



Improving structure and properties of lead phosphate glass through precipitation of few crystals from CeO₂



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Abstract

New lead-cerium phosphate glasses in the system $x\text{CeO}_2(50-x)\text{PbO}-50\text{P}_2\text{O}_5$ were successfully prepared by the melt-quenching process. The amorphous and/or crystalline character of the as prepared compositions were confirmed by both X-ray powder diffraction (XRD) and electron diffraction patterns (EDP) related to transmission electron microscopy (TEM). The surface morphology and the analytical amounts of glasses constituents have been studied by scanning electron microscopy (SEM) equipped with Energy-dispersive X-ray spectroscopy (EDX) apparatus. It was found that P_2O_5 as a host network can dissolve extremely high concentration from CeO_2 without crystallization of the host glass network. Some cerium phosphate (CeP_2O_7) clusters can be formed and precipitated in the main amorphous network. Formation of such type of clusters has an effective influence on enhancing material structure and properties, since the hardness number of the studied materials is highly enhanced. The chemical shift ^{31}P NMR of glasses is improved toward increasing shielding process by the effect of CeO_2 addition.

Key words: cerium oxide, morphology precipitated, hardness, shielding process.

1. Introduction

It was reported previously that some specific types of rare earth oxides such as CeO_2 and Nd_2O_3 have dominant influences on the structure, mechanical and magnetic properties of glasses and glass ceramics [1-5]. A number of previous studies have been performed to shed some light on the practical and manufactured uses of glasses containing cerium oxide [6]. In addition, cerium oxide, which has been reported to be used as decolorizing glass and eye protective glasses [6, 7], has been further commercially used since it has been established that cerium has a clear use, depending on its material, as an excellent ultra-violet absorption. Recently, several experimental results have been carried out on cerium silicate [8] and borate glasses [9], suggesting that CeO_2 enters the host glass network as an intermediate, both as a glass modifier and as a former at normal circumstances [1-4,8,9]. Under excessive conditions, such as exposure the glass to irradiation

processes, the irradiated glass becomes unusable for optical applications. Alternatively, CeO_2 can be referred to as Radiation Resistant Glasses (RRG) to preserve their shape and physical characteristics even after exposure to a high dose of nuclear radiation. The function of cerium polyvalent Ce^{4+} and Ce^{3+} gives irradiated glasses good protection from the effects of irradiation. This can be done in ways in which Ce^{3+} captures holes and Ce^{4+} traps electrons created by irradiation effects. As a consequence, recombination between the trapped electron and the capture holes is avoided and the main product is thus permanent defect centers. Cerium oxide (CeO_2) has been used in many types of materials that subjected to irradiation as a stabilizer or sensitizer agent. In order to improve irradiation resistance and luminescence properties, a small doping percentage has been added to certain types of glasses [10-12]. Glasses or glass ceramics that have a superior ability

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to dissolve rare earth (RE) without precipitation are given special attention. This criterion makes glasses very suitable for the production of RE-optical glasses. The addition of even small portions of CeO₂ to glasses contributes to improved structure and physical characteristics. In such situations, both in photovoltaic equipment and in the medical and military fields, glasses may be commonly used.

A variety of studies have been performed on various glass types, including borate, silicate and borosilicate glasses [2, 8, 9]. The structural function of CeO₂ was clearly determined in such glasses. However to our knowledge, it has not studied its function in both binary CeO-P₂O₅ and ternary CeO₂-PbO-P₂O₅. This work is therefore aimed at shedding some light on the various roles played by CeO₂ in changing the phosphate glass network structure and properties.

2. Experimental set-up

The [xCeO₂.(50-x)PbO.50P₂O₅, (0 ≤ x ≤ 40 mol%)] glasses were prepared by melt-quench technique. Reagent grade CeO₂, PbO and NH₄H₂PO₄ crystalline powders were used as raw materials. The powders were mixed in the desired proportions and melted in porcelain crucibles at temperatures ranging from 1250°C to 1320°C, except the sample containing 40 mol% CeO₂, the powder was added part by part to simplify the melting process and the temperature is raised gradually to 1470°C. This processes takes 2 hours from the first addition of the powder in the crucible to obtaining the final melt. The final product was check with both ²⁹Si and ²⁷Al NMR spectroscopy to confirm that there is no any contamination from both silica or alumina as residuals from the crucible. Also chemical analysis by EDEX confirm that the products' are free from any contaminations. The composition of each glass was X-ray diffraction to determine the vitreous states of the prepared samples. The samples were ground into a fine powder at Central Metallurgical Research and Development Institute XRD system with a Cu Kα radiation (λCuKα=0.15406 nm). The 2θ angle scan is changed from 5° to 70° and the time per step of 0.4 seconds.

The spectra were obtained at high external magnetic field 11.747T, at Larmor frequency of 160.47 MHz and spinning rate of 40 MHz. The obtained spectra did not contain any resonance peaks for Al or Si which confirm that there is no any contamination from the crucible during the high temperature melting process.

The Vickers micro-hardness test (H_v) was measured by Vickers Hardness Tester FALCON 500 with a load of 0.3 kg for 13s. The hardness was determined from the mean value of five indentations, after the sample surface was polished at room temperature. Transmission Electron Microscopy (TEM) is a common technique of transmission image

is used to evaluate its morphology more details about the shape and the size of the bulk material. TEM investigations were performed by a JEOL-JEM-2100 (Electron Microscope Unit, Mansoura University) equipped (EDP) with an electron diffraction pattern unit with an electron accelerating voltage of 200 KV.

Surface modification and microstructure of specimens were collected with a Scanning Electron Microscope (SEM) equipped with EDX unit, Mansoura University, using a JEOL-JSM-6510 LV Model, with a magnification up 400,000X. The obtained EDX spectra contains P, Pb, Ce and O only and there is no any peaks for Si or Al elements which assure that there is no any contamination from the crucible.

3. Results and discussions

Glasses have been successfully prepared in the xCeO₂.(50-x)PbO-50P₂O₅ with x reaches to 40 mol%. This compositional range appears wider compared to the compositions reported on the Al₂O₃ or ZnO phosphate glasses [13, 14]. The phenomenon of mixed former effect (between CeO₂ and P₂O₅) is considered as the main reason for obtaining amorphous glasses over wide composition range. Figure 1(a- e) shows the X-ray diffraction (XRD) spectra of as prepared glasses in the ternary forming range. As can be seen from figure 1 that, there is no detectable sharp diffraction peaks for the all investigated compositions (0, 15, 25, 30 and 40 mol% CeO₂). The broad diffraction pattern is only lowered in the glass of 40 mol% CeO₂ which may be considered due to small precipitation of CeP₂O₇ [ASTM Cards File No 30-0164 and ASTM Cards File No 16-0584] and CePb₃P₃O₁₂ [ASTM Cards File No. 42-0407] phases in the main amorphous structure [8,9].

Presence of such polycrystalline phases confirms that few of CeO₂ can simply separate from the main amorphous glass network and accumulated to form polycrystalline clusters from its own. In such situation PbO plays the role of glass modifier but CeO₂ plays a dual role both as a former and modifier [2, 5, 8, 9]. Therefore substitution of PbO with CeO₂ should result in decreasing (NBO) which was formed by the effect of PbO as a modifier in the phosphate network. In addition, some of CeO₄ tetrahedral units as a former species is increased via increasing CeO₂ contents. Decreasing NBO and increasing CeO₄ groups will result in increasing the total bridging bonds in phosphate network and as a consequence increases the shielding process around phosphorus atoms. The phenomenon of mixed former effect (between CeO₂ and P₂O₅) is considered as the main reason for obtaining amorphous glasses over wide composition. This was confirmed from figure 2, since the ³¹P NMR spectra have revealed the formation of an additional resonance peak at about -36 and -42 ppm for glasses of 30 and 40 mol% CeO₂. Presence of

such additional resonances lent support the increasing concentration of the bridging bonds around phosphorus atoms and as a consequence P-O-Ce₄ bonds are constructed. Insertion of cerium in the phosphate network leads to P/Ce reactivity with the formation of Q¹_{1Ce} and Q¹_{2Ce} species, i.e. phosphate connected to one other P and one (or two) Ce atoms.

This feature is also previously observed in potassium aluminophosphate glasses [15, 16].

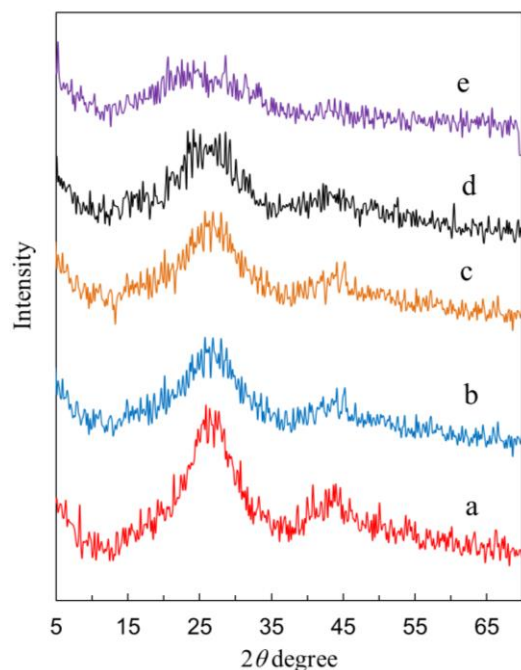


Figure 1. XRD spectra of glasses containing different concentrations from CeO₂, a=0, b=15, c=25, d=30, e=40 CeO₂ mol%.

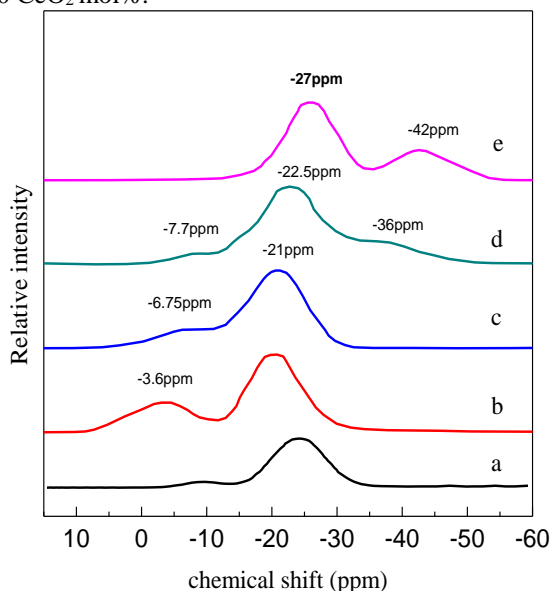


Figure 2. ³¹P NMR spectra of samples containing different CeO₂ concentrations. Where a=0, b=15, c=25, d=30, e=40 CeO₂ mol%.

Formation of the H_v is known as the resistance of the material to both scratching and indentation processes. Formation of Ce-O-P linkages increases the ability of the material to withstand more stress due to indentation process and as a result the hardness number should be increased with increasing CeO₂ contents as is noticed from Figure 3, such linkages is considered as the main reason for increasing the hardness number (H_v). The mixing effect between P and Ce is expected to have impact on morphological shape of the studied glasses.

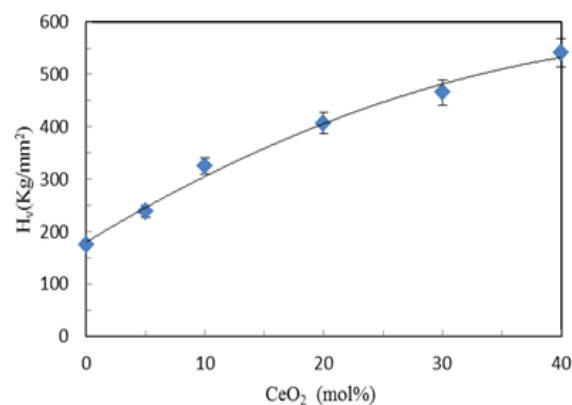


Figure 3. Change of Vickers hardness (H_v) number with increasing CeO₂ concentrations.

To follow the morphological changes occurred in the bulk network, TEM and EDP analysis should be carried out. Specifically, XRD can give a picture about the changes in the average glass network in terms of short or long range ordered structure. But TEM-EDP can follow and scan even small areas from the whole network structure. Then area enriched with CeO₂ which mixed with some of P₂O₅ can be simply determined. From the TEM micrograph, the EDP for specific chosen areas can be particularly and individually studied. Then, using TEM-EDP investigation, each part of the whole network can be checked and studied. Figures 4, 5 and 6 present the change of morphology of some selected glass compositions versus changing CeO₂ concentration (15, 30, and 40 mol% CeO₂).

The importance of the transition electron micrographs in this study is to verify if the well formed and precipitated clusters can be found in crystalline or amorphous form. It can be observed from figures (4-6) that the morphology of the studied materials is differed from one composition to another. In fact, the polycrystalline clusters are clearly obvious particularly at high content from CeO₂ ≥ 30 mol%. The well-formed clusters' are found in its poly-crystalline form, since EDP of accumulated particles have showed a clear spherical units connected together in the form of clustered species which are composed of agglomerated spherical particles. The samples contains 30 and 40 mol% CeO₂ (figures 5 and 6) have a morphology involves

high concentration from agglomerated species which confirms that there is a possible growth mechanism for the formation of agglomerated with increasing CeO_2 contents. The situation is different to high extent in glass of lower CeO_2 content (15 mol%), Figure 4 since accumulated particles take a different morphology, with EDP characterized the non-regular structure. The size of the spheroid clusters are not unique but changes from composition to another that means that the precipitated clusters may contain different concentrations from cerium.

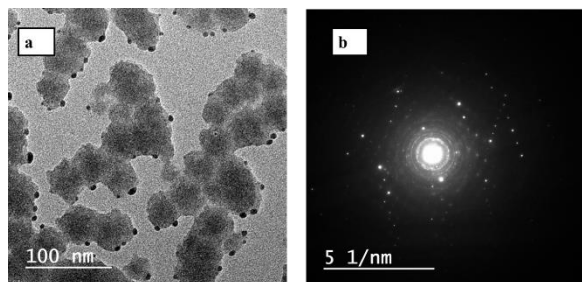


Figure 4. TEM and EDP of sample of 15 mol% CeO_2

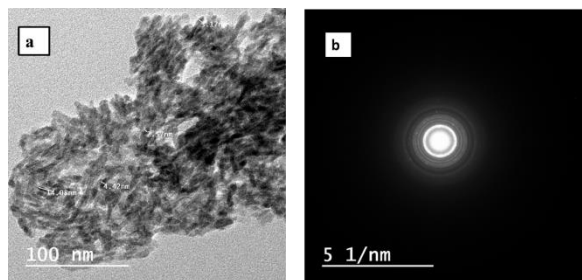


Figure 5. TEM (a) and EDP (b) for sample of 30 mol% CeO_2

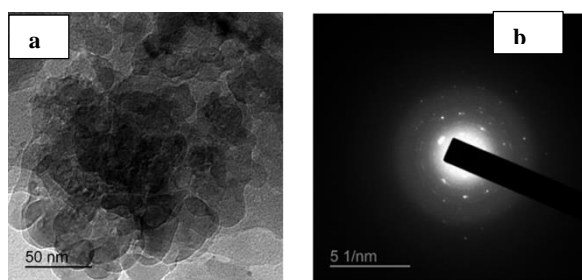


Figure 6. TEM (a) and EDP (b) for sample of 40 mol% CeO .

Figures 7(a and b) show scanning electron micrograph with its EDX spectra which reveals the surface morphology of the investigated sample. The analysis based on TEM-EDX spectroscopy, Figure 8 (b) revealed that the surface is enriched with Ce and O atoms as presented by presence several line spectra characterizing Ce ions. This agrees well with results obtained previously on cerium silicate and borosilicate glasses where the presence of crystalline clusters structure is documented. The atomic percent for P, O and Ce atoms are listed in table 1. The ratio

Ce/P is calculated and it was found to be around 1.15 which confirm the polycrystalline nature of the precipitated clusters [17].

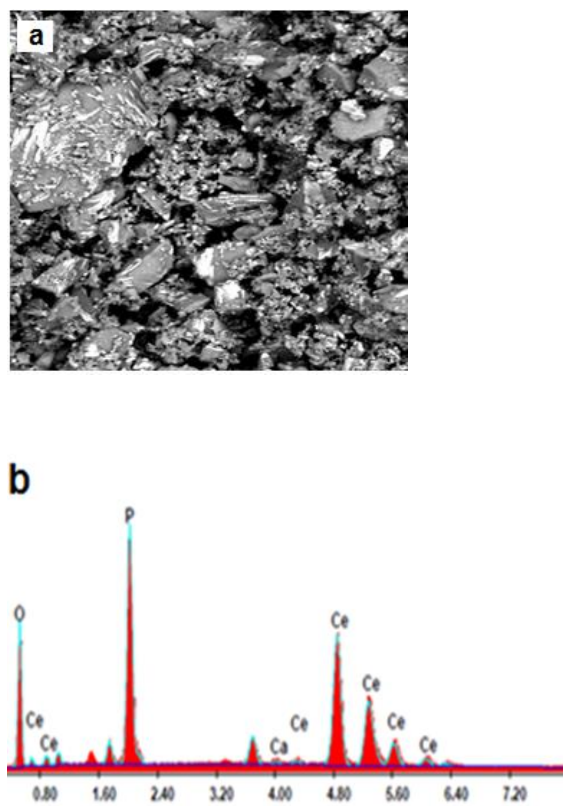


Figure 7. (a) and (b) are SEM and EDX of glass containing 40 mol% CeO_2

Table 1: Data regarding atomic% present in the investigated sample containing 40 mol% CeO_2

Element	Atomic%	KeV
Oxygen (O)	41	4. 0.525
Phosphorous (P)	5. 22	6. 1.82
Cerium (Ce)	7. 37	8. 4.8

4. Conclusion

Properties and structure of glasses in the cerium lead phosphate system were studied by different techniques. From XRD results, the amorphous nature is dominant in all investigated samples. Transmission and scanning electron microscopic analysis reveal that the precipitated clusters are in the form of nano-sphere having grain size in the range of 20–50 nm which is comparable to the crystallite size. Analysis based on EDX spectroscopy has showed that the ratio of cerium to phosphor is around 1.15 which agreed to high extend with that of crystalline CeP_2O_7 clustered species. ^{31}P NMR spectroscopy shows that

concentration of bridging bonds (BO) between cerium and phosphorous atom is increased with increasing CeO₂ content. Increasing of BO in the

phosphate matrix is considered the main reason for increasing hardness number (H_v) of the glass.

6. Conflicts of interest

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

7. References

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