Abstract
BiFe$_{1-x}$Ni$_x$O$_3$ ($x = 0.7, 0.8$ and $0.9$) polycrystalline ceramics are synthesized by a solid-state reaction, and their structural, absorption, leakage current and electrical properties are investigated. The X-ray diffraction measurements show that the lattice parameter values increase with increasing the substitution of Ni$^{2+}$ ions for Fe$^{3+}$ ions. The optical absorption spectra indicate that the band gap energy increases with increasing Ni$^{2+}$ ions. Leakage currents are much decreased by about three orders of magnitude with increasing Ni ions. The J-E hysteresis was also investigated. Both real and imaginary dielectric constants are investigated as a function of both frequency and temperature. The room temperature dielectric measurement with a wide frequency range of 1 KHz – 1 MHz reveals that the real and imaginary dielectric constants are decreased with increasing frequency of BiFe$_{1-x}$Ni$_x$O$_3$ ($x = 0.7, 0.8, 0.9$) ceramics. The real and imaginary dielectric constants are found to be increased with temperature. The temperature dependence of $\varepsilon'$ and $\varepsilon''$ exhibits an anomaly which shifted to lower temperature with increasing Ni$^{2+}$. The anomaly indicates the possible existence of spin-glass states with Ni$^{2+}$ ion substitution in places of Fe$^{3+}$ ions.

Keywords
Perovskite-like type structure . X-ray diffraction . Absorption spectra . Leakage current . Spin-glass state
Experimental

By using the solid-state reaction, BiFe$_{1-x}$Ni$_x$O$_3$ ($x = 0.7$, 0.8 and 0.9) were synthesized from highly pure Bi$_2$O$_3$, $(1 - x)$ Fe$_2$O$_3$ and 2xNiO powders. The weighed powders were milled mixed for half an hour at room temperature in air atmosphere. This milled powder was pressed into 16 mm diameter and 1 mm thickness discs under 1.5 Mpa pressure on a hydraulic press and then were rapidly heated to 750 °C and sintered for 30 min at atmospheric pressure. The calcined powder was milled again for half an hour. Then, they were pressed again into pellets of 16 mm diameter by applying a pressure of 1.5 Mpa. The pellets of the sample were found to be dark grey upon Ni substitution. For measurements of electrical properties, the ceramic pellets were coated on both surfaces with silver paint for good contacts.

The structure of the samples is characterized by X-ray diffractometer (X’Pert-Pro MPD, Philips) using CuKα radiation with $\lambda = 1.541874$ Å. The patterns were recorded in a 2θ interval of 20–60 with increments of 0.025 (2θ). The photo-absorption of BiFe$_{1-x}$Ni$_x$O$_3$ was measured by UV-visible diffuse reflectance spectrophotometer ShimadzuUV-3600. The electric properties were measured using the semiconductor characterization system SCS4200 (Keithly). The electric data were carried out as a function of temperature and frequency during heating of the samples from room temperature up to 280 °C and frequency range from 5 kHz to 5 MHz.

Result and discussion

Structural

Figure 1a demonstrates XRD patterns of sintered BiFe$_{1-x}$Ni$_x$O$_3$ ceramics, $x = 0.7$, 0.8 and 0.9. The patterns indicate that all samples have secondary phases (Bi$_2$FeO$_3$, Bi$_{25}$FeO$_{40}$, and NiFeO$_4$) in a perovskite structure. The secondary phase peaks Bi$_2$FeO$_3$ and Bi$_{25}$FeO$_{40}$ are usually observed in BiFeO$_3$ and its substituted samples because of the kinetic of their formation [24]. The new peak NiFe$_2$O$_4$ is observed corresponding to the phase associated with Ni ions which indicate that Ni ions are incorporated into the BiFeO$_3$ structure [25]. In addition, as a result of the highest Ni content in the samples, the reflection peaks of bismuth ferrite have disappeared which is in a good agreement with the previous results reported by Betancourt-Cantera et al. [25]. The new peak NiFe$_2$O$_4$ is observed corresponding to the phase associated with Ni ions which indicate that Ni ions are incorporated into the BiFeO$_3$ structure [25].

Figure 2 demonstrates the diffuse reflectance spectra of BiFe$_{1-x}$Ni$_x$O$_3$ samples with different doping concentration.
of the difference in ionic radius between the Ni$^{2+}$ (ionic radius 0.69 Å) and the Fe$^{3+}$ (0.64 Å).

**Optical properties**

The optical properties of BiFe$_{1-x}$Ni$_x$O$_3$ samples with $x$ = 0.7, 0.8 and 0.9 powder were investigated. Figure 2 illustrates the diffuse reflectance spectra (DRS) of BiFe$_{1-x}$Ni$_x$O$_3$ samples in the wavelength range of 250 to 700 nm. Kubelka-Munk function [27, 28] is used to estimate the absorption coefficient from the DRS data. Kubelka-Munk function is defined as:

$$F(R_e) = \frac{\alpha}{S} = \frac{(1-R_e)^2}{2R_e}$$

where $R_e = R_{\text{sample}}/R_{\text{pref}}$.

Here, “$\alpha$ is the absorption coefficient, $S$ is the scattering coefficient and $F(R_e)$ is the KM function”. Near the absorption edge, the relation between photon energy ($E = h\nu$), absorption coefficient and band gap energy ($E_g$) for insulating substance is represented as:

$$\alpha E = K (E-E_g)^n$$

$K$ is a constant, and $n$ is the exponent which depends on the type of transition [29].

The KM function can be used instead of the absorption coefficient $\alpha$ for the estimation of the optical energy gap ($E_g$) [21]. Figure 3 shows the method of calculating the optical gap in the case of a direct and an indirect transition of $x = 0.9$ sample as an example. It was noted that the calculation based on the direct transition shows more extended linear region as compared with the calculations based on indirect transition.

![Image of optical properties](image)

**Fig. 3** Direct and indirect optical band gap for BiFe$_{1-x}$Ni$_x$O$_3$ with $x = 0.9$

![Image of energy plots](image)

**Fig. 4** $(\alpha h\nu)^2$ versus $h\nu$ (photon energy) plots of BiFe$_{1-x}$Ni$_x$O$_3$ with different dopant concentrations
For this reason, we consider the direct transition for all samples. The direct band gap for BiFe$_{1-x}$Ni$_x$O$_3$ can be predicted from the slope and intercept of the $(\alpha h\nu)^2$ vs $(h\nu)$ linear portion [30]. Figure 4 illustrates this relation for samples with different Ni content ($x = 0.7$, 0.8, 0.9). For samples with doping concentrations of $x = 0.8$ and 0.9, the band gaps were suddenly reduced to about 2.5 eV. Such a sudden decrease in optical band gap due to high doping concentration can be attributed to the Mott semiconductor-metal transition [31].

The value of the optical band gap energy of the samples with $x = 0.8$ and 0.9 is consistent with previous report [22, 32, 33]. However, the optical band gap exhibits an increase at $x = 0.7$ ($E_g = 3.04$ eV). This can be interpreted as the results of the molecular orbital rearrangements [34].

Electric properties

The leakage current represents one of the problems which hinder the ferroelectric and transport properties of multifarious ceramics. This leakage current is produced due to the existence of defects and nonstoichiometric in the bulk samples. The improvement of multiferroic properties requires a reduction of its leakage current. Hence, the study of the leakage current represents one of the important issues in this research. For this purpose, the J-E curve was measured for the present samples (BiFe$_{1-x}$Ni$_x$O$_3$ ceramics) at room temperature. During the voltage change in positive and negative directions, the mean value of the leakage current (for five consecutive readings) was recorded automatically. We did not notice any
significant differences between the two directions of applied voltage which supports our previous results [35]. As shown in Fig. 5a, the leakage current density of BiFe$_{1-x}$Ni$_x$O$_3$ samples has a tendency to decrease with increasing of $x$ (Ni contents), and the value is dramatically decreased when $x = 0.9$ (see Fig. 5b). This result shows a significant improvement in the properties of the prepared samples which represented as the lowering in the leakage current values with Ni co-doping content. As we know, the main source of the leakage current is the charge defects such as $V^{3-}_{Bi}$ (bismuth vacancies) and $V^{2+}_O$ (oxygen vacancies). The oxygen vacancies are mostly generated from Bi volatility besides the changes from Fe$^{3+}$ to Fe$^{2+}$. The reduction in Fe$^{3+}$ species to Fe$^{2+}$ is possibly compensated by the substituted Ni$^{2+}$ ion, and thus, it decreases the probability of oxygen vacancies formation, which may cause the initial reduction in leakage current as shown in the lattice parameters shown in Fig. 1.

The electrical hysteresis (IV loop) for sample $x = 0.9$ is represented in Fig. 5c. It is clearly noted that the area of the hysteresis decreases with decreasing Ni content, the symmetry of the curve behaviour ($-20 \rightarrow 0 \rightarrow +20$) increase with decreasing Ni content, and the shift between the two minima (m1 and m2 in Fig. 5c of the cycle becomes close to each other with decreasing Ni content. This behaviour can be attributed to the existence of trapping and detrapping process beside the cle bipolar resistive element which decreases the effect of the space charge carrier.

Figure 6 a and b represent the dependence of the real and imaginary dielectric constant $\varepsilon'$ and $\varepsilon''$ on frequency at room temperature. It is evident that for all samples, the $\varepsilon'$ and $\varepsilon''$ decrease with the increasing of frequency. In the starting low frequency range both $\varepsilon'$ and $\varepsilon''$ values decrease gradually as the frequency increases and then decrease slowly and become almost constant up to 1 MHz for all samples. These results can be attributed to the well-known dipole relaxation phenomena. At high electric field frequencies, the electric dipoles become enable to switch or rotate with the applied electric field frequency [36]. Furthermore, the real and imaginary parts of the dielectric constant are decreased as the concentration of Ni ions increases. The oxygen vacancies in BiFeO$_3$ materials, which are mostly generated during the heat treatment, are the major origin of the determination of the insulation and the formation of Fe, according to $V^{x}_{O} + 2\text{Fe}^{3+} \rightarrow V^{x}_{O} + 2\text{Fe}^{2+}$, where $V^{x}_{O}$ is an oxygen vacancy and $V^{x}_{O}$ is an oxygen position. Following Le Charelier principle, the concentration of Fe$^{2+}$ would decrease if the content of Fe$^{3+}$ is reduced. Therefore, doping at Fe site would suppress the formation of oxygen vacancies and reduce the concentration of Fe$^{2+}$ [37].

The variation of the real and imaginary dielectric constants ($\varepsilon'$) and ($\varepsilon''$) of the BiFe$_{1-x}$Ni$_x$O$_3$ ($x = 0.7, 0.8$ and $0.9$) as a function of temperature measured at as elected frequencies is shown in Fig. 7. It shows a continuous increase with temperature up to the transition temperature $T_c$ then it comes to be decreased. The exhibited anomaly has been detected in three samples around 260 °C, 255 °C and 240 °C. The existence of these anomalies in the temperature range 240–260 was reported previously by several authors [24, 38–40]. These anomalies seem to be related to magnetic transition (spin-glass-like behaviour) [41]. The position of the anomaly was shifted with doping of Ni in BiFeO3 towards to lower temperature side.
The shift in the position of anomaly may be attributed to the increasing in the ionic radius of Ni$^{2+}$ (0.69 Å) which is larger than Fe$^{3+}$ (0.64 Å). These anomalies prove that the possibility of coupling between the electric and magnetic dipole moments of BiFe$_{1-x}$Ni$_x$O$_3$, which attributed to the magneto-electric coupling.

**Conclusion**

The high nickel dopant induced changes in the structure, optical absorption and leakage current; the J-E hysteresis and dielectric properties of BiFe$_{1-x}$Ni$_x$O$_3$ samples have been investigated. It is shown that the BiFe$_{1-x}$Ni$_x$O$_3$ crystallizes in the triclinic crystal structure. The cell parameters increase with increasing $x$ doping, and optical band gaps decrease with increasing $x$. Leakage current were much reduced with Ni$^{2+}$ ion doping, it was decreased by about three orders of magnitude. The area of the hysteresis decreases with decreasing Ni doping. It is also found that the doping of Ni$^{2+}$ ions can effectively reduce the leakage current density and improve the ferroelectric properties. The dielectric constants $\varepsilon'$ and $\varepsilon''$ were found to be decreased with increased frequency. The real $\varepsilon'$ and imaginary $\varepsilon''$ dielectric constants were found to be increased with temperature. The temperature dependence of $\varepsilon'$ and $\varepsilon''$ exhibited an anomaly which shifted to lower temperature with increasing Ni$^{2+}$ ion doping. The anomaly indicates the possible existence of spin-glass states with Ni$^{2+}$ ion substitution in the place of Fe$^{3+}$ ions.

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**References**

1. Hill, N.A.: J. Phys. Chem. B. 104(29), 6694–6709 (2000)
2. S. Kumari, D.K. Pradhan, R.S. Katiyar, A. Kumar: Elsevier, p. 571 (2018)
3. N.I. Ilic, B.D. Stojanovic: Elsevier, p. 527, (2018)
4. C.E. Ciomaga, L. Mitoseriu: Elsevier, p. s/ (2018)
5. Delshad, M., Safaei, A., Kazazi, M., Shahrahi, M.M.: Ceram. Int. 44(12), 14281–14285 (2018). https://doi.org/10.1016/j.ceramint.2018.05.032
6. Roginskaya, Y.E., Tomashpol’skii, Y.Y., Venevtsiev, Y.N., Petrov, V., Zhidanov, G.: Soviet. J. Exp. Theor. Phys. 23(47), (1966)
7. Küber, F., Schmid, H.: Structural Science. 46, 698–702 (1990)
8. Kiselev, S., Ozorov, R.P., Zhudanov, G.S.: Detection of magnetic order in ferroelectric BiFeO$_3$ by neutron diffraction. Sov Phys. 7, 742 (1963)
9. Ederer, C., Spaldin, N.A.: Curr. Opinion Solid State Mater. Sci. 9, 128 (2005)
10. Wang, Y., Zhou, L., Zheng, M., Chen, X., Liu, J.-M., Liu, Z.: Appl. Phys. Lett. 84, 1731 (2004)
11. Palkar, V., Kumara, K.G., Malik, S.: Appl. Phys. Lett. 84, 2856 (2004)
12. Sarkar, T., Elizabeth, S., Kumar, P.A.: J. Magn. Magn. Mater. 448(266), (2018)
13. Dai, H., Ye, F., Chen, Z., Li, T., Liu, D.: J. Alloys Compd. 734, 60 (2018)
14. Wen, X., Chen, Z., Liu, E., Lin, X., Chen, C.: J. Alloys Compd. 678, 511 (2016)
15. Yu, B., Li, M., Liu, J., Guo, D., Pei, L., Zhao, X.: J. Phys. D. Appl. Phys. 41(065003), (2008)
16. Kawae, T., Tsuda, H., Morimoto, A.: Appl. Phys. Express. 1, 051601 (2008)
17. Yau, C., Panal, R., Tran, K., Buchanan, R.: Appl. Phys. Lett. 86, 032907 (2005)
18. Kojima, T., Sakai, T., Watanabe, T., Funakubo, H., Saito, K., Osada, M.: Appl. Phys. Lett. 80, 2746 (2002)
19. Kumar, M.M., Srinivas, A., Suryanarayana, S.: J. Appl. Phys. 87, 855 (2000)
20. Liu, H., Liu, Z., Yao, K.: Phys. B Condens. Matter. 391, 103 (2007)
21. Kumar, V., Gaur, A., Kotnala, R.: J. Alloys Compd. 551, 410 (2013)
22. Gao, F., Yuan, Y., Wang, K., Chen, X., Chen, F., Liu, J.-M., Ren, Z.: Appl. Phys. Lett. 89, 102506 (2006)
23. Gao, F., Chen, X., Yin, K., Dong, S., Ren, Z., Yuan, F., Yu, T., Zou, Z., Liu, J.M.: Adv. Mater. 19, 2889 (2007)
24. Biswal, M.R., Nanda, J., Mishra, N.C., Anwar, S., Mishra, A.: Adv. Mater. Lett. 5, 531 (2014)
25. Betancourt-Cantera, L.G.: Bolarín-Miró, A.M., Cortés-Escobedo C.A.; Hernández-Cruz, L.E.; Sánchez-De Jesús, F.: J. Magn. Magn. Mater., 456, 381 (2018)
26. Ishiwata, S., Azuma, M., Hanawa, M., Moritomo, Y., Ohishi, Y., Kato, K., Takata, M., Nishibori, E., Sakata, M., Terasaki, I.: Phys. Rev. B. 72, 045104 (2005)
27. Yang, L., Mikhailic, S.J.: JOSA A. 22, 1866 (2005)
28. Kortüm, G.: Reflectance spectroscopy: principles, methods, applications. Springer Science & Business Media (2012)
29. Barton, D.G., Shein, M., Wilson, R.D., Soled, S.L., Iglesia, E.: J. Phys. Chem. B. 103, 630 (1999)
30. Butler, M.: J. Appl. Phys. 48, 1914 (1977)
31. Kim, K.J., Park, Y.R.: Appl. Phys. Lett. 78, 475 (2001)
32. Katsura, H., Balatsky, A.V., Nagaosa, N.: Phys. Rev. Lett. 98, 027203 (2007)
33. Van Minh, N., Quan, N.G.: J. Alloys Compd. 509, 2663 (2011)
34. Bhushan, B., Basumallick, A., Vasanthacharya, N., Kumar, S., Das, D.: Solid State Sci. 12, 1063 (2010)
35. Arafat, S., Ibrahim, S.: Mater. Sci. Appl. 8, 716 (2017)
36. Uniyal, P., Yadav, K.: J. Alloys Compd. 492, 406 (2010)
37. Zhang, Y., Yu, S., Cheng, J.: J. Eur. Ceram. Soc. 30, 271 (2010)
38. Chaudhary, Y.A., Mahajan, C.M., Jagtap, P.P., Bendre, S.T.: J. Adv. Ceramics. 2(2), 135 (2013)
39. Karim, S., Reaney, I.M., Levin, I., Sterianous, I.: Appl. Phys. Lett. 94(112903), (2009)
40. Gautam, A., Singh, K., Sen, K., Kotnala, R.K., Singh, M.: J. Alloys Compd. 517, 87 (2012)
41. Catalan, G., Scott, J.F.: Adv. Mater. 21, 2463 (2009)

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