Structural Analysis of PbO-B$_2$O$_3$-ZnO Glasses by High Energy Ball Milling (Attritor)

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Abstract Lead, boron and zinc oxides powder were subjected to the mechanical milling/alloying to study the structural transformation. The process was carried out at room temperature in a high energy ball milling (attritor). The compositional effects on the amorphization process of the ball-milled were investigated. The X-ray Diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) results indicated that zinc oxide was the residual phase after 10 hours of mechanical milling. The compositions play a significant role in powder morphology. The FT-IR sharp peaks are completely disappeared with higher lead oxide concentration. The formed glasses consist of chains of ortho- and penta- borate groups.

1. Introduction

Borate glasses have been used as electro-optic switches, electro-optic modulators, non-linear parametric converters and solid state laser materials by incorporating with heavy metal oxides. All these properties have some effect with respect to the dielectric properties of the medium. Therefore studies of dielectric properties have also got some interests [1]. Lead oxide has many extraordinary properties such as high refractive index, large density, high non-linear optical susceptibility and excellent infrared transmission. Moreover the high density of this glass makes it a candidate for radiation shielding material [2]. Although it is not a glass-forming oxide by itself, it can be incorporated in substantial quantities into the other glass-forming oxide systems such as SiO$_2$, B$_2$O$_3$ and P$_2$O$_5$ [3]. PbO is known to enter PbO–B$_2$O$_3$ glasses as only a modifier oxide up to 15 mol%. In this case PbO is entirely consumed to convert triangular BO$_3$ units into BO$_4$ tetrahedra. Above 15–20 mol% PbO some lead atoms start to be network former in the form of PbO$_4$ units. The fraction of PbO$_4$ units undergoes a monotonic increase when increasing the PbO content up to the glass formation limit. On the other hand, there is an increase in the concentration of BO$_4$ units and thus in the fraction N4 of four coordinated boron atoms up to a maximum around 50mol% PbO [4].

B$_2$O$_3$-based glasses are an important material for the insulation and textile fiberglass. Lead borate oxide glasses are highly transparent in the visible and near infrared regions. Moreover the ZnO-B$_2$O$_3$-PbO glasses have the desired characteristics against irradiation since the naturally occurring stable boron isotope is a good absorber of thermal neutrons and lead is known as a shielding material of gamma rays [5]. It is now well known that lead oxide (PbO) is unique in its influence on the glass structure and is widely used in
glasses because it enhances the resistance against devitrification, improves the chemical durability and lowers the melting temperature [6].

Mechanical milling/alloying (MM/MA) is a potential method for the preparation of various interesting solid-state materials and takes advantage of the perturbation of surface-bonded species by pressure to enhance thermodynamic and kinetic reactions between solids. Over the past decades, MM/MA has been widely developed for the fabrication of a wide range of advanced materials such as supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, amorphous alloys or ceramic materials and intermetallics. Mechanical alloying/milling is a solid state powder processing technique involving cold-welding and fracturing of powder particles. The constituent powder particles are repeatedly fractured and cold welded, so that powder particles with very fine structure can be obtained after milling [7] [8].

Until now, to the best of our knowledge, no detailed investigation has been carried out dealing with the effects of the synthesis parameters on the structure of lead borate zinc by mechanical alloying method. So the purpose of the present work is to study the effect of mechanical milling/alloying on the lead borate zinc with varying compositions.

2. Materials and Samples

Zinc oxide 99.9%, Boron oxide 99% and Lead (II) oxide 99.9% -325 mesh powders (Alfa Asar) were placed into 600 cm³ high energy ball milling attritor, rotating with 500 RPM. The powders were treated with hard steel balls at different milling times with the optimum balls to powder ratio equals to 20:1. The detailed compositions of the samples used in the present study are as follow, table 1:

<table>
<thead>
<tr>
<th>Sample code</th>
<th>PbO</th>
<th>B₂O₃</th>
<th>ZnO</th>
</tr>
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<tbody>
<tr>
<td>PBZ 1</td>
<td>20</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>PBZ 2</td>
<td>30</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>PBZ 3</td>
<td>40</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>PBZ 4</td>
<td>50</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>PBZ 5</td>
<td>60</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>PBZ 6</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

XRD was performed using D5000 powder diffractometer using Cu Kα radiation (wavelength λ = 0.15406 nm) with a nickel filter at 40 kV and 30 mA. The diffractometer was operated within range of 20° < 2θ < 60° with step-time = 1 seconds and step-size = 0.05 degree. Diffraction signal intensity throughout the scan was monitored and processed with DIFFRACplus software. Topas 2.1 Profile fit software was used to extract the peak parameters and the Pseudo Voigt function was used to model the peak shape. The as-received lead oxide was matched with ICDD (JCPDS) standard cards, (65-0129) orthorhombic phase with space group Pbcm(57) and (85-1289) tetragonal phase with space group P4/nmm(129). The zinc oxide powder was matched with card number 65-4311, while as-starting boron oxide was in amorphous state, figure 1.

3. Results and Discussion

The nature of the crystalline phases and the microstructure of the materials are the most important factors affecting its technical properties. Figure 2 presents the X-ray diffraction patterns of ball milled PBZ4 powder mixture. The mixture was milled for different periods up to 10 hrs. The XRD pattern of the as received powder shows only sharp peaks corresponding to the starting materials mixture; a mixture of different crystalline structures, two allotropic structures of
lead oxide and zinc oxide ICDD (JCPDS) (65-0129; 85-1289 and 65-4311) and a non-crystalline $\text{B}_2\text{O}_3$ were found as expected. As shown, after 30 minutes of high energy ball milling the lead oxide peaks shows a notable intensity reduction as a result of severe plastic deformation. The diffraction of (111) peak for orthorhombic PbO (29.08° of 2θ) dramatically decreases, whereas the tetragonal $\alpha$-PbO structure and zinc oxide phase stile stable. After ten hours of MM/MA all lead oxide peaks were disappeared and only zinc oxide phase was found. No additional new phases were detected throughout the MM/MA process up to ten hours.

Fig. 2. X-ray diffraction patterns of the mechanical milling PBZ4 sample.

![X-ray diffraction patterns of the mechanical milling PBZ4 sample.](image)

Fig. 3. X-ray diffraction patterns of the 10 hours mechanically milled sample.

![X-ray diffraction patterns of the 10 hours mechanically milled sample.](image)

The average grain size and the internal strain of lead oxide were calculated from the XRD patterns by the Hall–Williamson method [9]. After two hours of milling the crystallite size and micro-strain was 129.4 nm and 0.0549, while the five hours milled sample was 64.7 nm and 0.0516 respectively. The excessive cold working of the powder during mechanical milling leads to the formation of high density of defects that could hold responsible for the observed high strain in the sample.

According to XRD patterns shown in figure 3, increasing lead oxide content more than 40wt.%, up to PBZ3, a complete disappearance of all peaks related to lead oxide phases. As shown in XRD patterns, all higher lead oxide content contained the evidence of ZnO nanocrystalline peaks superimposed onto a broad amorphous background. Although continued milling could change the amounts of amorphous phases, this paper will focus on the comparison between the effects of different compositions after 10 hrs of ball milling. Although the same amount of ZnO was added, the crystalline peaks were of different intensities for the different compositions, indicating that there were different amounts of amorphous phase present in each composition.
As reported in [10], the amorphization process starts when the powders have experienced a certain number of critical loading events which depends on the impact energy. The unusual reactivity observed has been ascribed to the far-from-equilibrium working conditions, resulting in severe plastic deformations and local excited states. After ten hours of MM/MA the XRD pattern shows the partially amorphous nature of the samples. Increasing milling energy could produce a complete amorphous phase [7] [11]. It is reported that [12], lead borate glasses have a low melting temperatures and wide glass formation region, while zinc oxide shows a higher melting point temperature. This could be the main factor that affecting amorphization process due to impact energy. Also, the free energy due to lattice deformation plays a significant role in glass formability.

Figure 4 shows the macrostructure of the samples, indicating the colour change associated with 10 hours of mechanical milling. The morphology of the samples was investigated by SEM to reveal the particle size details and the morphological changes after mechanical milling. SEM micrograph of PBZ1 sample consists of laminar or plate like structure, fig. 5a. With increasing lead oxide content the laminar structure decreases and nearly not found with PBZ3. The PBZ4 and PBZ5 powder particles were fine irregular in shape with different sizes. Due to cold welding of the milled powder during mechanical milling, the large agglomerates are composed of several smaller grains. Sample PBZ6 shows fine particles and fibre like structure due to local melting through the mechanical milling/alloying process.
Glasses containing heavy metal oxide have attracted the attention of several workers in recent years for their excellent infrared transmission compared with conventional glasses [13]. Figure 6 shows infrared transmission spectra in the 400 – 4000 cm⁻¹ region of 10 hours mechanically milled powder. It is clear from figure 6 that, spectra of PBZ1 and PBZ2 specimens are nearly similar, having broad bands around 3700-2800 and 1600-1300 while at 700-870 cm⁻¹ range two bands overlapped. Sharp intense bands was observed at 2262, 1193, 646 and 547 cm⁻¹. Weak bands found at, 2513, 2360 and 883 cm⁻¹. For the PBZ3 sample, weak bands nearly disappeared and the intensity sharper decreases. With PBZ4 to PBZ6, weak band was observed at 1638 cm⁻¹ while other bands nearly disappear.

It is reported that [6] [14] [15], three domains could be separated in the infrared spectra of the borate glasses: the absorption wave number profile in 400 - 800 cm⁻¹ range is assigned to the bending vibrations of various borate segments, PbO bond vibrations; the medium absorption placed between 800 and 1200 cm⁻¹ is due to the B-O asymmetric stretching of tetrahedral BO₄ units; strong absorption bands that appeared in the 1200 - 1600 cm⁻¹ range are generated by the stretching vibrations of borate units in which boron atoms are connected to three oxygen (BO₃ units). While [12] shows that, broad band between 1300 and 1600 cm⁻¹ attributed to the stretching vibration of B–O–B in [BO₃] triangles. Also, transmission peak around 1050 cm⁻¹ causes one boron to change from the B3 state to B4 state. With higher content of PbO, the lead ions acting as glass-forming agent and a band around 470 cm has been observed due to PbO₄ vibrations [2] [14]. The absorption band at 470-530 cm⁻¹ is stretching mode of ZnO.
As shown in figure 6, the relative areas of the observed bands were increased with increasing milling time up to 6 hours. It is reported that [2], as the relative area of the 470 cm\(^{-1}\) peak increases, the stretching force of Pb–O bond tend to decrease. So, the bond length of Pb–O increases and may increase the molar volume as a result. The observed infrared transmission peak at 3216 cm\(^{-1}\) region of the glass containing metal oxides replacing parts of sodium oxide is due to the strong hydrogen bonded OH stretching vibrations, and the peak region 1620 cm\(^{-1}\) is due to the H–O–H vibrations of water, OH or B–OH groups. It is reported that [17] [15], the broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples.

It is reported that [18], Infrared absorptions are not infinitely narrow and there are several factors that contribute to the broadening. The collision between molecules is a factor. There is also the broadening of bands due to lifetime of the states involved in the transition. From quantum mechanics, the energy states of the system do not have precisely defined energies and this leads to lifetime broadening. There is a relationship between the lifetime of an excited state and the bandwidth of the absorption band associated with the transition to the excited state, and this is a consequence of the Heisenberg Uncertainty Principle. This relationship demonstrates that the shorter the lifetime of a state, then the less well defined is its energy.

4. Conclusion

- It is possible to obtain nanocrystalline/amorphous phases at room temperature of lead, boron and zinc oxides powders by mechanical alloying.
- Infrared spectroscopy data shows both triangular and tetrahedral borate groups at all compositions.
- With higher lead oxide content PbO\(_4\) vibrational band was observed at ~470 cm\(^{-1}\).
- The morphology of milled powder with 20 to 40 wt.% lead oxide content, was composed of laminar structure while fine particles and large agglomerates were observed with 50 and 60 wt.% PbO samples.
- Fiber like structure was formed after mechanical milling/alloying with 70 wt.% lead oxide content.

References


