

Physical properties and optical basicity of transition metal-doped borate glasses

Eldaly Abd Elrahman¹, Abdo Mohamed¹, saad Mohamed² and AboBakr Hamsa Mohamed^{1*}

¹ Physics department, faculty of science, Zagazig university

² Basic sciences department, faculty of engineering, Sinai university

*Corresponding author: hamsabakr@gmail.com

ABSTRACT: To study various properties of cobalt cations on glasses, a new borate $62\text{B}_2\text{O}_3-(20-x)\text{ZnO}-18\text{Na}_2\text{O}-x\text{CoO}$ glass system, with $x = 1.5, 1, 0.5$ and 0 mol.% was prepared by using the melt quenching technique. Traditional methods and usual formulas were used to calculate the molar volume (V_m) and measurement of density (ρ). Optical basicity (Λ_{th}) was determined using the formula suggested by Duff and Ingram. The dependence of density (ρ), molar volume (V_m), ion concentration (N), polaron radius (r_p), field strength (F), inter atomic distance (r_i), optical basicity (Λ_{th}), electronic polarizability (α_0^{-2}) and electronegativity (X_{av}) on Co^{2+} cations content were analyzed. The trend of density, field strength, ion concentration, electronegativity with composition shows an increasing behavior with CoO content, while molar volume, inter atomic distance, polaron radius, optical basicity and electronic polarizability exhibit a decrement behavior.

KEYWORDS: Borate glasses. Transition metals. Physical properties. Optical basicity.

Date of Submission: 16-04-2022

Date of acceptance: 18-05-2022

I. INTRODUCTION

Boric oxide (B_2O_3) is one of the most main glass formers [1, 2]. The boron atom in borate crystals and glasses ordinarily organizes with either four or three oxygen atoms forming $[\text{BO}_4]$ or $[\text{BO}_3]$ structural units [3, 4]. The concentration of these structural units is contingent on both the nature and the total concentration of the other modifiers [5]. Additionally, boron atom has a small cation size, and high bond strength. It has the aptitude to variation its oxidation state simply. The borate groups-include of (B-O-B) linkages- help in increasing the optical properties of glasses by affecting metal oxygen bonds and the bonds of the non-bridging oxygen atoms (NBOs) [6,7]. Alkali and/or alkaline oxides such as Na_2O , Li_2O , CaO , etc. are regularly used to decrease the fusion point as well as to increase the dielectric or optical properties of the glass [8].

Glasses doped with 3d transition metal ions have gained attention due to the relevance of their spectroscopic and electrical characteristics, as well as their appropriateness for a variety of glass filters, plasma display panels, solar energy converters, and a variety of electronic devices [9,10]. The electronic and optical properties of this TM-doped glasses might be enhanced by the slight addition of various oxide modifiers, such as ZnO [11]. ZnO enters the glass structure in the form of both network former and network modifier [12]. Zinc borate glasses take several technological applications in optoelectronic devices such as laser diodes, light-emitting and laser emission covering a wide visible area because of its great band gap [13]. Cobalt cations in different valence Co^{3+} and/or Co^{2+} exist in octahedral and/or tetrahedral positions. Despite of Cobalt cations require great stabilities in the normal environment; they develop the system performance while added. Cobalt cations enclosing glasses are employed in several applications such as lasers, lithium batteries, super capacitors, gas sensors and Q-switching devices [14-16]. Cobalt ion Co^{2+} ($3d^7$ configuration) existed as a strong colorant, which creates a strong blue color in glasses and its color shade variations with the coordination state variation [17]. The goal of the present work is to assess the eligibility of gradual doping of CoO on physical properties, optical basicity, electronegativity and electronic polarizability of a new Zn borate glassy system.

II. MATERIALS AND METHODS

The borate glass system of the formula; $(20-x)\text{ZnO}+62\text{B}_2\text{O}_3+ x\text{CoO} 18\text{Na}_2\text{O}$ where $x= 1.5, 1.0, 0.5$ and mol.% was prepared by using the melt quenching technique. The raw materials that used to prepare the glass system were pure Boric acid (H_3BO_3), sodium carbonate (Na_2CO_3), zinc oxide, (ZnO) and cobalt oxide (CoO). All weighted chemicals were powdered finely and thoroughly mixed in an agate mortar then melted in porcelain crucibles by an electrical oven at $1050\text{ }^\circ\text{C}$ for 45 minutes. The homogeneous melt was guardedly stirred and molding on copper sheet -at RT ($27\text{ }^\circ\text{C}$). The undoped glasses stay colorless, while CoO doped specimens show a clear blue color. As the CoO concentration augmented from 0.5 to 1.5 mol%, a gradual variation of the color from the light into dark blue occurs. The average density (ρ) was calculated by applying Archimedes' principle. Density values were explained by calculating the average of 3 attempts executed on different specimens with different shapes with error about 0.01 g/cm^3 . The molar volume (V_m) was calculated by using the data of density (ρ) and molar mass (M) with error about $0.01\text{ cm}^3/\text{mole}$.

III. RESULTS AND DISCUSSION

3.1-Optical basicity

The optical basicity of an oxide glass reflects ability of the glass to give a negative charge to the probe ion. It is also used as a quantity of acid-base properties of oxide glasses [18,19]. The theoretical bulk optical basicity of the multi-component glass was calculated by the method suggested by Duff and Ingram [20] according to the following equation:

$$\Lambda_{th} = \sum X_i \Lambda_i \quad (1)$$

where Λ_i and X_i are the respective optical basicity and molar concentration of the oxide component i as obtained from [21,22]. The average electronegativity was calculated using the following relationship:

$$\chi_{av} = \frac{0.75}{\Lambda_{th}} + 1.35 \quad (2)$$

The mean electronic polarizability (α_0^{-2}) of the oxide ions is a standout between the most important properties of the materials, which is most likely related to their application in the sphere of electronics besides optics [23]. The values of (α_0^{-2}) of the oxide ions were calculated using the empirical equation. [24]:

$$\alpha_0^{-2} = \frac{1.67}{1.67 - \Lambda_{th}} \quad (3)$$

The calculated values of the theoretical optical basicity, electronic polarizability and electronegativity for the investigated glass samples are listed in Table.1. This table clearly shows a decrement of the theoretical optical basicity and electronic polarizability beside an increment in the electronegativity with increasing CoO content. The decrease in optical basicity is caused by an decrease in the polarizability and increase in single bond strength of CoO where single bond strength of CoO oxide is greater than that of ZnO oxide. Thus, the field strength of Zn^{2+} ion is smaller than that of the Co^{2+} ion, which means that Zn^{2+} ion is much more polarizable than Co^{2+} ions. Lower polarizability of CoO means increased ability of an ion to attract electrons from the atoms bonded to it [25].

Similar results were obtained by Ibrahim and Sadeq [26] found that the values of optical basicity and electronic polarizability were decreased with CoO addition.

Table.1 Theoretical electronegativity, optical basicity, electronic polarizability of $xCoO-18\%Na_2O-(20-x)ZnO-62\%B_2O_3$, where $x=1.5,1,0.5$ and 0 mol%.

x (mol%)	Optical basicity Λ_{th}	Electronegativity χ_{av}	Electronic polarizability α_0^{-2}
0	0.6906	2.4360	1.7051
0.5	0.6899	2.4372	1.7038
1	0.6891	2.4384	1.7025
1.5	0.6884	2.4396	1.7012

3.2- Physical properties

The calculated densities (ρ) for all glass samples under investigation are tabulated in Table 2. It was found that the density augmentation from 2.47456 to 2.67857 (g/cm³) with the addition of CoO content at the expense of ZnO content (Fig. 1). This could be due to the higher density of CoO ($\rho = 6.44$ g/cm³) in compared with that of ZnO ($\rho = 5.61$ g/cm³). The molar volume (V_m) depends on the density (ρ) of glasses and as predicted in the current example, it follows a trend reverse to density [15]. The molar volumes (V_m) of glasses were decreased from 28.52859 to 26.31965 (cm³/mol) with augmentation of CoO concentration. This behavior is due to the decrease in the bond length or inters atomic spacing. The ionic radius of CO²⁺ ion (0.58 nm) is smaller than that of Zn²⁺ ion (0.083nm) [28]. Furthermore, the decrease in molar volume can be related to decrease in the non-bridging oxygen (NBO) in the glass matrix. This decrement in NBO is supported by the augmentation in E_g (28). The observed decrease of ionic radius (r_i) and polaron radius (r_p) with augmentation CoO content is most likely related to the augmented value of ion concentration (N) for Co²⁺ ions. The Co²⁺ ions are located among the layers and, accordingly, the distance between Co²⁺ ions and oxygen atoms are reduced. This leads to a strong augmentation in the Co-O bond strength, resulting in a stronger field around the Co²⁺ ions [24,27]. Other important parameters such as concentration of Co²⁺ (N), polaron radius (r_p) and interatomic distance of cobalt (r_i) are related to the density given by:

$$N = (\text{mol\% of TM}) \frac{\rho N_A}{M} = \frac{X \rho N_A}{M} \quad (4)$$

$$r_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \quad (5)$$

$$r_p = \frac{r_i}{2} \left(\frac{\pi}{6}\right)^{\frac{1}{3}} \quad (6)$$

The observed decrease of ionic radius (r_i) and polaron radius (r_p) with augmenting CoO content is most likely associated to the augmented value of ion concentration (N) for Co²⁺ ions. The Co²⁺ ions are located among the layers and, accordingly, the distance between Co²⁺ ions and oxygen atoms are reduced. This results in a strong augment in the Co-O bond strength, which resulting in a stronger field around the Co²⁺ ions [24,27].

Similar results were obtained by Abd-Allah and Nabhan, [30] found that the density of studied samples increased as CoO increased while the molar volume decreased. Siriprom et al., [31] found that the density was increased with increasing of CoO concentration. Mostafa et al., [32] found that as the CoO content increased from 1% to 12% (mol) in the glass samples, the bulk densities of glasses increased from 2.611 to 2.785 g/cm³. Ibrahim and Sadeq, [26] found that the measured density of the sample is increased with Co doping, while molar volume follows the opposite behavior typical for glasses. These results confirm our conclusion.

Table.2 The physical and structural parameters of glasses system ($x\text{CoO}-18\%\text{Na}_2\text{O}-(20-x)\text{ZnO}-62\%\text{B}_2\text{O}_3$, where $x=1.5,1,0.5$ and $0\text{mol}\%$).

X	0	0.5	1	1.5
Density (g/cm^3)	2.47456	2.58671	2.64399	2.67857
Molar volume (cm^3/mol)	28.52859	27.27924	26.67606	26.31965
Co concentration ($\times 10^{20}$)(cm^{-3})	0	1.105174	2.257506241	3.432117034
Inter atomic distance r_i (nm)	0	2.0838	1.6423	1.4283
Polaron radius r_p (nm)	0	0.8398	0.66092	0.57629
Field strength F (cm^2)	-	2.38152	3.02608	3.4705

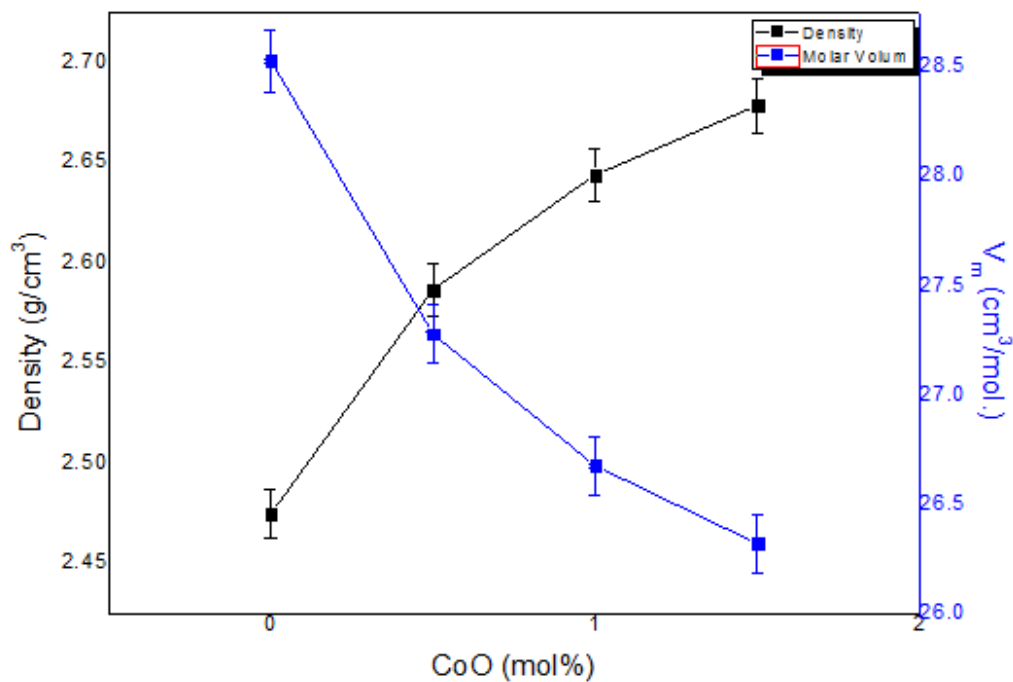


Fig.1: Molar volume and Density with different concentrations of Co^{2+} ions.

IV. Conclusion

The quaternary (x) $\text{CoO}-18\text{Na}_2\text{O}-(20-x)\text{ZnO}-62\text{B}_2\text{O}_3$ glasses, with $x = 1.5, 1.0$

, 0.5 and 0 mol%, have been successfully synthesized. The average electronegativity showed opposite trend with both of (Δ_{th}) and (α_0^{-2}). The measured density appeared augmenting behavior and molar volume appeared a reverse behavior with augmenting Co cations. Moreover, the most significant structural parameters were employed to study the augmentation toward the strong crystal field with the augmentation in the content of Co cations. These obtained results nominate these cobalt-borate glasses for promising applications such as optical devices.

REFERENCES

- [1] Subhashini, H.D. Shashikala, N.K. Udayashankar, J. Alloys Compd. 658 (2016) 996-1002.
- [2] A. Wagh, Y. Ravirakash, M. Ajithkumar, Trans. Nonferrous Met. Soc. China 25 (2015) 1185-1193.
- [3] A. Edukondalu, B. Kavitha, M.A. Samee, S.K. Ahmmed, S. Rahman, K. Siva Kumar, J. Alloys Compd. 552 (2013) 157-165.
- [4] A. Terczynska-Madej, K. Cholewa-Kowalska, M. Łańczka, Opt. Mater. 33 (2011) 1984-1988.
- [5] A. Edukondalu, S. Rahman, K. Siva Kumar, D. Sreenivasu, Vib. Spectrosc. 71 (2014) 91-97.
- [6] M. Farouk, A. Samir, F. Metawe, M. Elokr, Optical absorption and structural studies of bismuth borate glasses containing Er^{3+} ions, J. Non-Cryst. Solids 371-372 (2013) 14-21.
- [7] S.M. Salem, S.F. Mansour, I.I. Bashter, M.S. Sadeq, A.G. Mostafa, Effect of mixed heavy metal cations on the A.C. conductivity and dielectric properties of some borosilicate glasses, Ceram. Int. 44 (2018) 14363-14369
- [8] A. Hidayat, M. Diantoro, Z. Muniroh, B. Zaini, A.A. Mustikasari, Nasikhudin, A. Taufiq, Sunaryono, N. Mufti, The 4th international conference on advanced materials science and technology IOP publishing 1234567890 IOP Conf, Series: Mater. Sci. Eng. ??? (2017) 202.
- [9] C.R. Bamford, Color Generation and Control in Glass, Glass Science and Technology, vol. 2, Elsevier Science Publisher, Amsterdam, 1977??????.
- [10] G. Fuxi, Optical and Spectroscopic Properties of Glasses, Springer, Berlin, 1992??????.
- [11] R. Mimouni, K. Boubaker, M. Amlouk, J. Alloys Compd. 624 (2015) 189-194
- [12] T. Raghavendra Rao, Ch. Venkata Reddy, Ch. Rama Krishna, U.S. Udayachandran Thampy, R. Ramesh Raju, P. Sambasiva Rao, R.V.S.S.N. Ravikumar, Correlation between physical and structural properties of Co^{2+} doped mixed alkaline zinc borate glasses, Journal of Non-Crystalline Solids 357 (2011) 3373-3380.
- [13] Lihua Ding, Yunxia Yang, Xiongwei Jiang, Congshan Zhu, Guorong Chen, J. Non-Cryst. Solids 354 (2008) 1382.
- [14] M.A. Hassan, F. Ahmad, Z.M. Abd El-Fattah, Novel identification of ultraviolet, visible Cr^{6+} , Cr^{3+} optical transitions in borate glasses, J. Alloys Compd. 750 (2018) 320.

- [15] F. Ahmad, E. Hassan Aly, M. Atef, M.M. ElOkr, Study the influence of zinc oxide addition on cobalt doped alkaline earth borate glasses, *J. Alloys Comp.* 593 (2014)250.
- [16] T. Satyanarayana, I.V. Kityk, M. Piasecki, P. Bragiel, M.G. Brik, Y. Gandhi, N. Veeraiyah, Structural investigations on $\text{PbO-Sb}_2\text{O}_3\text{-B}_2\text{O}_3\text{:CoO}$ glass ceramics by means of spectroscopic and dielectric studies, *J. Phys. Condens. Matter* 21 (2009) 16.
- [17] F. Ahmad , E. Hassan Aly , M. Atef , M.M. ElOkr , Study the influence of zinc oxide addition on cobalt doped alkaline earth borate glasses, *Journal of Alloys and Compounds* 593 (2014) 250-255.
- [18] J. Santhan Kumar, J. Lakshmi Kumari, M. SubbaRao, SandhyaCole, *Opt. Mater.*35 (2013) 1320.
- [19] Xinyu Zhao, Xiaoli Wang, Hai Lin, Zhiqiang Wang, ??? *Physica B* 403 (2008) 2450.
- [20] Z.X. Mo, H.W. Guo, P. Liu, Y.D. Shen, D.N. Gao, Luminescence properties of magneto-optical glasses containing Tb^{3+} ions, *J. Alloys Compd.* 658 (2016) 967-972.
- [21] V. Dimitrov, S. Sakka, ??? *J. Appl. Phys.* 79 (1996) 1736.
- [22] R.W. Young, J.A. Duffy, G.J. Hassall, Z. Xu, *Ironmaking Steelmaking* 19 (1992) 201.
- [23] Yasser B. Saddeek, Kamal A. Aly, Safaa A. Bashier, Optical study of lead borosilicate glasses, *Physica B* 405 (2010) 2407-2412.
- [24] M. Farouk, Effect of Co^{2+} ions on the ligand field, optical, and structural properties of ZnLiB glasses, *Optik* 140 (2017) 186-196.
- [25] VesselinDimitrov, Takayuki Komatsu, ??? *J. Solid State Chem.* 196 (2012) 574.
- [26] A. Ibrahim, M.S. Sadeq, Influence of cobalt oxide on the structure, optical transitions and ligand field parameters of lithium phosphate glasses, *Ceramics International* 47 (2021) 28536-28542.
- [27] H.Y. Morshidy, M.S. Sadeq, Influence of cobalt ions on the structure, phonon emission, phonon absorption and ligand field of some sodium borate glasses, *Journal of Non-Crystalline Solids* 525 (2019) 119666.
- [28] P. Yasaka, Y. Ruangthaweeep, P. Mangthong, J. Kaewkhao, Physical and optical investigation of ZnO-BaO-TeO_2 glass systems, *Materials Today: Proceedings* 5 (2018) 14199-14203.
- [29] A.A. El-Daly , M.A. Abdo , H.A. Bakr , M.S. Sadeq , Impact of cobalt ions on the phonon energy and ligand field parameters of some borate glasses, *Journal of Non-Crystalline Solids* 555 (2021) 120535.
- [30] Wesam Abd-Allah, Eman Nabhan, Effect of CoO and Gamma Irradiation on the Infrared Absorption Spectra of Lithium Borate Glasses, *Silicon* 10 (2018)

49-57.

[31] W. Siriprom , K. Teanchai , N.Srisittipokakun and J. Kaewkhao , Effect of CoO addition on the optical and physical properties of silicoborate glasses, *Key Engineering Materials*. 675-676 (2016) 318-321.

[32] Ahmed M. A. Mostafa , Mohamed A. M. Uosif , Ziyad A. Alrowaili , Reda Elsaman , Ahmed A. Showahy , Yasser B. Saddeek, Shams A. M. Issa , Antoaneta Ene and Hesham M. H. Zakaly , The Influence of CoO/P₂O₅ Substitutions on the Structural, Mechanical, and Radiation Shielding of Boro-Phosphate Glasses, *Materials* 14 (2021) 6632.