Structural Role of Nd2O3 as Dopant Material in Modified Borate Glasses and Glass Ceramics

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Abstract

Glasses in the system xNd$_2$O$_3$-(46-x)B$_2$O$_3$-27CaO-24.4Na$_2$O-2.6P$_2$O$_5$ (0 ≤ x ≤ 4 mol%) have been prepared via conventional melt quenching technique. X-ray diffraction (XRD) spectra have showed that the amorphous structure is dominant in glasses of Nd$_2$O$_3$ concentrations ≤ 0.5 mol%. But formation of a more ordered structure is confirmed at higher Nd$_2$O$_3$ values. Result based on differential scanning calorimetry (DSC) shows an increase in glass transition temperature ($T_g$) with increasing Nd$_2$O$_3$ at expense of B$_2$O$_3$ contents. Vicker hardness ($H_v$) and density ($D$) are used to correlate the glass structure with its properties. The measured density is found to be increased whereas the molar volume is decreased with increasing Nd$_2$O$_3$ content. The calculated molar volume ($V_m$) and free spaces ($V_f$) are both decreased due to filling process which is suggested to be carried out by Nd$^{3+}$ of larger size than that of B$^{3+}$. Decreasing of $V_m$ and $V_f$ can reflect the increase in bridging bonds in the glass network which in turns results in increasing of both $T_g$ and of the investigated compositions.

1. Introduction

A family of rare earth (RE) elements is considered between the elements of the lanthanide group which shows pronounced biological activity as they are capable of replacing Ca$^{2+}$ in investigated glass matrix [1–2]. Most of the recent studies have concentrated on enhancing the bioactivity of glass materials by the effect of RE ions [3–8]. These advances include the preparation of special glass materials, or the introduction of certain useful elements in the matrix of the simple glass materials [9].

The research interest in the branch of borate glass systems is due to their anomalous behavior. Borate glass has been studied most recently in contrast with other traditional glasses due to its good optical and mechanical properties [8, 10]. Borate glass systems are well known to have a stable structure against ambient humidity, good corrosion resistance in mechanical strength and chemical toughness. Borate oxide glasses are one of the most suitable for doping with RE$^{3+}$ ions among the potential host glasses. [8–14].

Due to its high transparency, low melting point, high thermal stability, different coordination numbers and strong solubility of rare-earth ions, borate glass is an especially suitable optical medium [15, 16]. In addition, RE-doped alkali borate glasses are interesting for the study of the effects of alkali ions, especially around rare-earth ions, on the glass forming network. Depending on the type and concentration of the modifier oxide, the addition of an alkali oxide has a strong effect on boron coordination and structural groups [13,17,18].

In the present work, the properties and structure of some glass ceramics containing Nd$_2$O$_3$ have been investigated in terms of its promising features for biomedical applications due to the electronic configuration of Nd$_2$O$_3$. Although studies of such glasses have continuously been increasing, they still have been poorly studied as biomaterials. Most current research focuses on improvement the bioactivity
of the base glass materials. These improvements include incorporation of some useful elements through the basic glass materials. Also, the present work aimed to introduce Nd$_2$O$_3$ into the glass matrix in order to research the effects of glass composition on the compatibility and strength of the material, due to the bioactivity effects of the rare earth elements.

2. Materials And Methods

2.1 Preparation of glasses

In the present work, glasses in the system xNd$_2$O$_3$-(46-x)B$_2$O$_3$-27CaO-24.4Na$_2$O-2.6 P$_2$O$_5$, ($0 \leq x \leq 4$ mol%) have been prepared via conventional melt quenching method. Materials were obtained from mixtures of reagent grade CaCO$_3$, Na$_2$CO$_3$, H$_3$BO$_3$, Nd$_2$O$_3$ and (NH$_4$)$_2$HPO$_4$ thoroughly mixed and placed in a Pt-Au crucible. The batches were first heat treated from room temperature to 600 °C with a slow heating rate of 2°/min to remove NH$_3$ and H$_2$O and were then melted at 1000-1200 °C during 20-30 min before being quenched by pouring the melt between two metallic plates. Melting time and temperatures were optimized to limit P$_2$O$_5$ volatilization and maintain the overall glass weight losses under 2 %.

2.2 XRD measurements

X-Ray diffraction measurements are carried out with Shimadzu X-ray diffract meter (Dx-30, Metallurgy institute, El Tebbin-Cairo). The peak position and intensity values used to identify the type of material were compared with patterns in the international powder diffraction file (PDF) database complied by joint committee for powder diffraction standards (JCPDS).

2.3 Density measurements

By applying Archimedes principle, the densities of the prepared samples were measured with benzene as the immersion liquid. The density was calculated using the formula:

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_b \quad (1)$$

where, $W_a$ is the weight in air, $W_b$ is the weight in benzene, and $\rho_b$ is the density of benzene.

2.4. Molar volume calculations

The molar volumes ($V_m$) were calculated using the equation that follows:

$$V_m = \frac{M_T}{\rho} \quad (2)$$

in which $V_m$ is molar volume (cm$^3$/mol), $M_T$ is the molecular weight of the glass sample (g/mol) and $\rho$ is the density (g/cm$^3$) of the sample.
2.5 Microhardness

The SHIMADZU-HMV-G20S (Shimadzu, Kyoto, Japan), microhardness tester was employed to determine microhardness number ($H_v$) of the prepared samples at an ambient temperature under a weight of 50 g and a retention period of 15 s. For certainty of the measurement, ten indentations were taken at different points on the surface of each specific sample. The consequential traces of the indentations were captured and after unloading the corresponding length of the indentation imprint diagonals recorded by a high resolution microscope. The microhardness ($H_v$) values were calibrated with the help of the formula:

$$H_v = 1.854 \frac{F}{d^2}$$ (3)

where $H_v$ is Vickers hardness in Hg/mm$^2$, $F$ is the applied force in newton and $d$ is the mean length of the diagonals of the indentation in meters.

3. Results And Discussion

3.1. XRD spectroscopy

The glasses of low Nd$_2$O$_3$ ($x = 0$ and 0.5 mol %) were colorless, transparent and amorphous in nature. The addition of Nd$_2$O$_3$ at expense of B$_2$O$_3$ has been shown to be very effective in enhancing the crystallization of the glasses. Precipitation of the small sized crystals in the main glass network lowers the sample transparency and the glass in such a case is partially devitrified.

The XRD spectra revealed that an amorphous structure is the characteristic feature of the samples containing $\leq 0.5$ mol% Nd$_2$O$_3$. Transformation into a crystalline structure occurred after introducing higher Nd$_2$O$_3$ concentrations. It is shown from figure 1(a, b) that the XRD spectra contains two broad diffraction bands located between 20-30° and 40-55°. Presence of these broaden bands reflects the amorphous structure of the glasses of low Nd$_2$O$_3$ concentration (0 and 0.5 mol%). On the other hand, the glasses of higher Nd$_2$O$_3$ concentrations become relatively opaque due to formation or precipitation of some crystalline species. Presence of sharp and intense diffraction line plectra in glasses of more Nd$_2$O$_3$ content figure 1(c, d, e) can be correlated to formation of the more ordered crystalline phases in the matrix of the investigated materials.

Comparisons between X-ray sharp diffraction line spectra of the studied materials with that of Ca$_3$(PO$_4$)$_2$, (CaB$_4$O$_7$) and (NdBO$_3$)) crystals were made. It is concluded from the comparison that calcium phosphate, calcium borate and Nd-borate crystalline species are the most formed species. It was found that metaborate (CaB$_2$O$_4$) nanoparticles and tetraborate (CaB$_4$O$_7$) nanoparticles are the main crystalline phases. In addition, crystalline apatite (Ca$_3$(PO$_4$)$_2$) structure is well formed also by the effect of Nd$_2$O$_3$ addition.
The diffraction peaks observed at 2 theta values of 23°, 26°, 31.8°, 41.2°, 47°, 48° are belong to calcium tetraborate [ICDD PDF 83-2025]. The XRD peaks at 2 theta values of 23.3°, 24.8°, 28.3°, 32°, 47° matching with the (111), (210), (220) and (022) the rhombic structure of calcium meta-borate [ICDD PDF 32-0155].

Figure 2 represents the change of the determined crystallinity with increasing Nd$_2$O$_3$ concentration. Then from the figures 1 and 2 one may expect that the crystallization process is offered mainly by effect of Nd$_2$O$_3$, since the material containing even limited addition of Nd$_2$O$_3$ (> 0.5 mol%) is crystallized. The number of diffraction lines in glasses of 1, 3 and 4 mol% Nd$_2$O$_3$ is the same but change in intensities is the most observed parameter. This means that the types of the well-formed crystalline phases are the same but the content of the separated phases increases with increasing Nd$_2$O$_3$ concentrations. These modifications are summarized in figure 2, which reflects a change in the structure throughout changes of crystallinity in glass. It can be seen from this figure that with increasing Nd$_2$O$_3$ concentration, the crystallinity increases to reach its saturated values in the region between 3 and 4 mol%. This interpretation may account on the presence of several diffraction lines in spectra of glasses modified by more than 0.5 mol% Nd$_2$O$_3$ (spectra c, d, e). Some of the well-formed crystalline phases, such as crystalline apatite (calcium phosphate crystals), are categorized as bioactive phases that are useful for the material to be used in the field of biodental and bioactive use [19-26].

There are two parameters that can play a role in improving the process of crystallization in the glasses being tested. The first is the replacement of B$_2$O$_3$ with Nd$_2$O$_3$, as mentioned above. Secondly, the thermal heat treatment process (THT) is alternatively applied also to improve the crystallization behavior. The latter can be applied on sample containing 4 mol% Nd$_2$O$_3$ which characterized with its higher crystallinity in comparison with composition of lower Nd$_2$O$_3$. The temperature at which THT process can be considered can be extracted from DSC curves.

### 3.2 DSC, thermal treatments, glass transition temperature and Vicker hardness

The maximum crystallinity is found in composition of 4 mol% Nd$_2$O$_3$ under the effect of glass composition. To assure the stability of the well-formed crystals, the sample of 4 mol% Nd$_2$O$_3$ is also investigated under the effect of thermal treated at a specific temperature based on differential scanning ceilometer (DSC) data. As can be shown from figure 3, the DSC curve clearly shows one endothermic peak and one exothermic peak. The endothermic peak corresponds to the glass transition (T$_g$) while the exothermic peak indicates the crystallization point of the glass (T$_c$). The glass transition temperature (T$_g$) as well as crystallization temperature (T$_c$) are estimated by the slope intercept method. The nature of the DSC curves is typical for other glass compositions. The crystallization temperature was found to be around 800°C. The glass is therefore thermally treated at this temperature. It can be shown from figure 4 that the state of crystallization didn’t changes with thermal heat treatment, since XRD spectra of the as prepared and treated samples are nearly not differed. This means that the glass ceramic of 4 mol% Nd$_2$O$_3$ is the most recommended composition containing the maximum concentration of crystals.
The thermal analysis of the glasses was carried out because any change in the coordinating number of atom-forming networks or in the formation of non-bridging oxygen (NBO) or bridging bonds (BB) can simply be expressed by the change of \( T_g \) with the composition. The variation of \( T_g \) with compositions is shown in figure 5. It can be seen that with the rise of \( \text{Nd}_2\text{O}_3 \) content, which is the network intermediate here, \( T_g \) increases monotonically. It is documented that with the increase of bridging bonds in the main borate glass network, \( T_g \) and crystallization temperature \( T_c \) are generally increased [20, 27-30]. It is believed that \( T_g \) depends on the strength of chemical bonds in the structure. \( \text{Nd}_2\text{O}_3 \) in general, plays the role of a network intermediate which has been consumed to increase the bonds between different structural units with the increase of its content in the glass system. Increase of bridging oxygen indicates the increase in the strength of chemical bonds, which in turn increases both \( T_g \) as shown in figure 5.

### 3.3 Density, molar volume, free volume and packing density

It was found that the density of glass samples increases with increasing \( \text{Nd}_2\text{O}_3 \) concentration as shown in figure 6. This is due to the higher molecular weight of \( \text{Nd}_2\text{O}_3 \) (336.4822 g/mol) than the host structures of the glass samples (\( \text{B}_2\text{O}_3 \) is 69.6202 g/mol) [19-22]. Therefore, the molar volume (\( M_v \)) shows a reverse behavior to density as shown in figure 6. The \( M_v \) is the parameter that describes the volume occupied by the unit mass of a glass plus the free volume (\( V_f \)) surrounded the structural unit forming the network of the glass. In general, the unit mass is increased upon increasing \( \text{Nd}_2\text{O}_3 \) at the expense of \( \text{B}_2\text{O}_3 \). In addition, the free spaces (\( V_f \)) associated with borate or NdO\(_4\) units is decreased as a result of its occupation with \( \text{Nd}^{3+} \) ions which is of larger size than that of \( \text{B}^{3+} \). Then, substitution of \( \text{B}_2\text{O}_3 \) with \( \text{Nd}_2\text{O}_3 \) is therefore decreases the free volume with a manner which depends on the ionic radius of the glass modifier oxide [23]. As a result, increase of density and decrease of free volumes (\( V_f \)) are the two factors played the role of decreasing (\( M_v \)) of the investigated glasses. The decrease of the molar volume is due to adding \( \text{Nd}^{3+} \) of larger ionic radius (1.123 Å) into interstitial of host structure as the ionic radius of \( \text{B}^3 \) is (0.400 Å) lead to reducing the free spaces formed around the structural units. Therefore, substitution of \( \text{B}_2\text{O}_3 \) with \( \text{Nd}_2\text{O}_3 \) decreases the molar volume via reducing the concentration of free spaces which have been filled with \( \text{Nd}^{3+} \) ions of larges sizes. Decreasing of open spaces with increasing \( \text{Nd}_2\text{O}_3 \) means that the packing density should be increased with decreasing the total molar volume of the glass samples [22-24]. Then increasing \( P_d \) (density) and decreasing void spaces in the glass network are considered as the main causes in increasing \( T_g \) and \( H_v \) of the investigating samples.

### 4. Conclusions

\( \text{Nd}_2\text{O}_3 \) containing \( \text{B}_2\text{O}_3\)-\text{CaO}-\text{Na}_2\text{O}-\text{P}_2\text{O}_5 \) glasses were prepared by conventional melt-quenching technique. The amorphous or crystalline nature of these samples was confirmed by X-ray diffraction (XRD). The calculated crystallinity increases with increasing \( \text{Nd}_2\text{O}_3 \) contents. The measured density, the glass transition temperature \( T_g \) and Vicker hardness number are also increased upon \( \text{Nd}_2\text{O}_3 \) addition. The calculated molar volume \( V_m \) and free spaces are both decreased due to filling process by \( \text{Nd}^{3+} \) of larger...
size than that of B$^{3+}$. Decreasing of $V_m$ and $V_f$ are the main reasons for increasing the packing density in the glass network.

**Declarations**

**Ethical Statement**

Authors declare that we have no conflict of interest. We are agreed upon all the Ethical Rules applicable for this journal.

**Declaration of Competing Interest (No funding)**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Consent for Publication**

Authors asgreed to publish this work in SILICOn . This declaration ensures that the Publisher has the Author's permission to publish this work.

**Availability of data and materials**

As authors, we are increasingly make our research data available and Data will be made available on request.

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