

# Mechanism of Cluster Formation on Cerium Borosilicate Glasses Based on TEM-EDP and SEM-EDEX Investigations

Salma Ahmeed<sup>1</sup>, Gomaa El Damrawi<sup>2\*</sup>

<sup>1</sup>Physics Department, Sirte University, Sirte, Libya

<sup>2</sup>Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

Email: \*gomaeldamrawi@gmail.com

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## Abstract

Cerium oxide has a great capacity to remove nonbridging oxygen atoms (NBO) from the glass network and serves as glass former units. The well formed CeO<sub>4</sub> units played the role of decreasing NBO from the silicate network and cause a reduction in the concentration of tetrahedral boron groups (N<sub>4</sub>). The highest content of NBO in glass of lower CeO<sub>2</sub> (1 mol%) has a dominant role in constructing crystalline clusters in the glass. Higher CeO<sub>2</sub> concentration leads to formation of an amorphous glass network as documented by XRD and TEM-EDP spectra. Coordination of cerium with oxygen atoms gives uniform units of spherical morphology in the pure CeO<sub>2</sub> as well as in cerium rich glass. Clustered species has a great benefit in the field of application, used as a shielding material for ionized radiations.

## Keywords

TEM-EDP, SEM-EDEX, Cluster Formation, Cerium Borosilicate Glasses

## 1. Introduction

The changes in both structure and properties of borosilicate glasses [1] [2] [3] with addition of different types of glass constituents have been shown to depend on the field strength (*i.e.* charge/radius) of the cation introduced. In borosilicate glasses containing alumina or ceria or both, an increased bridging oxygen (BO) fraction is induced with the increase in CeO<sub>2</sub>/Na<sub>2</sub>O molar ratio. The increase in BO bonds is correlated to the higher field strength of the Ce<sup>2+</sup> as compared to Na<sup>+</sup> cation. As a result, some of Na<sub>2</sub>O as a modifier can be preferentially associated with the higher field strength cation Ce<sup>2+</sup> and as a result CeO<sub>4</sub> as a glass

former unit is the product which in turn increases the number of bridging bond, BO [1] [2] [3] [4] [5].

Understanding and interpreting of data based on structural changes upon addition of cerium oxide in silicate [3], borate [6] [7] [8] and borosilicate glasses [1] [2] are of major interest. This is maybe because many commercial borosilicate glasses that contain some amount of such oxides are suitable in the field of applications. Similarly both boron and silicon can also be affected by  $\text{Al}_2\text{O}_3$  and  $\text{CeO}_2$  which undergo a considerable change in their coordination [1] [3]. The simultaneous introduction of  $\text{CeO}_2$  within glass network brings even more complexity when defining the structure of such glasses [5] [6] [7] [8] [9].

The structure changes of the borosilicate glasses were severally reported to depend on structural factors called R and K ( $R = \text{modifier}/\text{B}_2\text{O}_3$  and  $K = \text{SiO}_2/\text{B}_2\text{O}_3$ ) [1] [2] [3]. The condition of  $R > k$  forces  $\text{Na}_2\text{O}$  to participate between both the borate and the silicate glass networks [1] [2] [3]. As a result, the degree of mixing between the silica-rich and boron-rich network is strongly enhanced and homogeneous borosilicate network is produced. The structure of glass and therefore its properties are deeply influenced by changing both R and K.

Studies based on  $\text{CeO}_2$  in borate and silicate glasses have been recently reported [1] [2] [3] [4]. On the other hand, role of cerium oxide in complicated borosilicate glasses, to our knowledge, is not explored. Therefore the present work is devoted to determining the structural role of cerium oxide in the borosilicate glasses. More clarification will be considered by using the advantage of additional, XRD, EDP, SEM and TEM techniques.

## 2. Experimental

### 2.1. Preparation of Glass

The chemically pure  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$  and  $\text{Na}_2\text{CO}_3$  were used to prepare all glass samples from the starting materials. Stoichiometric powders were carefully mixed and melted for 50 minutes in a platinum crucible at  $1340^\circ\text{C}$  -  $1450^\circ\text{C}$ . Subsequently, melts were quenched on a metal plate that was pre-heated to  $350^\circ\text{C}$  to avoid cracking progress.

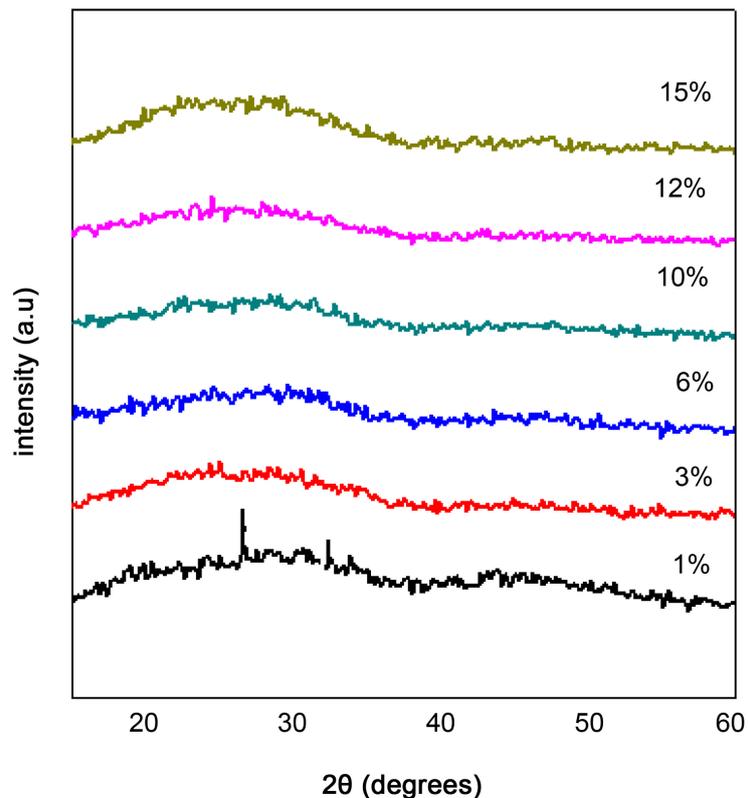
### 2.2. Experimental Techniques

A Shimadzu X-ray type Dx-30 diffractometer is used for X-ray diffraction measurements. The values of the maximum peak and intensity are used to determine the material type that is compared to patterns in the joint committee for powder diffraction 108 standards' international powder diffraction file (PDF) database (JCPDS). A transmission electron microscope (TEM) of type JEOL-JEM-1011 was used for the determination of the size and shape of the studied samples. Microstructural data was tested using the JSM-7500F field emission scanning electron microscope. The machine operated with an accelerated voltage of 25 kV. All samples were sputter-coated with a thin layer of gold (3 - 4 nm) to avoid sample charging and increase the signal-to-noise ratio.

### 3. Results and Discussion

#### 3.1. XRD Spectroscopy

**Figure 1** shows XRD patterns of the glass samples containing different concentration from  $\text{CeO}_2$ . There is no evidence for crystal formation in the sample of  $\text{CeO}_2 > 1$  mol%. At lower concentration, there are weak diffraction peaks which may be situated at  $26^\circ$ ,  $32^\circ$  and  $34^\circ$ . This weak diffraction peaks were identified as the stable sodium silicate phase enriched with NBO atoms [JCPDS 40-0376] [10] [11]. After further increasing of  $\text{CeO}_2$ , the intensity of these peaks disappeared and started to emerge in the amorphous background in glasses of higher  $\text{CeO}_2$  concentration. Based on the present results, the mechanism proposed is that both metasilicate and disilicate phases nucleate concurrently at the very early stages of nucleation [8]. As the content of cerium oxide increases, nucleation and growth of metasilicate becomes restricted. As a result, the relative number of metasilicate ( $\text{Na}_2\text{SiO}_3$ ) crystals decreases, and they are no longer observed after addition of one mol%  $\text{CeO}_2$ , since significant amount of glassy phase is the dominant. We can thus safely state that equilibrium state has not been reached and that metasilicate is a metastable phase and its constituent may be changed with more cerium oxide addition. As a result, another structural species containing  $\text{CeO}_4$  are evidenced to be formed. Therefore, disappearance of diffraction peaks in spectra of glasses may be considered as a result of decreasing



**Figure 1.** XRD patterns of borosilicate glasses containing different concentrations from  $\text{CeO}_2$ .

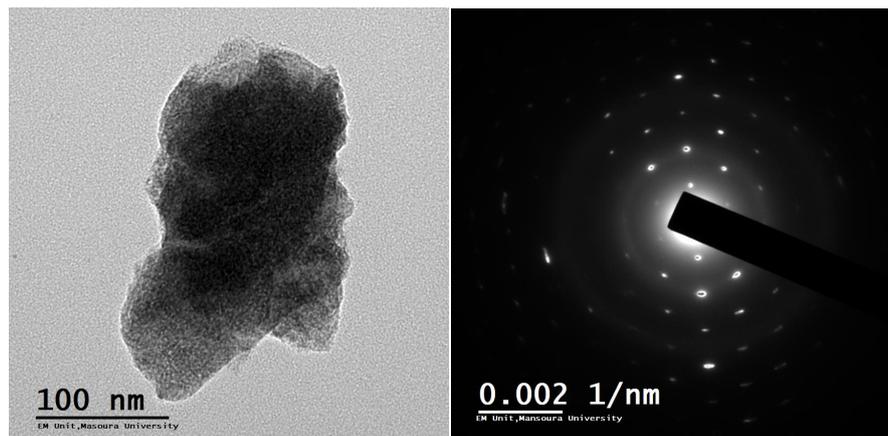
concentration of  $Q^2$  (silicate units of 2NBO) species which perform metasilicate  $Na_2SiO_3$  phases. As a result, phases containing less NBO atoms (disilicate) are the dominant upon  $CeO_2$  addition. Decreasing  $Q^2$  and increasing  $Q^3$  upon increasing  $CeO_2$  concentration might be considered the main reasons for increasing the amorphous nature of the glasses.

It has been found that more addition of  $CeO_2$  to the glass network resulted in spreading of  $CeO_2$  over silicate structural groups to form two-dimensional amorphous phase (silicate precursor) containing nanocrystalline cerium silicate of undefined structure [8] [9] [10].

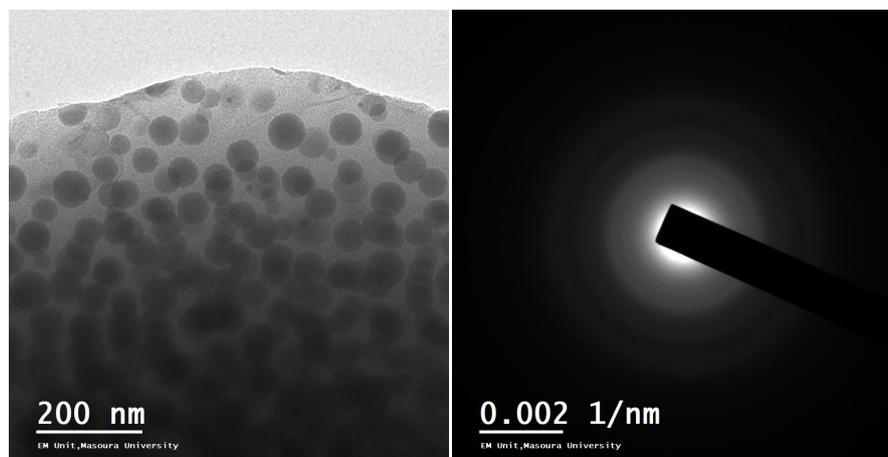
At extremely high cerium oxide concentration, the structural units of the tetragonal  $Ce_2Si_2O_7$  disilicate began to form at expense of  $Na_2SiO_3$  that resulted in increase of disorder in a glassy phase [12].

### 3.2. Morphology and Phase Analysis, TEM and EDP

Evidences based on XRD data are in a good agreement with that obtained from TEM and EDP, **Figure 2** and **Figure 3**. Both confirmed that well-formed structural species are constructed in its ordered state in glasses of low  $CeO_2$  contents.



**Figure 2.** TEM and EDP of glass containing 1 mol%  $CeO_2$ .



**Figure 3.** TEM and EDP of glass containing 20 mol%  $CeO_2$ .

Samples of 1 & 20 mol% CeO<sub>2</sub> are presented as examples in **Figure 2** and **Figure 3**. It can be observed from these figures that at lower CeO<sub>2</sub> contents (1 mol%, for example), sub crystallized species are still formed within the glassy state. The crystal size and morphology of the crystalline phases is shown to depend on the glass composition [8] [9], particularly on CeO<sub>2</sub> concentration. The size of the well-formed ordered species in glass of 1 mol% CeO<sub>2</sub> is higher than that of glass containing higher CeO<sub>2</sub> concentration, since it lies in the region of 70 - 110 nm in low ceria glass, since it lies in the region of 70 - 110 nm in low ceria glass.

Cerium has a great capacity to remove NBO from the silicate and serves the role of a glass former, as seen by the reduction in cluster size as CeO<sub>2</sub> level increases. This would be accompanied by sodium silicate clustered phases decreasing in size and content. Furthermore, some of the modified cerium species are detached from the original glass phases to produce smaller species of sphere-like structures that characterize the CeO<sub>2</sub> phases [6] [12], as seen in **Figure 3**.

Since cerium and sodium oxide can act as modifiers, the micro-crystallized clustered species are clearly visible in glasses containing 1 mol % CeO<sub>2</sub>. Ordered species are always represented by such diffractions [6] [12]. The size of the aggregation clustered species, on the other hand, appears to diminish with increasing CeO<sub>2</sub> level (see **Figure 3**). CeO<sub>2</sub> has the potential to remove more and more NBO and Na ions from the silicate and borate networks in this circumstance, reducing the content and size of the well-formed clusters.

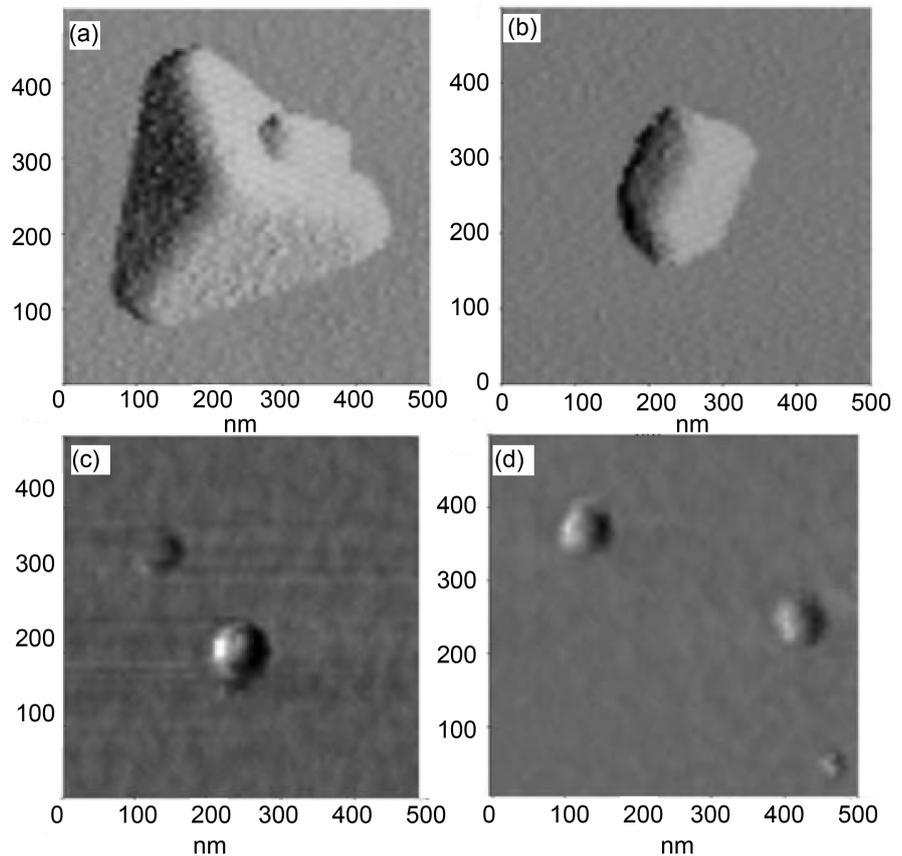
The linkage between distinct species weakens and almost completely separates when CeO<sub>2</sub> concentration increases, as seen by TEM and EDP, forming a sphere-like structure representing changed cerium units. These species, which contain around 20 mol% cerium oxide, may be easily detected with a size less than that of glasses containing 1 mol% cerium oxide (see **Figure 3**).

Features observed by Means TEM (**Figure 3**) is supported to a great extent with that detected by atomic force microscope **Figure 4** which clarified that irregular amplitude of images of cerium occurs in microparticles size (MPs; a, b) and spherical like shape of cerium oxide is found in nanoparticles (NPs; c, d).

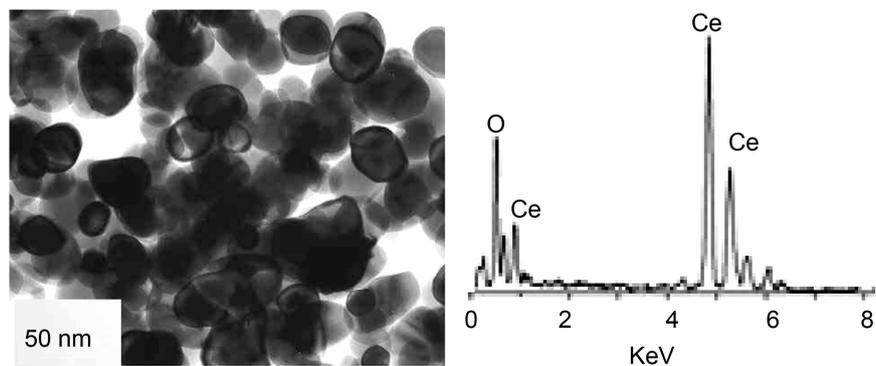
Generally increasing CeO<sub>2</sub> content at the expense of B<sub>2</sub>O<sub>3</sub> in borosilicate glasses will lower the size of Na<sub>2</sub>SiO<sub>3</sub> units through withdrawing of Na<sub>2</sub>O which is taken to form Na<sub>2</sub>CeO<sub>4</sub> units of lower size. Formation of the latter affects the nature of glass matrix, since less ordered network is the main product. Macro size species are found in nonspecific shape as presented from TEM micrograph and AFM (**Figure 2** and **Figure 4(a)**, **Figure 4(b)**) [12]. On the other hand, non-sized species are found in spherical like shapes (**Figure 3** and **Figure 4(c)**, **Figure 4(d)**).

### 3.3. EDS-Spectroscopy

In order to extract the structural role of CeO<sub>2</sub>, it is important in this study to compare EDS spectra of pure CeO<sub>2</sub> with that of cerium containing glass. **Figure 5** represents TEM and EDS spectra of pure cerium oxide. It is shown that most



**Figure 4.** Typical atomic force microscopy (AFM) amplitude images of cerium microparticles (MPs; (a), (b)) and cerium oxide nanoparticles (NPs; (c), (d)).



**Figure 5.** TEM and ESD spectra of pure  $\text{CeO}_2$ .

of line spectra are concentrated around 4 - 6 KeV (Ce bonded to oxygen with covalent bond). Little of Ce are bonded with ionic bond (spectra at about 1 KeV). Coordination of cerium with oxygen atoms gives uniform units of spherical morphology [5]. As seen from TEM micrograph representing pure  $\text{CeO}_2$ , spherical shaped units are seen to be greatly distributed in a layers manner, **Figure 5**.

Different observation is observed from EDS spectra of cerium containing glasses, since intensity of Ce line spectra at about 1 KeV is more higher in sample containing 1 mol%  $\text{CeO}_2$  (**Figure 6**) when it compared with sample of both

pure  $\text{CeO}_2$  (Figure 5) and one containing 20 mol%, Figure 7. This observation supports that both concentration of NBO and the modifier in the silicate network are relatively high. Formation of cerium as former is not evidenced, since there is no resolved Ce peak at higher energy (4 - 6 KeV). Reverse behavior is observed in cerium rich glasses, since the reduction in peak intensity at 1 KeV is shown (for both pure and high  $\text{CeO}_2$  glass) and new different cerium spectral peaks (3 lines) are clearly formed in the region of (4 - 6 KeV). This leads that  $\text{CeO}_2$  changes its role from modifier to former to form  $\text{CeO}_4$  groups. As a result the size and concentration of polycrystalline species ( $\text{Na}_2\text{SiO}_3$ ) [12] [13] should be changed.

It is shown from this figure that most of cerium is a modifier. Since intense peak at about 1 KeV is only resolved. There are no peaks that are evidenced between 4 - 6 KeV. In addition, it found that the concentration of Na atoms (18%) is higher

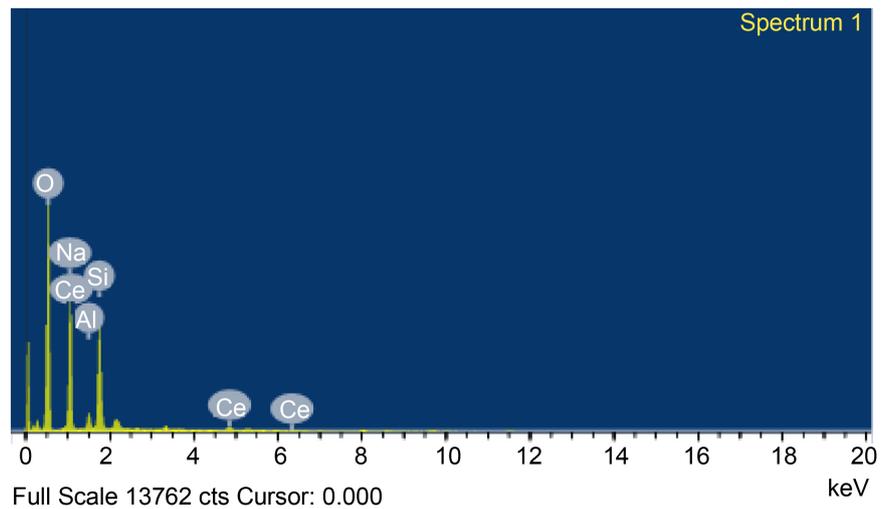


Figure 6. EDS spectra of borosilicate glass containing 1 mol%  $\text{CeO}_2$ .

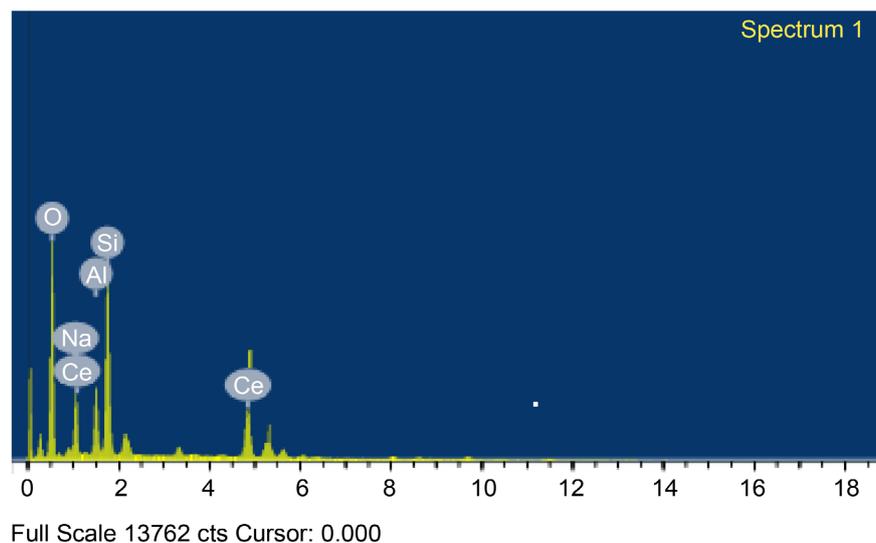
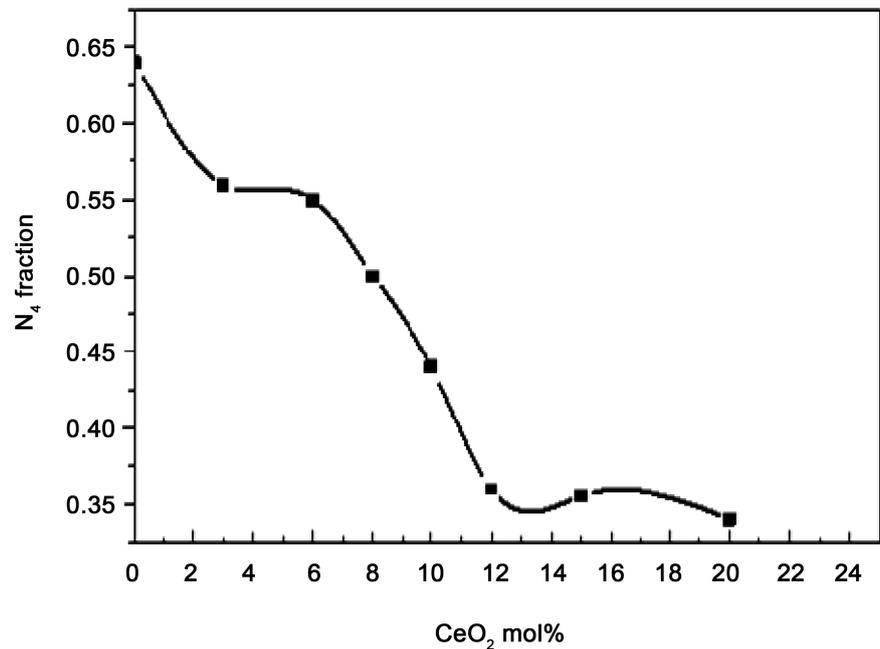


Figure 7. EDS spectra of borosilicate glass containing 30 mol%  $\text{CeO}_2$ .



**Figure 8.** Fraction of boron tetrahedral as a function of CeO<sub>2</sub> concentration.

than that of glasses contains higher cerium oxide. The concentration of Na decreases reaches 8% and Ce increase (from 0.48% to 5%) with increasing CeO<sub>2</sub> contents.

In such a case CeO<sub>2</sub> plays the role of glass former, since three peaks are evidenced between 4 - 6 KeV. It can be noted from EDS spectra of the investigated glasses that, the total Na<sub>2</sub>O concentration in the glassy phase is highly reduced upon CeO<sub>2</sub> addition. The corresponding Na concentration (16 by atom) of glass of 1 mol% CeO<sub>2</sub> is lowered to 8 for glass of 20 mol% CeO<sub>2</sub>. Reverse behaviour is noticed for silicon, its atomic content in low CeO<sub>2</sub> concentration was 9.8 and it increased to reach 16 upon more addition of CeO<sub>2</sub>. Increasing Si and decreasing Na concentration is interpreted on bases of formation of more shielded silicate units upon increasing CeO<sub>2</sub> content. In addition some of Na<sub>2</sub>O should be with drowning from the original phase and consumed to build CeO<sub>4</sub> groups. This in turn results in reduction of its (Na<sub>2</sub>O) content in the original glass phase. These considerations are found to correlate with that obtained by NMR spectroscopy **Figure 8**. The decreasing trend of the fraction of tetrahedral boron (N<sub>4</sub>) detected by <sup>11</sup>B NMR spectroscopy (**Figure 8**) may be referred to most of Na<sub>2</sub>O as a modifier is with drowning by CeO<sub>2</sub> to form tetrahedral cerium species. Presence of the latter was highly evidenced from EDS spectroscopy, since new spectral lines at about 5 KeV are grown at expense of EDS lines at 1 KeV.

#### 4. Conclusions

Cerium oxide has the effect of removing nonbridging oxygen atoms (NBO) from the glass network and serves. CeO<sub>2</sub> entered the glass network as a strong glass former.

The well formed  $\text{CeO}_4$  units cause a reduction in the concentration of tetrahedral boron groups ( $\text{N}_4$ ). At lower  $\text{CeO}_2$  (1 mol%) the latter has a good ability to form crystalline clusters in the glass. Higher  $\text{CeO}_2$  concentration leads to formation of amorphous glass network as documented by XRD and TEM-EDP spectra. Clustered species has a great benefit in the field of application, used as shielding material for ionized radiations.

### Data Availability as Authors

We increasingly make our research data available and Data will be made available on request.

### Consent to Participate

All of the listed authors have approved the manuscript before submission, including the names and order of authors.

### Consent for Publication

All of the listed authors agree to publish this work in this Journal and agree to all of the publishing rights.

### Conflicts of Interest

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

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