



Structural Characterization of Neodymium Oxide doped with Borate glasses

Mona Shaalan^{1*}, Gomaa El-Damrawi¹, Abdelmagued Hassan¹, and Mohamed Hamed Misbah²

¹ Physics Department, Faculty of Science, Mansoura University, Mansoura 35511, Egypt

² Institute of Nanoscience & Nanotechnology, Kafrelsheikh University, Kafrelsheikh 33511, Egypt

* Correspondence to: mona.shaalan@yahoo.com

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Abstract: The effect of different contents of Nd₂O₃ on the structure of xNd₂O₃ – (46-x) B₂O₃ – 27 CaO – 24.4 Na₂O – 2.6 P₂O₅ (0 ≤ x ≤ 4 mol%) has been investigated using NMR and FTIR (Fourier transform infrared) absorption spectroscopy was used to investigate the glasses. The effect of Nd₂O₃ on NMR parameters has been studied in terms of modifying both boron and Neodymium coordination. ¹¹B NMR spectroscopy was used to measure the quantitative proportion of four coordinated boron (N₄). FTIR spectral analysis, on the other hand, yields the fraction of total tetrahedral structural units B₄ (BO₄ + Nd₂O₄). The potential of Neodymium oxide to participate as a network modifier improves with increasing its content, as evidenced by decreasing both percentage of boron tetrahedral units (N₄) and the chemical shift of boron nuclei (δ), confirming the role of Nd₂O₃ as a modifier.

keywords: NMR Spectroscopy, FTIR Spectroscopy, Neodymium Oxide, Borate glasses

1. Introduction

More insight into the development of bioactive materials as borate glass ceramics for technical, dental, and bone tissue regeneration and healing applications was recently conferred by several authors [1-3]. Because inorganic hydroxyapatite nanocrystals and organic collagen protein are the major component constituents of bone tissue. The effect of bioactive glasses and glass-ceramics chemical composition on their interaction with the physiological system and bonding between living tissue and the glass surface has been previously observed. [4,5]. The effect of crystallization of the glass has centered the proper interest for bioactive glass-ceramic materials in the biomedical field [6]. As a result, glass-ceramic materials often have a very fine microstructure with few or no residual pores. These qualities increase the final product's mechanical properties.

Borate oxide glasses are one of the most suitable for RE³⁺ doping. [7,8]. The influence of rare-earth ions on the structural characteristics of borate glasses has received considerable attention. Therefore, it is used in combination with other oxides which leads to improved chemical durability. Rare earth

elements with the highest abundance offer unique properties, such as antibacterial or imaging applications. Due to the electronic configuration of lanthanides, rare earth-containing bioactive glasses are attractive materials for biological applications such as brachytherapy, luminescence-based imaging, and magnetic resonance imaging. Although such glasses are increasingly being researched, they remain understudied as biomaterials [9].

In this study, we concentrate our research on a specific type of borate glasses containing Nd₂O₃. This is because this type can reveal high surface hardness with a low thermal expansion coefficient. Such characteristics made the glasses to be more resistant to fatigue stresses and temperature changes. The addition of a network modifier to B₂O₃ has been shown to break down the B-O bonds, enabling BO₃ triangles to convert into BO₄ tetrahedral units. [10]. The main aim of this paper is to investigate the effect of Nd₂O₃ on the structure of xNd₂O₃ – (46-x) B₂O₃ – 27 CaO – 24.4 Na₂O – 2.6 P₂O₅ (0 ≤ x ≤ 4 mol%) using different techniques like NMR and FTIR to reveal the correlations between structure and properties of glass doped with rare-earth.

1. Experimental methods

2.1. Glass preparation:

The nominal $x\text{Nd}_2\text{O}_3-(46-x)\text{B}_2\text{O}_3-27\text{CaO}-24.4\text{Na}_2\text{O}-2.6\text{P}_2\text{O}_5$ ($0 \leq x \leq 4$ mol%) glass composition was prepared through the melt-quenching process using a porcelain crucible. Nd, HBO_3 , Ca, Na, NH_4P (chemical precursors) were used as a starting material. The required amount of the last precursor was heated at 300 °C for about 90 min to exclude water and ammonia. Then, the required amounts of the other precursors were well-mixed and added to the porcelain crucible, and melted at 1000-1200 °C. To maintain uniformity, the melt was constantly stirred and then poured between two stainless-steel plates. The glass materials were kept in a desiccator until the characterization process.

2.2. Characterization:

^{11}B and ^{31}P NMR spectra of the powdered glass samples were recorded using JEOL RESONANCE GSX-500 high-resolution solid-state MAS NMR spectrometer. The spectra were obtained at a high external magnetic field (11.747T) and a frequency of 160.4 MHz. The glass samples were measured with a single pulse length of 0.5 - 1.0 ms and a pulse delay of 2.5 s, and an accumulation of 200-300 scans was produced on the glass samples. Fourier transform Infrared Spectroscopy (FTIR) spectra were collected Bruker spectrometer FTIR. At room temperature, spectra in the wavenumber range of 400 to 4000 cm^{-1} at 2.0 cm^{-1} were recorded. The powdered glass samples were blended at 1:100 in weight with KBr for the FTIR examination in absorption mode. Each glass had at least three samples tested. Each sample's spectrum is derived from a total of 20 scans. The resulting spectrum was normalized to that of a blank KBr pellet, which meant subtracting a pure KBr spectrum from each glass spectra.

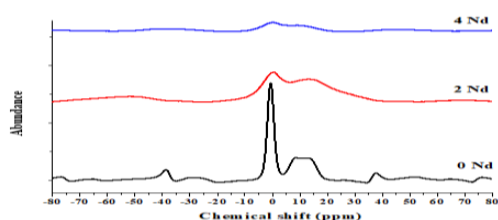


Figure 1: ^{11}B NMR for the base and modified borate glass containing respectively 2 and 4 mol% Nd_2O_3 .

2. Results and Discussion

3.1. ^{11}B MAS NMR Spectra

Figure 1 shows the ^{11}B MAS NMR spectra of $x\text{Nd}_2\text{O}_3 - (46-x)\text{B}_2\text{O}_3 - 27\text{CaO} - 24.4\text{Na}_2\text{O} - 2.6\text{P}_2\text{O}_5$ at $x = 0, 2$ and 4 mol% Nd_2O_3 . In the spectra of base glass (at $x = 0$), there are two main peaks at a chemical shift of about 0 and 10 ppm attributed to BO_4 and BO_3 , respectively [1]. With the addition of Nd_2O_3 the intensity of the peak assigned to BO_4 tetrahedra groups decreases, while that of BO_3 triangle groups increases. This indicates qualitatively that the relative concentration of BO_3 units increases while that of BO_4 decreases.

This strongly suggests that Nd^{3+} delays the transformation of BO_3 into BO_4 . It was thus considered that Nd^{3+} is sufficiently greater than that of Na^+ and Ca^{2+} to lead to the creation of BO_4 [2]. It therefore can suggest that the Nd/B ratio is important for the nature of the BO_3/BO_4 ratio because BO_4 decreases with getting exchanged out by Nd_2O_3 locations. Whenever a result of the previous facts and assumptions, it is believed that the quantity of BO_4 changes dramatically as Nd_2O_3 concentration rises.

The reduction in BO_4 concentration indicates that certain network modifiers are being removed in order to convert $\text{BO}_4 \rightarrow \text{BO}_3$. This is a surprising behavior, which is unexpected at this lower concentration of Nd_2O_3 compared to that of B_2O_3 . Indeed, the participation of 4 mol% of Nd_2O_3 in the glass network formation is assumed to be limited since its low concentration is not accessible to withdraw some modifier from the borate network. This indicates that Nd_2O_3 does not affect directly the $\text{BO}_4 \rightarrow \text{BO}_3$ transformation. Back conversion, as seen in rare-earth-doped borate glasses with high lead oxide concentration, is a phenomenon that has been seen in previous research [13]. In other words, there is another indirect role is played by Nd_2O_3 which has the main responsibility for back conversion of boron transformation. ^{11}B NMR for 0 Nd glass should contain a higher BO_4 fraction. The average full width at half maximum FWHM of ^{11}B NMR spectra is found to increase. It changes from 9 ppm to about 29 ppm upon the presence of 2 mol% rare earth. The fast increase in FWHM should be referred to as increasing asymmetric BO_3 units through the transformation of BO_4 to

asymmetric BO_3 . The smaller value of FWHM in the base glass leads that only symmetric borate groups are dominant. On the other hand, the higher value of FWHM in glasses containing rare earth support that the latter played the role of back conversion agent. BO_4 in such a case is highly transformed to asymmetric BO_3 units which in turn reduce BO_4 fraction. The formation of B-O-Nd bonds increases the cross-linked bonds in the glass network which leads to increased T_g particularly in samples of > 0.5 mol% Nd_2O_3 .

3.2. ^{31}P MAS NMR Spectra

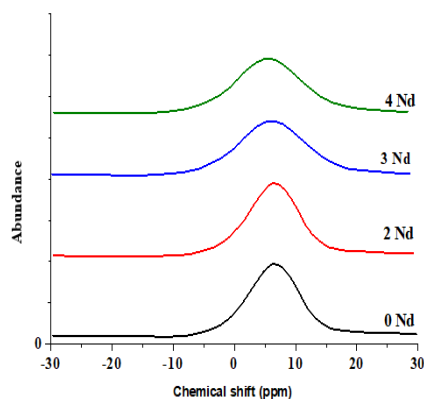


Figure 2: ^{31}P NMR spectra of borate glass Nd free and of glasses containing respectively 2, 3, and 4 mol% Nd_2O_3 .

The different Q^n species discovered in the glass network may be directly identified using ^{31}P MAS NMR studies. The phosphate tetrahedral are classified using the Q^n terminology where n represents the number of BOs per tetrahedral group. In phosphate glass, the nomenclature can be used to four different units (from Q^3 to Q^0) since Q^4 cannot be formed due to the presence of $\text{P}=\text{O}$ bond. In the present glass matrix, the concentration of P_2O_5 is about 2.6 mol %. Thus, orthophosphate (Q^0) is the dominant structural species that form the phosphate network, and there is no extra Q^n type because the modifier contents are very high exceeding seven times of phosphate concentration. Therefore, this composition is corresponding to (Q^0). This has been demonstrated by the recorded ^{31}P NMR spectra in Figure 2.

The dominant peaks are located in the + 2.1 to + 1.6 ppm range which corresponds to the Q^0 phosphate units (PO_4) $^{3-}$. Adding 2 mol% Nd_2O_3 does not influence the ^{31}P -NMR spectra, since chemical shift values are identical. It can be

observed that the glass free from Nd_2O_3 is as well as glasses containing 2, 3 and 4 mol % Nd_2O_3 has a single, symmetric Gaussian peak with a chemical shift of 2.2 ppm, which represents monophosphate (PO_4) $^{3-}$ units. The frequency peaks are thought to relate to orthophosphate Na_3PO_4 . The assignments are confirmed with spectra obtained from pure crystalline compounds [14]. Furthermore, ^{31}P NMR spectra of glass containing 4 mol% Nd_2O_3 is broader than that of glasses of lower Nd_2O_3 contents, the chemical shift is changed toward lower values. This might be attributed to the development of some ordered apatite phases that include Nd ions as a charge compensator. Furthermore, the little change in NMR chemical shift of the phosphate network with Nd_2O_3 addition might be attributed to Nd_2O_3 's minor alteration of the phosphate network. This indicates that the majority of Nd_2O_3 is utilized only to alter the borate network, resulting in a significant reduction in the fraction of boron tetrahedral units (N_4).

The chemical shift in ^{31}P NMR towards lower values and the slight increase in its FWHM (Table 1), with Nd_2O_3 content is following literature [15]. A little contribution from the Q^1 phosphate units (P_2O_7) $^{4-}$ is also found, with values ranging from - 7.0 to - 8.7 ppm. Their presence indicates the existence of phosphorus in the region of rising Nd_2O_3 concentration in the structure of tested glasses. The presence of Nd^{3+} cations in the structure of the studied glasses may explain the appearance of peaks attributed to diphosphate complexes in the spectrum. Their location has likewise shifted to the lower values, while their FWHM has changed dramatically. This might suggest the development of P-O-Nd type connections rather than P-O-Ca and P-O-Na type connections. It contributes to a modest increase in the polymerization degree of the phospho-oxygen subnetwork.

Table 1: NMR observed absorption peaks positions.

Content of Nd_2O_3	Chemical shift / (ppm)	FWHM / ppm	Intensity/ %
0 mol % Nd_2O_3	2.1	8.2	97
2 mol % Nd_2O_3	1.9	8.5	97
3 mol % Nd_2O_3	1.7	11	77
4 mol % Nd_2O_3	1.4	14	71

3.3. FTIR Spectroscopy of Nd₂O₃ doping borate bioglass

The information about the arrangement of the structure of borate when the quantity of Nd³⁺ ions increase up to 4 mol% can be obtained by using the FTIR technique. The FTIR spectra of the glasses are presented in Figure 3. Broad, strong and weak absorption bands can be seen in the investigated 400 – 4000 cm⁻¹ regions.

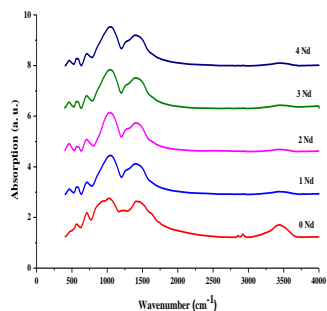


Figure 3: FTIR of the glass samples with different contents of Nd₂O₃.

The vibrations of the characteristic groups of atoms in the glass network are well known to be independent of the vibrations of the other surrounding groups in the glass [16]. The basic absorption bands of borate glasses are clear at three major bands, which are comparable to those reported by other studies [17, 18]. Figure 3 shows the FTIR spectra collected from the borate sample (0 Nd) Nd₂O₃ content in the glass matrix. The addition of Nd₂O₃ content in the glass makes the band around 690–750 cm⁻¹ become sharper and shifted to a higher frequency of 665–770 cm⁻¹. The appearance of split sharp FTIR spectral lines reinforces the idea of developing crystalline phases in glass due to the influence of Nd₂O₃ addition. The obtained broad bands may illustrate the amorphous nature of the investigated samples and are in agreement with the X-ray measurements of our prior study on the same glasses [19].

Overall, with the addition of Nd₂O₃, FTIR spectra show that the broadness of the peak ascribed to BO₄ groups decreases, while that of BO₃ increases. This indicates qualitatively that the concentration of BO₄ is decreased. This is aligned with the NMR spectroscopy data, which show a reduction in the intensity of the peak associated with the four coordinated boron atoms BO₄ compared to the three-coordinated

ones of BO₃ when Nd₂O₃ concentration increases. The major changes are found in the fraction of boron tetrahedral units (N₄), since a clear difference in (N₄) value is considered between the investigated glasses. To follow the evolution of the triangular and tetrahedral borate units in the studied samples we used the fraction of four-coordination boron atoms:

$$N_4 = A_4 / (A_3 + A_4) \quad (1)$$

where A₄ and A₃ denote the areas of the BO₄ and BO₃ units. Figure 4 shows the change of the fraction of the four-coordinated boron atoms, N₄, in comparison to the Nd₂O₃ content of the glass samples.

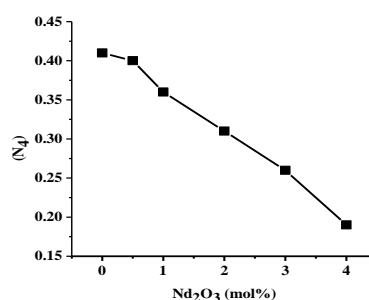


Figure 4: The fraction of the four-coordinated boron atoms, N₄, in comparison to the Nd₂O₃ content of the glass samples.

It is obvious that N₄ drops from 0.42 (at x = 0) to 0.18 (at x = 4). This indicates that the presence of Nd₂O₃ even with limited concentration results even at low concentrations leads to a sharp decrease in the concentration of BO₄ units in the borate network. The N₄ data of Nd₂O₃ free glass agree with previous observations. It was found that the maximum N₄ at about 4 mol% Nd₂O₃ [20]. The decrease in N₄ with increasing Nd₂O₃ implies that NBOs are being generated to maintain charge balance, however, the direct observation of boron's with non-bridging oxygens is challenging in these systems. Two main factors can play the role of decreasing N₄ in presence of even a small concentration from the rare earth oxide ≤ 4 mol%. The first one is referred to the relatively high concentration of the modifier oxide. For example, the number of BO₃ triangles available to be transformed to BO₄ would be increased to reach a specific maximum N₄ at 35- 40 mol% of alkali oxide [21]. On the other hand, more addition of the modifier leads to the creation of NBO in the borate network leading to decreasing N₄.

The second mechanism relates to lowering the rate and concentration of BO_3 triangle units which transformed to BO_4 groups throughout the addition of an extra glass former beside the main glass former oxide (B_2O_3) to the network of the glass [22]. The above two considerations are not satisfied in the investigated glasses, since the relative concentration of the modifier oxide is fixed around 30 mol% which is extremely lower than the concentration which refers to maximum N_4 . In addition, the concentration of the added Nd_2O_3 is very limited (≤ 4 mol%). This leads us to suggest that there is another unusual role for Nd as rare earth which itself plays the role of the sharp reduction in the fraction of tetrahedral boron (N_4).

2. Conclusion

Various techniques have been used to examine the structural characteristics of Neodymium borate glasses that are connected to the role of Nd_2O_3 . The following conclusions might be used to summarize the new features that have been discovered. FTIR and NMR spectroscopy has revealed that Nd_2O_3 in binary borate glasses primarily serves as a glass modifier in the form of Nd_2O_3 units. The predicted ordered Nd-B-Nd connection affects the conversion of triangular BO_3 units into BO_4 tetrahedra and results in a broadening of the spectrum. Rising the overall proportion of all four coordinated units B_4 is strongly linked with increasing Nd_2O_3 concentration, resulting in the creation of more structured structures. It can be seen from the represented data that the intensity characterizing BO_4 units is lower in glasses containing Nd_2O_3 when compared with that of the base glass. In addition, the full width at half maximum (FWHM) of glasses containing Nd is higher than that of Nd_2O_3 free glass. This leads that Nd ions are the main sources for creating broadening in the measured spectra. In glass containing Nd_2O_3 , the relative intensity of the peak owing to the BO_4 units reduces when compared to the intensity of the peaks attributable to the BO_3 unit. It indicates that the trace amounts of rare earth oxides (≤ 4 mol%), represented by Nd ions, have been reported to stimulate the modifier oxide to be more active for playing a role of borate back conversion and promote asymmetric units (borate units containing NBO). Then, a few

Nd_2O_3 additions to the borate glasses produce a partial back conversion from BO_4 to BO_3 groups.

4. References

1. Gupta R, Kumar A. (2008). Bioactive materials for biomedical applications using sol-gel technology. *Biomed Mater* **3(3)**: 034005
2. Jones JR. (2013). Review of bioactive glass: from Hench to hybrids. *Acta Biomater* **9(1)**:4457–4486
3. Mohamed N Rahaman, Delbert E Day, B Sonny Bal, Qiang Fu, Steven B Jung, Lynda F Bonewald, Antoni P Tomsia. (2011). Bioactive glass in tissue engineering. *Acta Biomater* **7(6)**:2355–2373
4. El-Damrawi, G., Doweidar, H., Kamal, H., & Hassan, A. (2018). Characterization of some bioactive glasses and glass-ceramics prepared by a hydrothermal method. *Silicon*, **10(2)**, 395-402
5. El-Damrawi G, Kamal H, Doweidar H, Dawood AE. (2016). Microstructure and in vitro bioactivity of metal substituted hydroxyapatite. *Br J Appl Sci Technol* **15(2)**:1–12
6. Ferraz M, Monteiro F, Manuel C. Hydroxyapatite nanoparticles: a review of preparation, *Journal of Applied Biomaterials & Functional Materials*, **2**, (2) [https:// doi.org/10.1177/2280800004002002](https://doi.org/10.1177/2280800004002002).
7. El Damrawi, G., Hassan, A.K., Kamal, H., Aboelez, M. and Labeeb, S (2016). Structural Investigations on $\text{Na}_2\text{O-CaO-V}_2\text{O}_5\text{-SiO}_2$ Bioglass Ceramics. *British Journal of Applied Science & Technology*, **16**, 1-9 <https://doi.org/10.9734/BJAST/2016/26683>
8. El-Damrawi, G., Hassan, A.K., Ehmead, S. and El Shahawy, A. (2017). Advantage of NMR and FTIR Spectroscopy to Determine Structure Role of CeO_2 in Complicated Borosilicate Glasses: New Approach. *New Journal of Glass and Ceramics*, **7**, 22-33 <https://doi.org/10.4236/njgc.2017.72003>
9. Fanshu Xia, Siyuan Liu, Yang Wang, Jiayi Mao, Xinxi Li, Yiqun Wang & Guorong Chen. (2015). Fast and intense green emission of Tb^{3+} in borosilicate glass modified by Cu^+ . *Scientific Reports*, | **5**:15387
10. Doweidar, H., El-Damrawi, G. and Al-Zaibani, M. (2013). Distribution of Species in $\text{Na}_2\text{O-CaO-B}_2\text{O}_3$ Glasses as Probed by FTIR. *Vibrational Spectroscopy*, **68**, 91-95 <https://doi.org/10.1016/j.vibspec.2013.05.015>
11. Maniu, D., Ardelean, I., Iliescu, T., Cinta, S., & Cozar, O. (1997) Raman spectroscopic investigations of the oxide glass system (1– x)

- ($3\text{B}_2\text{O}_3 \cdot \text{K}_2\text{O}$) $x\text{MO}$ (MO= V_2O_5 or CuO). *Journal of molecular structure*, **410**, 291-294.
12. Kashif, I., Abd El-Maboud, A., & Ratep, A. (2014). Effect of Nd_2O_3 addition on structure and characterization of lead bismuth borate glass. *Results in Physics*, **4**, 1-5
 13. Pisarski, W. A., Goryczka, T., Wodecka-Duś, B., Płońska, M., & Pisarska, J. Structure and (2005) properties of rare earth-doped lead borate glasses. *Materials Science and Engineering: B*, **122(2)**, 94-99
 14. El-Damrawi, G., Gharghar, F., Ramadan, R. and Aboelez, M. ^{11}B NMR (2016) Spectroscopy of Lead Borate Glasses: Additive Effect of Cerium Oxide. *New Journal of Glass and Ceramics*, **6**, 57-63. [http://dx. doi.org/ 10.4236/njgc.2016.64007](http://dx.doi.org/10.4236/njgc.2016.64007)
 15. Doweidar, H., Gohar, I.A., Megahed, A.A. and El-Damrawi, G.. Structure-Transport (1991). Relationships in Lead Borate Glasses Containing V_2O_7 . *Solid State Ionics*, **46**, 275-281. [http:// dx. doi. org/ 10.1016/ 0167-2738 \(91\) 90226-2](http://dx.doi.org/10.1016/0167-2738(91)90226-2).
 16. Zheng A., Sh Liu, F. Deng, ^{31}P NMR of (2017). Phosphorus Probes as Reliable and practical acidity scales for solid and liquid crystals, *Amer. Chem. Soci.***117**, 12475-12531
 17. El-Damrawi, G., Gharghar, F. and Ramadan, R. Structural Studies on New $\text{CeO}_2 \cdot (50-x)$ $\text{PbO} \cdot 50\text{B}_2\text{O}_3$ (2016). Glasses and Glass Ceramics. *Journal of Non-Crystalline Solids*, **452**, 291-296
 18. ElBatal, F. H., Marzouk, S. Y., Nada, N., & Desouky, S. M.. (2007). Gamma-ray interaction with copper-doped bismuth-borate glasses. *Physica B: Condensed Matter*, **391(1)**, 88-97
 19. Shaalan M.A., Gomaa El-Damrawi, A.K. Hassan, M. Hamed Misbah. Structural (2021). Role of Nd_2O_3 as Dopant Material in Modified Borate Glasses and Glass Ceramics. *Journal of Materials Science: Materials in Electronics* **32**:12348–12357 [https:// doi.org/ 10.1007/ s10854 - 021- 05866 - x](https://doi.org/10.1007/s10854-021-05866-x)
 20. Verhoef AH, Den Hartog HW (1995). Infrared spectroscopy of network and cation dynamics in binary and mixed alkali borate glasses. *J Non Cryst Solids* **182**, 221–234.
 21. Kamitsos EI, Patsis AP, Kararkassides MA, Chryssikos GD. (1990). Infrared reflectance spectra of lithium borate glasses. *J Non-Cryst Solids*; **126**:52