater. Biostructures, 14(3), 751-760 (2019); https://chalcogen.ro/751\_IrfanM.pdf

[9] M.M. Hossain, Heliyon, 5(4), e01436, (2019); <u>https://doi.org/10.1016/j.heliyon.2019.e01436</u>
[10] P. Vlazan, M. Stoia, M. Poienar, and P. Sfirloaga, Ceramics International, 43(8), 5963-5967 (2017); <u>https://doi.org/10.1016/j.ceramint.2017.01.120</u>

[11] F. Wang, I. Grinberg, and A.M. Rappe, Physical Review B, 89(23), 235105 (2014); https://doi.org/10.1103/PhysRevB.89.235105

[12] M. Adachi, N. Fujita, Y. Norimatsu, and T. Karaki, Ferroelectrics, 334(1), 91-96 (2006); https://doi.org/10.1080/00150190600692625

[13] M. A. Faridi, S. Tariq, M. I. Jamil, A. Batool, S. Nadeem, and A. Amin, Chinese Journal of Physics, 56(4), 1481-1487 (2018); <u>https://doi.org/10.1016/j.cjph.2018.06.003</u>

[14] S. Raja, R. R. Babu, K. Ramamurthi, and S. M. Babu, Ceramics International, 44(3), 3297-3306 (2018); <u>https://doi.org/10.1016/j.ceramint.2017.11.104</u>

[15] D. Nie, J. Zhang, W. J. Deng, X. Chen, Z. Q. Mao, and L. Y. Tang, Chinese Journal of Chemical Physics, 30(1), 97-102 (2017); <u>https://doi.org/10.1063/1674-0068/30/cjcp1608154</u>

[16] W. Tang, Y. Zhang, C. Yuan, X. Liu, B. Zhu, L. Meng, C. Zhou, F. Liu, J. Xu, J. Wang, and G. Rao, Journal of the American Ceramic Society, 104(5),2181-2190 (2021); https://doi.org/10.1111/jace.17567

[17] Y.Q. Xu, S.Y. Wu, C.C. Ding, L.N. Wu, and G.J. Zhang, Chemical Physics, 504, 66-71 (2018); <u>https://doi.org/10.1016/j.chemphys.2018.03.007</u>

[18] B. Song, X. Wang, C. Xin, L. Zhang, B. Song, Y. Zhang, Y. Wang, J. Wang, Z. Liu, Y. Sui, and J. Tang, Journal of Alloys and Compounds, 703, 67-72 (2017); https://doi.org/10.1016/j.jallcom.2017.01.180

[19] C. Pascual-Gonzalez, G. Schileo, and A. Feteira, Applied Physics Letters, 109(13),132902 (2016); https://doi.org/10.1063/1.4963699

[20] Y. Shen, and Z. Zhou, Chemical Physics Letters, 454(1-3), 114-117 (2008); https://doi.org/10.1016/j.cplett.2008.01.079

[21] Y. Liang, and G. Shao, RSC Advances, 9(13), 7551-7559 (2019); https://doi.org/10.1039/C9RA00289H

[22] A. Sohail, S. A. Aldaghfag, M. K. Butt, M. Zahid, M. Yaseen, J. Iqbal, Misbah, M. Ishfaq, A.

Dahshan, Journal of Ovonic Research, 17(5), 461-469 (2021).

[23] H. Shafique, S. A. Aldaghfag, M. Kashif, M. Zahid, M. Yaseen, J. Iqbal, Misbah, R. Neffati, Chalcogenide Letters, 18(10), 589-599 (2021).

[24] M. Yaseen, H. Ambreen, U. Shoukat, M.K. Butt, S. Noreen, S. Rehman, J. Iqbal, S. Bibi, A. Murtaza, And S. Ramay. Journal of Ovonic Research 15(6), 401-409 (2019); https://chalcogen.ro/401\_YaseenM.pdf

[25] B. Bouadjemi, T. Lantri, M. Matougui, M. Houari, R. Bentata, Z. Aziz, and S. Bentata, Spin, 10(02), 2050010 (2020); <u>https://doi.org/10.1142/S2010324720500101</u>

[26] M. Yaseen, M. K. Butt, A. Ashfaq, J. Iqbal, M.M. Almoneef, M. Iqbal, A. Murtaza, and A. Laref, Journal of Materials Research and Technology, 11, 2106-2113 (2021); https://doi.org/10.1016/j.jmrt.2021.02.017

[27] A. Mahmood, S. M. Ramay, H. M. Rafique, Y. Al-Zaghayer, and S. U. D. Khan, Modern Physics Letters B, 28(10), 1450077 (2014); <u>https://doi.org/10.1142/S0217984914500778</u>

[28] D. P. Rai, A. Shankar, A. P. Sakhya, T. P. Sinha, B. Merabet, R. Khenata, A. Boochani, S. Solaymani, and R. K. Thapa, Materials Chemistry and Physics, 186, 620-626 (2017); https://doi.org/10.1016/j.matchemphys.2016.11.045

[29] M. Rizwan, H. Hameed, U. Mushtaq, M. I. Khan, S. S. A. Gillani, and M. H. Farooq, Physica B: Condensed Matter, 605, 412493 (2021); <u>https://doi.org/10.1016/j.physb.2020.412493</u>

[30] Q. Mahmood, and M. Hassan, J. Alloys. Compd. 704, 659-675 (2017); https://doi.org/10.1016/j.jallcom.2017.02.097

[31] C. Jing, C. Xiang-Rong, Z. Wei, and Z. Jun, Chin. Phys. B. 17, 1377 (2008); https://doi.org/10.1088/1674-1056/17/4/037

[32] M. K. Butt, M. Yaseen, I. A. Bhatti, J. Iqbal, A. Murtaza, M. Iqbal, M. mana AL-Anazy, M.H. Alhossainy, and A. Laref. Journal of Materials Research and Technology, 9(6), 16488-16496 (2020); https://doi.org/10.1016/j.jmrt.2020.11.055

[33] G. Nazir, A. Ahmad, M. F. Khan, and S. Tariq, Computational Condensed Matter, 4, 32-39 (2015); <u>https://doi.org/10.1016/j.cocom.2015.07.002</u>

[34] B. Sabir, G. Murtaza, R. A. Khalil, and Q. Mahmood, Journal of Molecular Graphics and Modelling, 86, 19-26 (2019); <u>https://doi.org/10.1016/j.jmgm.2018.09.011</u>

[35] Q. Mahmood, B. U. Haq, M. Yaseen, S. M. Ramay, M. G. B. Ashiq, and A. Mahmood, Solid State Commun. 292, 1723 (2019); <u>https://doi.org/10.1016/j.ssc.2019.01.011</u>

[36] D.R. Penn, Physical Review, 128(5), 2093 (1962); <u>https://doi.org/10.1103/PhysRev.128.2093</u>
[37] R. Khenata, M. Sahnoun, H. Baltache, M. Rérat, A.H. Rashek, N. Illes, and B. Bouhafs, Solid state communications, 136(2),120-125 (2005); <u>https://doi.org/10.1016/j.ssc.2005.04.004</u>

[38] S. Saleem, S.A. Aldaghfag, M. Yaseen, M.K. Butt, M. Zahid, A. Murtaza, and A. Laref, The European Physical Journal Plus, 137(1), 121 (2022); <u>https://doi.org/10.1140/epjp/s13360-022-02352-z</u>