Influence of La-impurities and plasma treatment on the structural and optical properties of some bismuth calcium borate glasses

N. M. Ebrahem1 · Hosam M. Gomaa2 · H. A. Saudi1 · R. M. El Shazly3 · W. M. El-Meligy1 · F. M. El-Hossary4

Received: 29 May 2021 / Accepted: 16 October 2021 / Published online: 25 October 2021 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

Abstract
This research work aims to the estimation of the effect of the addition of La2O3, by different amounts in wt. %, to the matrix of the bismuth calcium borate glass. The fast cooling procedure was used to prepare the suggested compositions. XRD was used to inspecting the internal structural phases of the prepared samples, where XRD patterns confirmed the amorphous natures of all samples. It was found that the La-additives act to increase the glass density, micro hardness, and optical absorption. While the plasma treatment using N2 acted to reduce both the relative intensity of XRD and the optical absorption.

Keywords Lanthanum · Glass · RF Plasma · Hardness · Elastic deformation · Optical measurements

1 Introduction

Though the last few decades, different glass systems doped with rare earth elements has great importance because of their special properties and potential applications in solid-state lasers, optical amplifiers and three-dimensional displays, planar waveguide, optoelectronic devices such as short wavelength lasers, sensors and, high-density frequency domain optical data storage (Chimalawong and Kirdsiri 2012; Parandamaiah et al. 2015). By a short survey on the applications of lanthanum-based materials, it can be concluded that such materials have a widespread in optical devices. For example, Lanthanum is used in equipment such as color televisions, fluorescent lamps, energy-saving lamps, and glasses. La2O3 is used in the glasses fabrication to improve their optical properties for infrared adsorbing-glasses that used to fabrication the lenses of the camera and telescopes. Also,
Lanthanum is used in large quantities in nickel-metal hydride rechargeable batteries. By the way, in 1974 the French researchers at the University of Rennes had discovered types of lanthanum-based fluoride glasses called ZBLAN, which is composed of zirconium, barium, lanthanum, aluminum, and sodium. This glass showed potential applications as an optical fiber material that can be used in fabrication-processes in communications tools and medical devices (Gong and Krishnan 2019). Bismuth oxide based glasses have much interest because of their premium optical properties which make them a good applicant in the range of glass ceramics, reflecting windows, layers for optical and electronic devices, third order optical nonlinear materials and other photonic devices Editor (Bale and Rahman 2012). Bi$_2$O$_3$ is known as a heavy metal oxide and the glass containing Bi$_2$O$_3$ have minimum rates of crystallization, higher density, great optical basicity, high optical susceptibility, high refractive index, high polarizability and nontoxicity (Lakshminarayana et al. 2017; Rani et al. 2015). Also, the boron-oxygen groups frequently participate to nonlinear optical effects along with alkaline earth cations, the thing that makes them good candidates for nonlinear and optoelectronic applications (Yasaka et al. 2014). Glasses doped with rare earth ions can be used as luminescence materials due to high emission efficiencies alike 4f-4f and 4f-5d electronic transitions in the RE$^{3+}$. Because of shielding imparts of the outward 5S and 5P orbitals on the 4f electrons, the 4f-4f transition gives a particularly sharp fluorescence patterns from the ultra violet to the infra-red region (Uma et al. 2016; Kaewjjang and Maghanemi 2014). Also, material surface modification is a very important issue in industrial applications, which always adjust the output quality with processing costs. For example, various surface plasma treatment techniques are applied to restore mechanical performance and to increase the life of materials for use in different applications (Chakrabarti and Das 2007). Radio frequency (rf) plasma with nitrogen gaseous used for surface modification alter the surface characteristics of materials while maintaining the bulk properties. (rf) plasma nitriding is superior and most developed method having a lot of advantages over the other methods. In an (rf) plasma process, nitrogen is one of the active elements which improve the corrosion resistance and wear of alloys J. Non- crystalline solids (El- Hossary et al. 2014). Plasma treatment modifies the surface properties of materials resulting in changes extending from a few nanometers to ~ 10 micro meters without affecting the bulk property of the material, a diversity of chemical structures can be generated also surface chemistry can be controlled. Plasma treatment affords control over hardness, chemical inertness and wettability. Plasma modified materials exhibit amended response characteristics when in connect with biological environment (Kaewkhao et al. 2016). A. M. Shams. et al. studied the enhancement mechanical properties of YBiBO$_3$ glasses using La$_2$O$_3$. This study found that the increment of La$_2$O$_3$ increased the bridging oxygen atoms, the cross-link density and the number of coordination (Issa et al. 2020). F. EL-Hossary et al. investigated the effect of (rf) plasma time on the carbonitriding treatment of titanium. They examined the effects of different plasma-processing times on mechanical Properties and the microstructure of plasma-carbonitrided Ti. The surface micro hardness and the thickness of the compound layer of carbonitrided Ti increment with the plasma processing time (Raaif and El-Hossary 2007). Studying the optical properties of oxide glasses gives us a good sight about their internal electronic environments. For profitable comparison between different optical parameters of the studied glass samples, the transmittance $T$ and the absorption $A$ were measured and plotted. One of the most important optical parameters is the optical absorption coefficient which gives useful information about the electronic
Influence of La-impurities and plasma treatment on the structural...  Page 3 of 11

state in depressed wavelength and high energy region. It also helps in determining the type of absorption process identified and other obtained linear optical parameters as well El-Hossary et al. (2014), Kaklamani et al. (2013). The aim of the present work is to prepare and characterize a new class of superior vitreous materials based on bismuth borate glasses co-doped with lanthanum oxide, to study optical properties and to investigate mechanical hardness of the glass system before and after plasma treatment.

2 Experimental details

Glass samples were prepared by melt quenching technique with chemical compositions, xLa$_2$O$_3$-0.4Bi$_2$O$_3$-0.4B$_2$O$_3$-0.2CaO where x = 0, 0.02, 0.04, 0.06, and 0.08. After mixed all different chemicals manually in a porcelain crucible in batches of 30 g, resulting homogeneous mixture was heated at 1100 °C for 2 h. Then quickly poured, annealed at 300 °C for 2 h and then quenched to room temperature to remove any internal stress and excessive OH$^-$ in the mixture. Circular samples (diameter = 3 cm) with thickness 4 mm were polished and cleaned with distilled water and ethanol. Then, these samples were nitrided using radiofrequency (rf) plasma inductively coupled operated in continued mode. Briefly the (rf) plasma was included of a quartz reactor tube that evacuated to base pressure of 2 × 10$^{-2}$ mbar. (100%N$_2$) gas was introduced to the glass samples for 20 min. The plasma power input was fixed at 200 Watts and an rf power generator adjusted at 13.65 MHz. After plasma-treatment, these samples were stored under vacuum (8.5 × 10$^{-2}$ mbar). X-ray diffraction (XRD) measurements were carried out using Japan diffractometer employing Cu-Kα radiation. A Vicker’s micro-hardness measurements were made for the surfaces using a standard micro-hardness tester (Shimadzu Corporation HMV$^{-2}$, 50–60 HZ, Japan) for specimen indentation with a contact load of 300 g for 10 s before and after plasma treatment. Finally the optical spectra were recorded using Jasco Spectrometer in the region from 190 to 2500 nm with a resolution of 4 nm.

3 Result and discussion

3.1 Structural characterization and phase identification

Figure 1 illustrates the normalized x-ray diffraction patterns for x = 0, 0.02, 0.04, 0.06, and 0.08. Those patterns do not show any sharp peak, only a broad hump that characterizes the amorphous solids. It’s clear that the relative Intensity of the observable hump increase as the La-impurities increase. Like this behavior may affect the optical parameters especially the value of the extinction coefficient, also it may indicate somehow conversion from the short-range order phase to the long-range order one, which may mean an increase in the density value as the La-impurities increase. Figure 2 shows the influence of the Nitrogen plasma, (100% N$_2$), treatment on the relative Intensity of XRD, for sample x = 0.08 as a representative sample; where the relative intensity decreased after plasma treatment, which may mean relaxation action similar to that of the annealing processes. To clarify the validity of the previous conclusions, the density was measured for each sample, and then plotted in Fig. 3 for comparison, where the density is very sensitive to any changes that may occur in the internal structural of a solid material. Figure 3 confirmed the results obtained from XRD-analysis, where the density of the glass increased when La-impurities was increased.
Such increase in density values may be attributed to the increase of the molecular weight values when adding lanthanum oxide, which is of high density (6.51 g/cm$^3$).

### 3.2 Micro-hardness

The Vickers micro-hardness values $H_v$ were calculated for all studied samples, before and after the plasma treatment, according to the previous standard formula (Gomaa et al. 2020; Maghanga’ 2018; Halimah et al. 2017; Amer et al. 2019), where $F$ is the indentation load and $d$ is the diagonal length impression, as seen in Fig. 4. It’s clear that the incorporation of La-impurities acted to increase the glass hardness (resistance to elastic deformations) as a result of the strength of the atomic bonds in the glass structure induced by dopants (Gomaa et al. 2020; Maghanga’ 2018; Halimah et al. 2017; Amer et al. 2019).
et al. 2021; Abouhaswa et al. 2021; Saudi and Kameesy 1253; Chris Jofeh Arup 2009). On the other side, the plasma treatment causes the hardness of each sample to increase to twice its value before treatment, which may due to a relaxation process as a result of the plasma energies.

3.3 Optical parameters

Figure 5 depicts both the optical absorbance and the optical transmittance for all studied samples in the range from 400 to 800 nm. Obviously, La-free and La-doped samples have an optical transmission window in the region of visible-near IR, which nominate them from different optoelectronic applications, like the optical switches and or UV-filters. As seen in Fig. 5, the
increase of La-impurities caused an increase in the optical absorbance because of the relative increase in the value of the bulk density by adding La$_2$O$_3$ (6.51 g/cm$^3$) and the increase in the number of oxygen atoms it was found that the plasma treatment causes the optical absorption to decrease to one-half of its value, as seen in Fig. 6 for sample x = 0.08. Such result may suggest the studied glasses as a base of fabrication somehow of optical gas sensors.

Based on the Absorbance and transmittance measurements some optical constants and optoelectronic parameters can be calculated, like the optical absorption coefficient $\alpha$, optical band gaps, extinction coefficient $K$, and the linear refractive index $n$.

$$\alpha = 2.303 \frac{A}{t}$$  \hspace{1cm} (2)

$$\alpha(\lambda) = \frac{B}{E} (E - E_{direct})^{\frac{1}{2}}$$  \hspace{1cm} (3)

Fig. 5 Optical absorbance (thin lines) and transmittance (Bold lines)

Fig. 6 Optical absorbance spectra of x = 0.08 before and after Plasma treatment
Influence of La-impurities and plasma treatment on the structural...

Figure 7 exhibits the absorption coefficient as a function of the wavelength, for all samples, it’s clear that the absorption coefficient decreases as the wavelength increases in the range 450 to 800 nm. Moreover, $\alpha$ increased when $\text{La}_2\text{O}_3$ content increased. Since the absorption coefficient $\alpha$ expresses the amount absorbed optical energy per unit volume of a sample for an optical process (Saudi 2016; Saudy et al. 2013), it can stated that the light penetration length in the studied glasses decreases with the increasing in $\text{La}_2\text{O}_3$ content. Using Tuac’s relations the optical band gaps for direct and indirect allowed transition were obtained, as seen in Figs. 8a, b, respectively. It was found that when La-impurities increase both optical band gap decrease from 2.6 to 2.5 eV for direct allowed transition, and from 2.44 to 2.34 eV for indirect allowed transitions, so it can be stated that the incorporation of La cations on the glass composition modify its electronic structure. Figure 9 shows the extinction coefficient $K = (0.08 \alpha \lambda)$, for all samples, versus the energy of the incident light. The extinction coefficient is defined as the parameter which describes the interaction between the electromagnetic radiation and the solid material (Karabulut and Yuce 2011; Saudi et al. 2015; Elkatlawy et al. 2020), where its value refers to the amplitude of the damping oscillation of the electric field component of the incident light. The K-Value increase as the energy increase from 1.55 eV to 2.47 eV, then starts an increase to reaches its maximum of around 2.9 eV, this result refers that the studied glasses allow radiation to pass through them high energy loss/max decay in the region of 1.55–2.47 eV.

\[
\alpha(\lambda) = \frac{B}{E} \left( E - E_{\text{indirect}} \right)^2
\]

\[
K = \frac{\alpha \lambda}{4\pi}
\]

\[
n = \frac{1 + R}{1 - R} + \sqrt{\frac{4R}{(1 - R)^2 + K^2}}
\]

\[
R = 1 - A - T
\]
The influence of La$_2$O$_3$ content on the K-value, where when La$_2$O$_3$ content increased the K-value increased, in other words the increment of La$_2$O$_3$ increase the optical energy loss. Figure 10 shows the linear refractive index as a function of the wavelength, for all samples, where the values of the refractive index were obtained from the measured transmission according to relation (Kodigala 2010; Hassanien et al. 2020; Hassanien 2019; Mott and Davis 1979; Saddeek et al. 2016; Nahrawy et al. 2018).

4 Conclusion

Some La-free and La-doped bismuth calcium Borate glasses were prepared according to the chemical formula, x (La$_2$O$_3$) 0.4 (Bi$_2$O$_3$) 0.4 (B$_2$O$_3$) 0.2 (CaO) where x = 0, 0.02, 0.04, 0.06, and 0.08, where the fast cooling rate technique was the consider procedure in the preparation process. The results indicated that the mechanical characterization
of a bismuth boron matrix mixed with lanthanum and a small amount of calcium oxide strengthens the vitreous structure, resulting in higher values of hardness. A significant increase in the hardness values was observed after plasma treatment of the glass samples due to the formation of a surface layer of nitride on the surface of the glass. Addition of La$_2$O$_3$ to this studied glass reduced the optical transmittance and increased the absorption coefficient, which means that the length of light penetration decreased with increasing the content of La$_2$O$_3$. The refractive index was calculated and found to increase with the increase in La$_2$O$_3$ contents, while the optical transmission decreased. Plasma treatment of $x = 0.08$ showed improvement in the glass transparency but did not change the absorption edge.
Declarations

Conflict of interest  All the authors declare that there is no conflict of interest.

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