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Structural Role of Cerium Oxide in Lead Silicate Glasses and Glass Ceramics

Gomaa El-Damrawi[1]*, Amal Behairy[2]

[1]Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt
[2]The High Institute of Engineering and Technology, New Damietta, Damietta, Egypt
Email: *gomaaeldamrawi@gmail.com

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Abstract

Silicate glasses and glass ceramics in the system CeO_2-PbO-SiO_2 have been studied as a function of the structure factors R and K. The latter two factors are defined as: R = (CeO_2 + PbO)/SiO_2 and K = (SiO_2/CeO_2) molar ratios. In this glass, PbO is fixed at 50 mol% and CeO_2 increases at the expense of SiO_2. NMR investigations have revealed that increasing R which is accompanied with decreasing K leads to reasonable decrease in the shielding of silicon atoms. The chemical shift (δ) showed an increasing behavior due to increasing non-bridging oxygen atoms (NBO) in silicate network. It is evidenced that NBO in cerium free glass is much lower than that of glasses containing CeO_2. Increasing R is clearly leading to higher chemical shift and higher NBO. This reflects that CeO_2 has an effective structural role, since it would be consumed in all cases as an intermediate oxide. The main portions from CeO_2 and PbO inter as glass modifiers which are consumed to form NBO atoms. A limited portion of CeO_2 acts as glass former which consumed to form tetrahedral cerium containing NBO due to modification by PbO as a modifier oxide. Increasing R = [(CeO_2 + PbO)/SiO_2] from 1 to 2.34 leads to a frequent increase of NBO in the average glass network. FTIR spectroscopy of the glasses showed a clear shift of the main absorbance peak toward the low wavenumber with increasing R which confirms the increasing silicate units containing NBO atoms. XRD of the investigated materials revealed the presence of some nanostructures from cerium silicate crystalline phases. Formation of separated phases containing micro clusters is found to depend on NBO concentration, since NBO can facilitate process of phase separation. Majority of modifier are consumed to form NBO in the glass network and the rest are aggregated or separated to form silicate phase riches with cerium cations. In such case, some of silicon atoms are electrically compensated with both Pb and Ce cations.

Keywords

Cerium in Glasses, Crystalline Clusters, NMR Feature, Glass Ceramics

1. Introduction

Glass ceramics containing PbO are useful to be studied because of their importance in several fields of applications [1] [2] [3] [4] [5]. PbO can easily resist devitrification process and enhances durability of the glasses. Recently, the continuous progress of the materials containing cerium and lead oxide has been requiring immediate attention in viewpoint of both academic [6] [7] and bio-applications [8] [9] [10] [11]. Structural role of PbO and CeO_2 as network intermediates is documented in several types of glasses [3] [4] [5]. This dual role is depending on their content, glass composition and the type of glass. PbO can modify silicate network similar to alkali oxide particularly at low concentration [12] [13]. In such situation, the modifiers are consumed to form silicate units containing NBO atoms [12] [13] [14]. In glasses enriched with lead, PbO_4 species would be formed and directly affects the glass structure through forming Pb-O-Si bonds [5] [13].

Structure of cerium borate and borosilicate glasses has been recently investigated via FTIR and NMR spectroscopy [6] [7] [15] [16] [17]. The obtained results have proved that cerium ions have a role of a network intermediate. Although several investigations have been done to characterize micro-structure of lead silicate glasses, the role of PbO and CeO_2 in studied silicate glass ceramics has not been fully explored. Our aim, in this study is to offer more information on the short range structure of cerium lead silicate glass ceramics in a wide range of composition. In particular, we focus on the short range ordered structure around the Si atoms via ^{29}Si NMR techniques. In addition, the role of cerium ions as an agent for phase separation and crystallization has also to be studied. In this regard, glasses are investigated with SEM, FTIR, XRD spectroscopies and the obtained data is compared with that of base glass, free from CeO_2.

2. Experimental

Glass samples containing different concentrations from CeO_2, PbO and SiO_2 have been prepared by mixing the desired components in silica crucibles. The crucible and its content was transferred into an electric furnace and the temperature is raised gradually to reach the limit suitable for melting. The melting temperature is ranged between 1350˚C -1450˚C, depending on the material composition. The melt was swirled severally to ensure homogeneity and to get bubble free matrix. Finally, the melt was poured between two stainless steel plates. The obtained samples are transferred to another furnace and annealed at 350˚C to reduce internal stress. The samples are obtained in disc like shape of 2 mm thickness and 5 mm radius.

2.1. ^{29}Si NMR Measurements

Fine powdered samples of different compositions have been investigated by using JEOL GSX-500 high-resolution solid state MAS NMR spectrometer of magnetic field of 11.74 T (Mansoura University-EGYPT). Spectra of silicon nuclei were recorded at a frequency of 99.3 MHz. A spinning rate of 7 kHz has been applied by using zirconia sample holder. An electric Pulse of 2.62 µs length and of 30 s recycle delay are used. Several scans (10,000 - 12,000) were acquired to get high resolution NMR spectra.

2.2. X-Ray Diffraction Method

XRD measurements were undertaken using a Bruker D5005 diffractmeter, at 40 kV - 30 mA power. Scans were taken between 10˚ - 70˚ with 0.04˚ increments, 15 - 30 seconds/increment.

2.3. Infrared Spectra (IR)

The FTIR absorption spectra were obtained, by KBr pellets technique, at room temperature in the range 400 - 4000 cm^{-1} using Mattson 5000 FTIR spectrometer with a spectral resolution of 2 cm^{-1}. The glass powder of 0.02 g was mixed with a 0.2 g of KBr and pressed to form a thin disc. At least three samples of each glass were analyzed. The spectrum of each sample is obtained due to collected 20 scans. The obtained spectrum was normalized to the spectrum of blank KBr pellet; *i.e.* a pure KBr spectrum was subtracted from each glass spectrum. In addition, the spectra were corrected to the background and dark currents using two-point baseline correction. Then the spectra were normalized by making the absorption of each spectrum varies between 0 and 1 arbitrary unit. In addition such normalization is necessary to eliminate the concentration effect of the powder sample in the KBr disc.

3. Results and Discussion

NMR spectra of glasses having different R values (1, 1.2. 1.86 and 2.34) are shown in **Figures 1(a)-(d)**. As shown from this figure, there is a remarkable shift in center of the main peak position of ^{29}Si NMR spectra with increasing R, *i.e.* increasing CeO_2 concentrations. The NMR resonance peak centered at −87.3 ppm in cerium free glass (spectrum a) is shifted clearly toward much higher value (−75.4 ppm) in glass of 20 mol% CeO_2 (R = 2.34). Increasing chemical shift of the silicate nuclei with increasing (PbO + CeO_2) concentration is attributed to the modification role of both cerium and lead oxides. In addition, decreasing of SiO_2 concentration as a result of increasing CeO_2 and decreasing K will result in increasing NBO per SiO_2 groups.

In terms of Q^n notation, (Q is silicon atom and n is the number of bridging bonds between Si and oxygen atoms), chemical shift value of base glass (−87.3 ppm) is attributed to mixture of Q^3 and Q^2 (silicate unit containing three and two bridging oxygen atoms as a major portion). In addition, little of Q^2[OPb] configurations may also be present [18] [19]. The main NMR resonances centered at −83.3, −77.8, and −75.4 ppm in glasses of R = 1.2, 1.68 and 2.34 (CeO_2 = 5, 15 and 20 mol% CeO_2) show that silicate network is frequently deshielded by the effect of increasing the modifier oxide concentration. In glass of R = 1.2 and

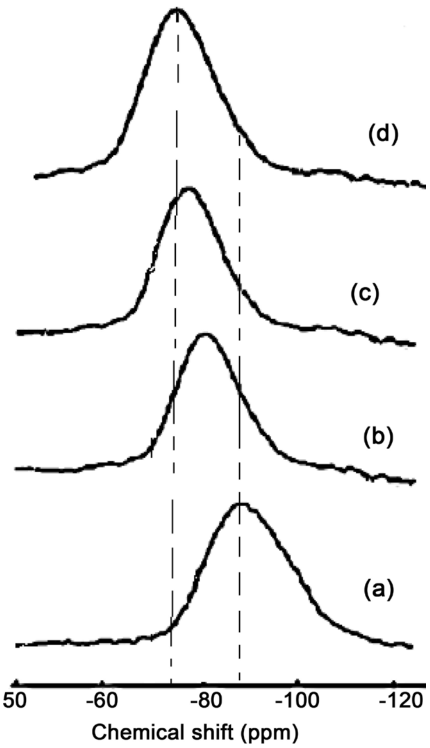


Figure 1. NMR spectra of silicon nuclei of cerium free, R = 1 (a) and of glasses containing 5 and 15 and 20 mol% CeO_2, R = 1.2, 1.86 and 2.34 ((b)-(d), respectively).

containing 5 mol% CeO_2, Q^2 species are the dominant. On the other hand, glasses containing 15 and 20 mol% CeO_2 (R = 1.68 and 2.34) contain Q^1 and Q^0 species respectively. In addition few silicate units containing cerium oxide in the second coordination sphere are suggested to be present.

The concentration of different silicate units (Q^n, $n = 0$ - 4) could be quantitavely obtained by an integration process which is applied to all NMR spectra of silicon nuclei. Figure 2 is presented as an example for the deconvolution process. From spectral analysis, the corresponding percentage of Q^1 = 17%, Q^2 = 55%, Q^3 = 20%, and Q^4 = 8% characterize binary lead silicate glass are simply evidenced. On the other hand, the values of Q^0 = 29%, Q^1 = 44%, Q^2 = 23%, Q^3 = 4% and Q^4 = 0% are obtained values characterize ternary cerium lead silicate glass of R = 1.86. This leads one to confirm that the major portion from CeO_2 and PbO can be introduced as glass modifier, since silicate units contain a mixture from Q^1 and Q^0 types are formed with higher concentration than that of Q^2 and Q^3 in glass free from CeO_2. In such glass, some of Q^n would contain Ce or Pb or both in the second coordination sphere of silicon. As a result, Si-O-Ce and Ce-O-Pb configurations are formed. These linkages are known to deshield the silicon nuclei in comparison with Si-O-Si linkages.

Figure 3 presents the change of the average isotropic chemical shift (δ) of ^{29}Si nuclei upon increasing R. It can be shown from this figure that δ increases (from −87.3 to −75.4 ppm) with increasing R values *i.e.* CeO_2 contents. This change leads to increasing NBO. Beside, some Si-O-Ce or Si-O-Pb are formed at expense

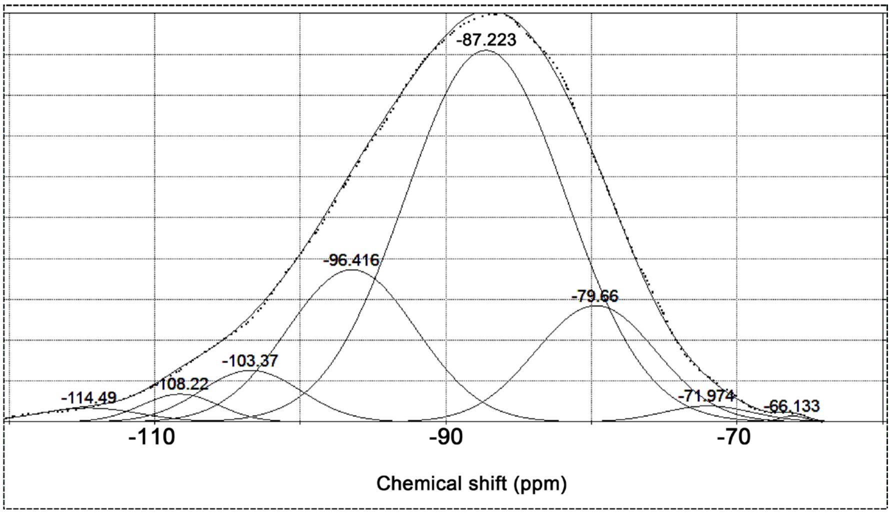


Figure 2. Separation of NMR spectrum of 50PbO-50SiO$_2$ glass into different component bands.

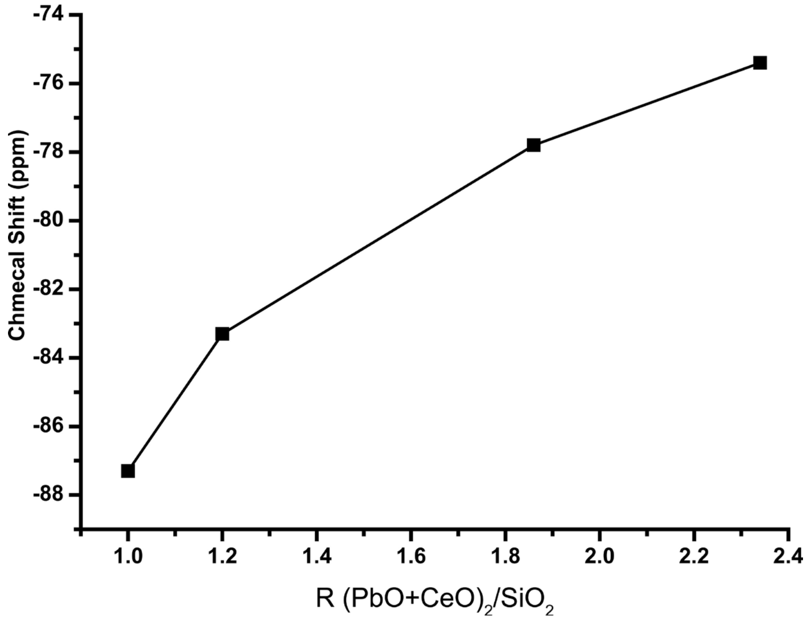


Figure 3. Relation between chemical shift of silicon nuclei and (PbO + CeO$_2$)/SiO$_2$ molar ratio.

of the more stronger Si-O-Si bonds. This assures that cerium oxide inters the glass as an strong glass modifier. In addition, silicate units of the type Ce[2OSi] containing NBO atoms are formed. As a result NBO, Si-O-Ce and Pb-O-Si bonds can deshield silicate units relative to stronger Si-O-Si bond in glasses of higher modification levels. Increasing deshielding upon increasing CeO$_2$ concentration is the main reason of increasing chemical shift with increasing CeO$_2$ concentration as represented in **Figure 3**.

To determine the structural role of CeO$_2$ as an effective modifier, it is useful to compare FTIR spectra of cerium containing glasses with that of free CeO$_2$. As an example, **Figure 4** shows FTIR spectra of cerium free glass and for glass samples

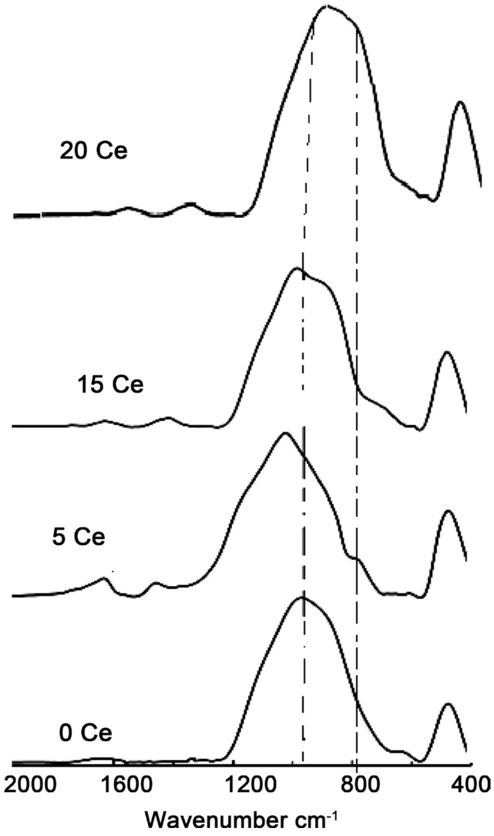


Figure 4. FTIR spectra of cerium free glass (R = 1) and of that containing 5 (R = 1.2) and 15 (R = 1.86) and 20 (R = 2.34) mol%.

contains 5, 15 and 20 mol% CeO_2 as an example. The main band at ca. 960 cm^{-1} in glass free from cerium oxide is shifted progressively towards 860 cm^{-1}, since the activity of Q^2 and Q^1 species containing Ce linkages are present in glass containing 5 and 15 mol%. In addition, week envelope represents Q^0 is appeared at about 770 cm^{-1} in the spectra of glass containing 20 mol%CeO_2. These changes are clearly evidenced in glass of higher CeO_2 oxide (15 and 20 mol% CeO_2), see **Figure 4**. As is shown from this figure, band characterizes Q^0 (at 770 cm^{-1}) [20] [21] [22] [23] is simply resolved which confirms that loos silicate units would be formed in high CeO_2 to SiO_2 molar ratio.

The nature of XRD pattern is known to depend upon the content of NBO in the main glass forming units such as $[Q^nSiO_4]$ and $[Q^n(PO)_3]$ species [7] [8] [9]. In this regard, the relative ratio of modifier to former is high enough to yield pyrosilicate (Q^1, 3NBO) and orthosilicate (Q^0, 4NBO) units which have been documented from NMR results. The nonbridging oxygen should be electrically balanced by positive ions (Ce^{2+}). Accumulation of Ce^{2+} cations around NBO in silicate network will result in producing crystalline clusters of cerium orthosilicate type [7] [8] [9]. These considerations are supported from comparison between XRD pattern of vitreous CeO_2 and of that of cerium silicate glass. Both spectra offer sharp diffraction lines at the same position. The intensity of the diffraction pattern of cerium silicate glass is appeared to be lower than that of the pure CeO_2. This may because the clusters formed from Ce and O ions are distributed within amorphous silicate units which play the role of lowering the total crystallite species. This argument is further supported, since the sharp diffraction peak is superimposed on a broad hump (between 20˚ - 40˚) which is a characteristic feature of the main amorphous glass network. This observation is simply strengthened from XRD spectra of cerium free glass, Figure 5, since amorphous distribution of glass constituents is the dominant.

Glass contains SiO_2 and PbO doesn't greatly affect the process of crystallization or clustring, but the main changes were found to depend on CeO_2. Figure 6 showed that there is a great difference between morphology of glass containing

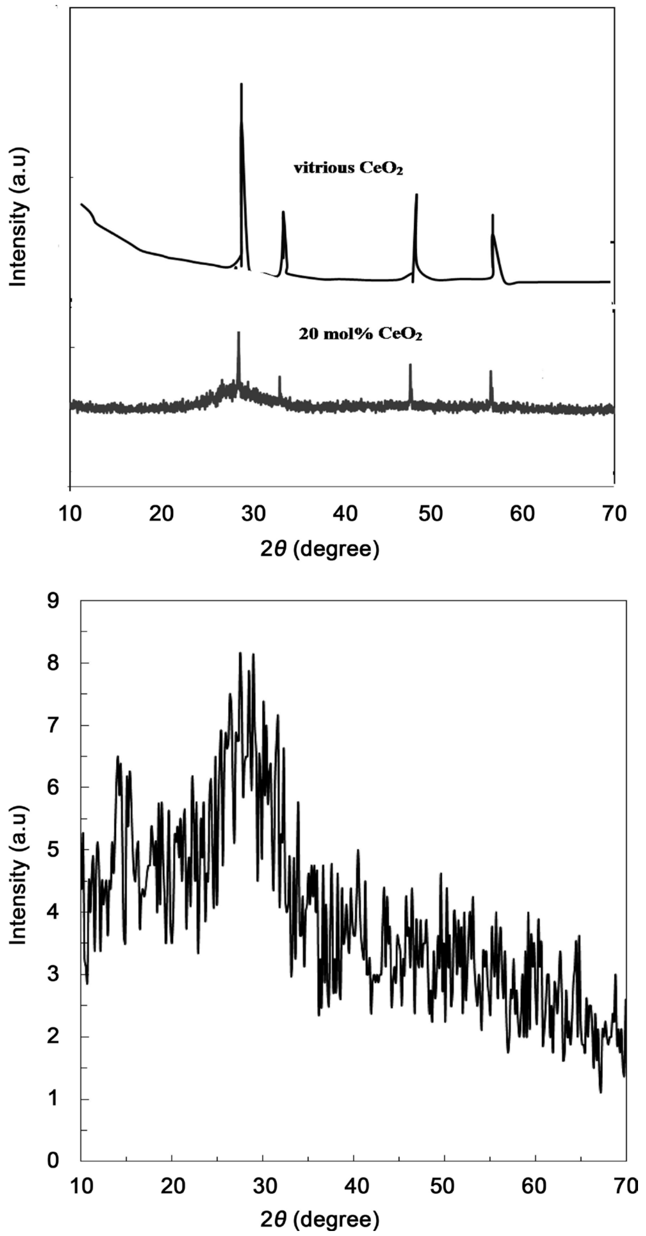
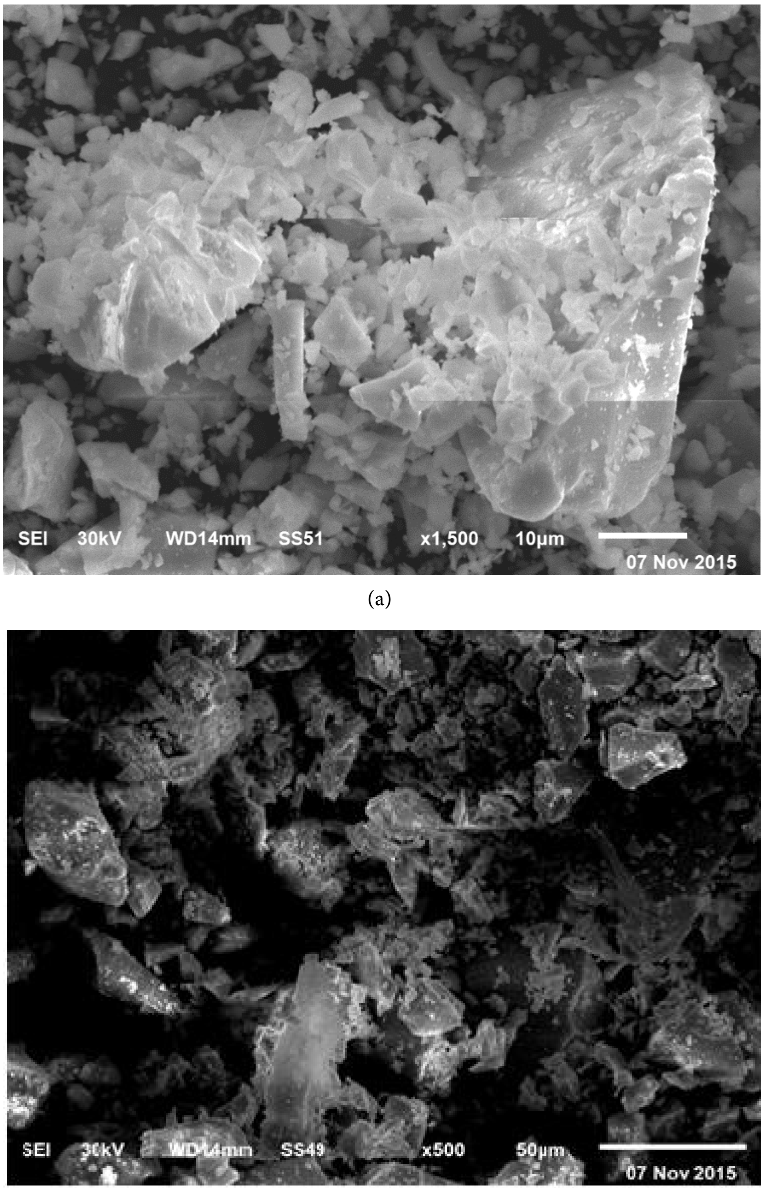


Figure 5. XRD patterns of glass free from CeO_2 (below) and that of glass containing 20 mol% CeO_2 together with vitreous CeO_2.



(a)

(b)

Figure 6. SEM of glass containing 20 mol% CeO_2 (a) and of glass free from CeO_2 (b).

20 mol% CeO_2, **Figure 6(a)** and of cerium free glass, **Figure 6(b)**, since crystalline clusters from cerium silicate phases are clearly resolved in the morphology of sample containing 20 mol% CeO_2.

4. Conclusion

NMR investigation has revealed that increasing of CeO_2 at the expense of SiO_2 at a constant concentration of PbO increases chemical shift (δ) of ^{29}Si nuclei through increasing (NBO) in silicate network. NBO atoms in cerium free glass are much lower than those of glasses containing CeO_2. Higher concentration of CeO_2 leads to higher chemical shift and higher NBO. The structural role of CeO_2 is definitely determined as a modifier oxide in the investigated lead silicate network. FTIR analysis revealed that increasing CeO_2 will result in increasing silicate units which are enriched with NBO atoms The major modifiers are consumed to form NBO in silicate network and the few are aggregated to form crystalline silicate phase riches with cerium oxide. XRD patterns of cerium containing glasses reflect the crystalline order of the glasses which is totally differed from that of cerium free glass, since amorphous character is the dominant.

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