



## The Effect of Cerium Oxide on the Structural Modifications of Hensch Borate Bioglass and Glass-Ceramics

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**Abstract:** Glasses of modified Hensch borate Bioglass containing gradient concentrations of cerium ions were prepared via an ordinary melting quenching route. Structural, mechanical, and morphological studies on the synthesized samples including X-ray diffraction (XRD), Scanning electron microscopic image supported with energy dispersive x-ray (SEM/EDAX), Fourier transforms infrared (FTIR) in combination with <sup>31</sup>P NMR spectroscopy were performed. It was noticed that samples containing less than 1 mol% CeO<sub>2</sub> are amorphous and their crystallinity increases with increasing Cerium content. The addition of more than 0.8 mol% CeO<sub>2</sub> can boost nucleation and crystallization processes, as well as the formation of various crystalline phases. Spectroscopic measurement in combination with deconvolution analysis technique (DAT) employed to calculate the number of tetrahedrally coordinated units of both boron and cerium atoms and therefore their structural role can be elevated.

**Keywords:** Cerium oxide; borate glass; FTIR; NMR; Vickers Hardness

### 1. Introduction

During the last decades, most research groups studied the formation and different applications of materials that contain the hydroxyapatite (HA) phase. HA is the mineral inorganic constituent of the human bones that assumed biocompatible with human hard tissues and shows osteoconductive properties [1-2]. Therefore, HA is considered a superior material with low mechanical characteristics compared with natural human bone. Bioactive glass-ceramics are being studied as fillers and bone graft alternatives to pure HA.

Unlike silicate glasses, without the creation of a borate-rich layer, bioactive borate glasses can generate hydroxyapatite right on the surface of the unreacted glass. This is because the borate matrix saturated with BO<sub>3</sub> groups, like phosphate glasses, is easily soluble in bodily fluids. Borate glasses can react to completion with no substantial change in dissolution kinetics because there is no diffusion layer [3, 4].

Previous research on bio-borate glasses has confirmed that the application based on

bioactive borate glasses appears to be very useful, especially for bone growth and the efficacious healing of diabetic bone wounds [5-7]. Despite their excellent -bioactive properties, bioactive borate glasses have significant drawbacks, including low mechanical strength and fracture toughness. Because of this disadvantage, they can only be used in a few applications. In this thesis, we will conduct some scientific trials to improve mechanical performance while maintaining the benefit of good bioactivity. In this regard, rare earth oxides such as CeO<sub>2</sub> can be added to the glass matrix to convert the brittle bioactive glass into harder glass-ceramics containing some crystalline active phases. The following considerations must be carried out to satisfy the extremely good bioactivity and material strength:

The glass or glass-ceramics matrix should be prepared in such a way that it can contain extremely variable concentrations of BO<sub>3</sub> units in both ring and non-ring configurations. The bioactivity was previously known to be

proportional to the glass's solubility, which is primarily determined by the  $\text{BO}_3$  content [8, 9]. The cerium oxide should act as a glass former in the glass matrix, forming  $\text{CeO}_4$  units at the expense of insoluble brittle  $\text{BO}_4$  units. This means that in the glass network,  $\text{CeO}_4$  tetrahedral units should be formed at the expense of  $\text{BO}_4$  units only. The prepared sample's matrix must contain a crystalline cerium borate phase that is appropriate for strength achievement. Crystalline cerium calcium phosphate phases are also formed with care. At the beginning of crystal formation, the glass is suggested to be transparent. This results in a fine mixing of the various structural units that comprise the main glass network. Furthermore, the size difference between amorphous and crystalline units should be very small [10-12].

Very advanced and powerful techniques, such as NMR spectroscopy of  $^{11}\text{B}$ ,  $\text{Na}$ , and  $^{31}\text{P}$  resonances, should be used to guide us through the very limited changes that can be considered after  $\text{CeO}_2$  addition. To recognize the effect of matrix on glass properties, the durability and hardness properties of some of the investigated samples should be reported [13].

Finally, the experimental results for both network extents of cerium-free and cerium-rich glasses should be reported. The preceding considerations may reflect our primary goal and objective from this study.

## 2. Materials and Techniques

Modified Hench Borate Bioglass consists of  $x\text{CeO}_2.(45-x)\text{B}_2\text{O}_3.24.5\text{Na}_2\text{O}.24.5\text{CaO}.6\text{P}_2\text{O}_5$  were thermally synthesized through the melting process. Analytical grade cerium oxide provided by Sigma Company in combination with orthoboric acid, ammonium dihydrogen orthophosphate, sodium carbonate, and calcium carbonate supplied by Raysan Co. were used as sources for  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ , and  $\text{CaO}$  respectively. Samples composition were introduced in the table (1)

Precalculated amounts of chemicals were mixed and melted in porcelain crucibles at temperatures ranging between 1100-1200 °C depending on composition. The melts were then poured over a stainless-steel mold of required dimensions and allowed to cool gradually to room temperature. X-ray diffraction patterns

were recorded via PANalytical X-Pert PRO operated at 30 Kv voltage adopting Cu target with wavelength  $\lambda = 1.54$  nm at Bragg's angles between 4 and 70°. Vickers's hardness numbers ( $H_V$ ) was calculated as the average value of 10 indentations in triplicate samples via FM-7 microhardness tester with a fixed load of 25 g.

**Table (1)** sample name abbreviations and composition

Abbr.	$\text{CeO}_2$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{P}_2\text{O}_5$
Ce0	0.00	45.0	24.5	24.5	6.0
Ce0.5	0.50	44.5	24.5	24.5	6.0
Ce0.8	0.80	44.2	24.5	24.5	6.0
Ce1	1.00	44.0	24.5	24.5	6.0
Ce2	2.00	43.0	24.5	24.5	6.0
Ce4	4.00	41.0	24.5	24.5	6.0
Ce8	8.00	37.0	24.5	24.5	6.0
Ce12	12.0	33.0	24.5	24.5	6.0
Ce20	20.0	25.0	24.5	24.5	6.0

## 3. Results and Discussion

### 3.1. X-ray diffraction and Vickers microhardness

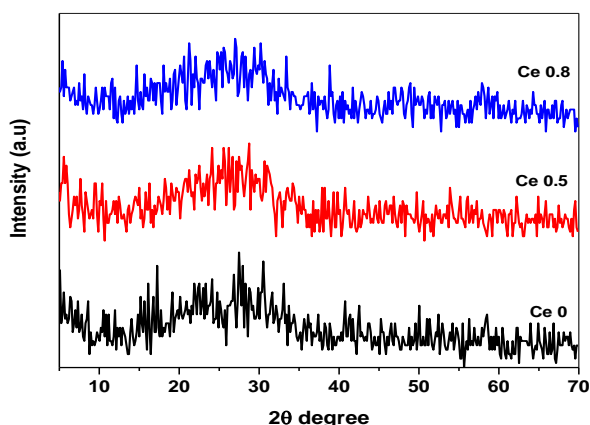
Figures 1 and 2 reveal the XRD pattern of both lower and higher contents of synthesized samples containing ceric oxide in different mass fractions. Samples that contain less than 0.8  $\text{CeO}_2$  (Figure 1) reveal a wide halo at about 25°, supporting the non-crystalline nature of prepared glasses, while other samples with a higher cerium oxide content up to 20 mole% (Figure 2) reveal intense sharp peaks superimposed over the non-crystalline diffraction halo indicating the formation of crystalline phase within the amorphous glassy matrix. The sharp intense peaks were compared with previously studied glasses with the nearly same composition and indexed to their respective phases [14]. Formed phases were compared to that of calcium cerium borate  $\text{Ca}_2\text{CeB}_2\text{O}_7$  and sodium cerium borate  $\text{Na}_4\text{CeB}_2\text{O}_7$ , in combination with different calcium phosphates including  $\text{Ca}_2(\text{P}_2\text{O}_7)$  and  $\text{CaCe}(\text{PO}_3)$  which considered amongst the most bioactive and biocompatible glass phases [15-16].

The percent of crystallinity was determined from the area under associated crystalline peaks ( $A_c$ ) relative to that under both crystalline ( $A_c$ ) and amorphous ( $A_a$ ) bands in the XRD pattern,

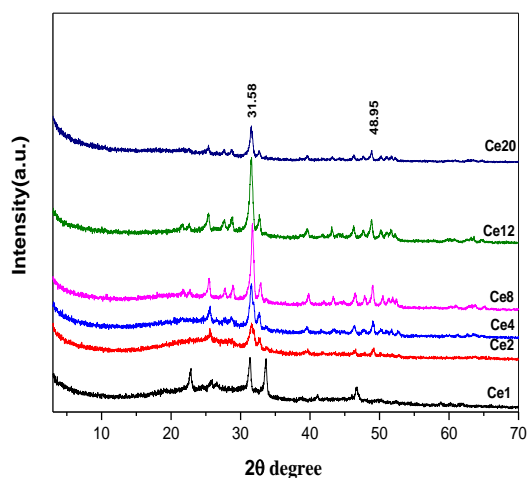
according to the following equation.

$$\text{Crystallinity \%} = \frac{A_c}{A_c + A_a} \times 100. \quad (1)$$

The percent of crystallinity is considered an indication for the bioactivity and tendency to form HA phase [17, 18]. Therefore, crystallinity considered sensitive to the variations in CeO<sub>2</sub> content as shown in Figure (3).



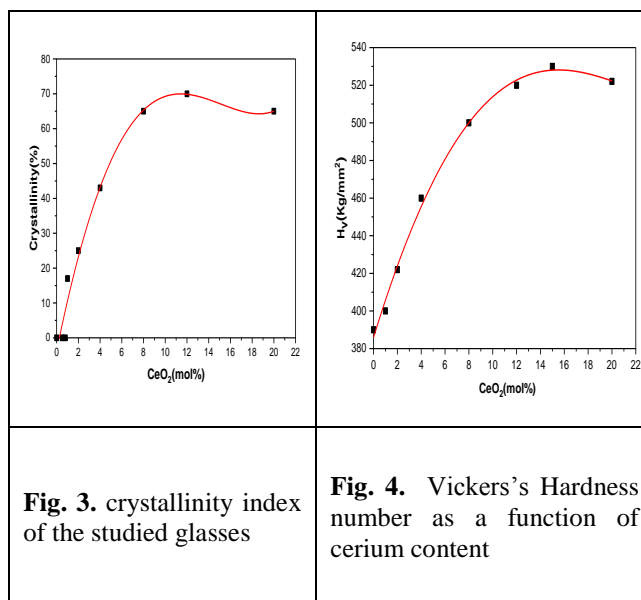
**Fig. 1.** XRD pattern of synthesized glass doped with up to 0.8 mol% Cerium oxide



**Fig. 2.** XRD pattern of glasses containing Cerium oxide from 1 mol% up to 20 mol%

**Table 2** crystallinity and Vickers microhardness number with CeO<sub>2</sub> content

Ce <sub>2</sub> O (mol%)	20	12	8.0	4.0	2.0	1.0	0.8	0.5	0.0
Crystallinity %	65	70	65	43	25	17	..	..	..
H <sub>v</sub> (kg/mm <sup>2</sup> )	40	40	40	42	46	50	52	53	52
	0	0	0	2	0	0	0	0	2



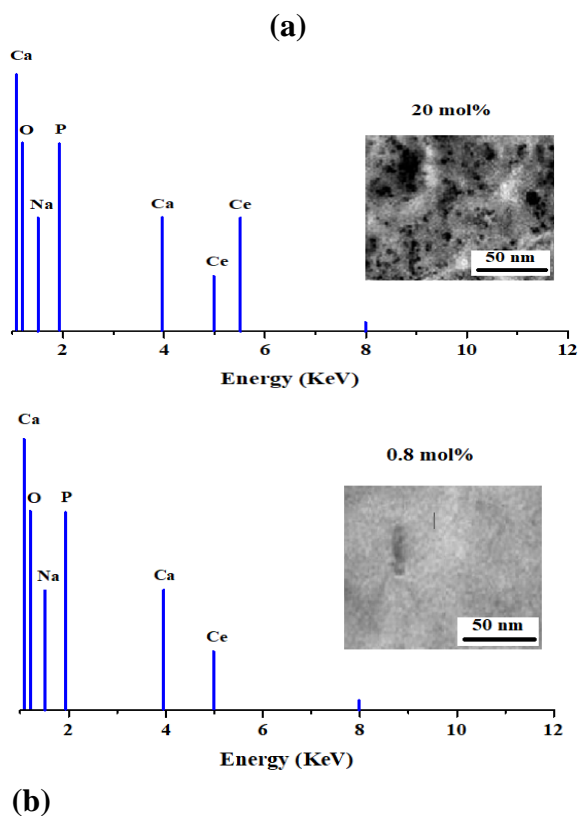
**Fig. 3.** crystallinity index of the studied glasses

**Fig. 4.** Vickers's Hardness number as a function of cerium content

The percent crystallinity was found to be correlated to the hardness number of the studied samples and behaves nearly the same behavior. Calculated crystallinity % and Vickers microhardness number in correlation to cerium content were shown in Figures 3 & 4, and listed in table 2.

### 3.2. Scanning Electron Microscopy supported Energy Dispersive X-ray (SEM/EDAX)

Figure 4 reveals scanning electron micrograph images (SEM) that represent the topographic nature of the surface of two selected samples in the lower and higher cerium concentration regions. Significant differences in the topography of the studied samples with low CeO<sub>2</sub> (0.8 mol %) and with the higher CeO<sub>2</sub> content (20 mol %) were observed. It was clear that change in the cerium content results in the appearance of large crystalline species within the amorphous matrix as supported by XRD results. EDAX peaks were also interpreted in terms of cerium transitions within the molecular states of L<sub>α</sub> and M<sub>α</sub> originally located at about 4.8403 and 0.8831 keV respectively in combination with other transitions of constituting glass partners including Ca L<sub>α</sub>, Ca K<sub>α</sub>, Na K<sub>α</sub>, O K<sub>α</sub> and P K<sub>α</sub> at about 0.3413, 3.6905, 1.041, 0.5249 and 2.0134 keV respectively shown in Figures 5a, b [19].



**Fig. 5.** SEM/EDAX images of extreme samples (a) 0.8 mol% and (b) 20 mol% CeO<sub>2</sub>.

### 3.3. NMR and FTIR Correlation

NMR experiments offer direct information about the Q<sup>n</sup> units in the glassy matrices containing multi-former oxide or intermediate partner with four coordinated oxygen. It is shown in Figure (6) that the chemical shift value of glasses with lower cerium oxide content up to 2 mol% (9 ppm) as a dominant structural species corresponding to orthophosphate units while the addition of cerium oxide changes the values of the chemical shift to about (2ppm) in the higher concentrations up to 20 mol% CeO<sub>2</sub> interpreted in terms of the interaction between cerium cation that coordinated with PO<sub>4</sub> groups forming a new cerium phosphate crystalline phases.

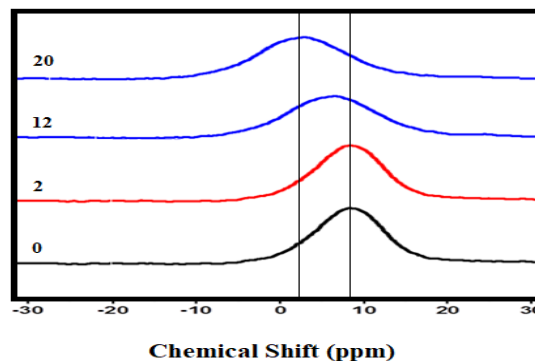
It was concluded that CeO<sub>2</sub> addition may be consumed in the phosphate and borate network modification causing an observed reduction in the number of four coordinated units (B<sub>4</sub>) [20].

$$B_4 = \frac{BO_4 + CeO_4}{BO_4 + CeO_4 + BO_3} \quad (2)$$

Such fact can be combined with the number of tetrahedral borate units that can be calculated from the deconvolution analysis technique (DAT) previously reported by different authors.

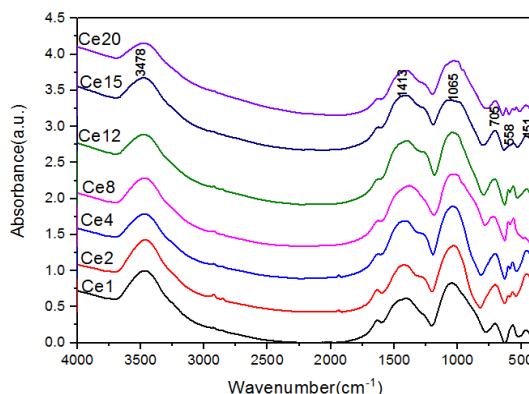
Deconvoluted technique applied for both NMR and FTIR spectral data to calculate both B<sub>4</sub> and N<sub>4</sub>. Figure (7) reveals FTIR optical absorption data of studied borate glasses containing different amounts of CeO<sub>2</sub> concentrations. While Figure (8) shows an exemplified analyzed sample in both techniques.

$$N_4 = \frac{BO_4}{BO_4 + BO_3} \quad (3)$$

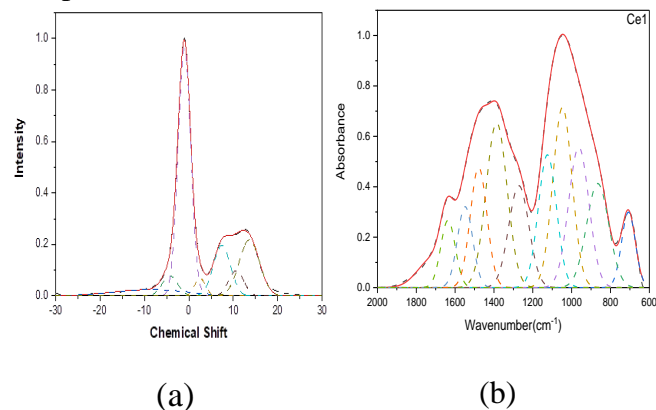


**Fig. 6.** NMR spectra of selected samples containing different CeO<sub>2</sub> concentrations

The concentration or fraction of CeO<sub>2</sub> as former CeO<sub>4</sub> units can be estimated from the difference between these two values (B<sub>4</sub>-N<sub>4</sub>) [21]

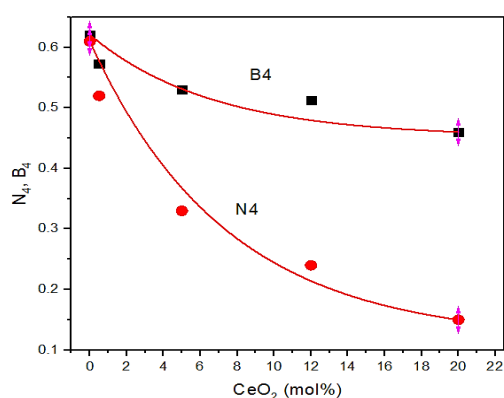


**Fig. 7.** FTIR absorption spectra of the studied samples



**Fig. 8.** deconvoluted spectra of selected sample containing 1 mol% CeO<sub>2</sub> (a) NMR and (b) FTIR

Figure (9) below shows the obtained values of both  $N_4$  drawn from the FTIR spectral data analysis with the  $B_4$  values obtained from the NMR spectral data analysis. It was clear that  $B_4$  values are usually greater than that of  $N_4$  except for the sample free of cerium oxide and generally constituting only  $BO_4$  and  $BO_3$  structural units. Samples containing cerium oxide as a former partner usually contain tetrahedral cerium structural units  $CeO_4$  that cannot be separated or measured using the NMR analysis route. Therefore, the difference between these values introduces a suggested measure for these units and specifies the role of cerium in the structure.



**Fig. 9.** Variation of  $N_4$  and  $B_4$  with the change of the cerium oxide content in the samples

#### 4. Conclusions

Modified Hench Borate Bioglass containing variable amounts of cerium oxide up to 20 mol% were thermally synthesized through melting process. XRD data reveals formation of amorphous glasses containing up to 0.8 mol% cerium while samples containing higher concentration of cerium shows formation of crystalline phases attributed to the presence of cerium oxide as nucleating and crystallizing agent. The percent crystallinity also calculated from XRD data and their logarithmic behavior was discussed and correlated with the Vickers microhardness number. SEM/EDAX approves the presence of cerium ions as a glass former within the glassy matrix. FTIR/NMR spectroscopic data were used to calculate the fraction of tetra-coordinated units adopting DAT technique.

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