

^{11}B NMR Spectroscopy of Lead Borate Glasses: Additive Effect of Cerium Oxide

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Abstract

Glasses and glass ceramics in the system $x\text{CeO}_2 \cdot (50 - x)\text{PbO} \cdot 50\text{B}_2\text{O}_3$ ($0 \leq x \leq 50$) have been studied, for the first time, by NMR and FTIR techniques. Effect of CeO_2 substitution with PbO on NMR parameters has been discussed in terms of changing both boron and cerium coordination. The quantitative fraction of four coordinated boron (N_4) has been simply determined from ^{11}B NMR spectroscopy. On the other hand, the fraction of total tetrahedral structural units B_4 ($\text{BO}_4 + \text{PbO}_4 + \text{CeO}_4$) is obtained from FTIR spectral analysis. It is not possible to get the fraction of cerium oxide directly from the applied spectroscopic tools. Therefore, a simple approach is applied, for the first time, to determine CeO_4 fraction by using the different criteria of both ^{11}B NMR and FTIR spectroscopy. The fraction of B_4 species is equal to N_4 , within the experimental error, of the same glasses in the composition region of up to 10 mol% CeO_2 . On the other hand, there is a clear difference between both N_4 and B_4 values in glasses of higher CeO_2 content (>10 mol%). The related difference showed a linear increasing trend with increasing the content of CeO_2 in the glass. This was discussed on the bases of structural role of CeO_2 which acts as a glass former in the region >10 mol%, while, at lower concentration, it consumed as a glass modifier.

Keywords

New Approach, Cerium Oxide, Boron Fraction

1. Introduction

Borate glasses containing CeO_2 and PbO are used in wide field of applications. This may be due to their distinction features including wide glass forming region and low thermal expansion [1]-[4]. Several investigations have been reported on the structure of

lead containing glasses [2]-[6]. It was concluded that glass and glass ceramics containing high concentration from PbO are of great importance from the viewpoint of glass formation. This may be because PbO in such a case enters the network of the glass as a former.

In the low PbO content (up to 50 mol%), majority of PbO act as a network modifier. The reverse behavior is found in binary CeO₂-B₂O₃ glasses, since cerium oxide acts as a glass former [3] [4]. Each atom of PbO added is used to convert two BO₃ species into two BO₄ units. The fraction of BO₄ groups increases with increasing PbO contents reaching maximum value ~0.50 - 0.53 [7]-[10] at equal amount of PbO and B₂O₃ oxides. Further increase of PbO content decreases the number of BO₄ units by forming nonbridging oxygen atoms in glass network. In such situation Pb ions are mainly surrounded by two BO₄ tetrahedral units and in part by BO₃ units with NBOs [11]. But major portion of CeO₂ enters the network of the glass as a modifier at extremely high contents (40 - 60 mol %) [3].

In this paper, the structure of CeO₂-PbO-B₂O₃ glasses is investigated by means of FTIR absorbance and NMR techniques with an aim to determine the structure role of cerium in ternary cerium lead borate glasses. In this regard, there is a remarkable lack and shortage information about the role of ceria in glass ceramics.

2. Experimental Details

2.1. Glasses Preparation

The glass samples were prepared by mixing and fusing the desired amount of CeO₂, PbO, and H₃BO₃ compounds in alumina crucibles. The melting process was carried out at different temperatures depending on the glass compositions. The glasses were prepared with a wide variety of the cerium oxide concentration which is varied from 2.5 to 50% CeO₂. The melt was swirled frequently and then poured on stainless steel plate and pressed by another plate to get disc like shape.

2.2. ¹¹B NMR Measurements

All samples were measured with JEOL GSX-500 high-resolution solid-state MAS NMR spectrometer in a magnetic field of 11.4 T. ¹¹B MAS NMR spectra were recorded at a frequency of 160.4 MHz and spinning rate of 15 KHz. The glass samples were measured with a single pulse length of 0.5 - 1.0 ms and a pulse delay of 2.5 s, and an accumulation of 200 - 300 scans is obtained.

3. Results and Discussion

3.1. Binary Borate Glasses

NMR spectra of both 50CeO₂-50B₂O₃ and 50PbO-50B₂O₃ binary glasses are presented in **Figure 1**. It is clear from this figure that there is a great difference between the features of the two spectra. In case of PbO-B₂O₃ glass (free from cerium), well resolved resonance peaks characterizing BO₃ (both in ring and nonring) and BO₄ groups are

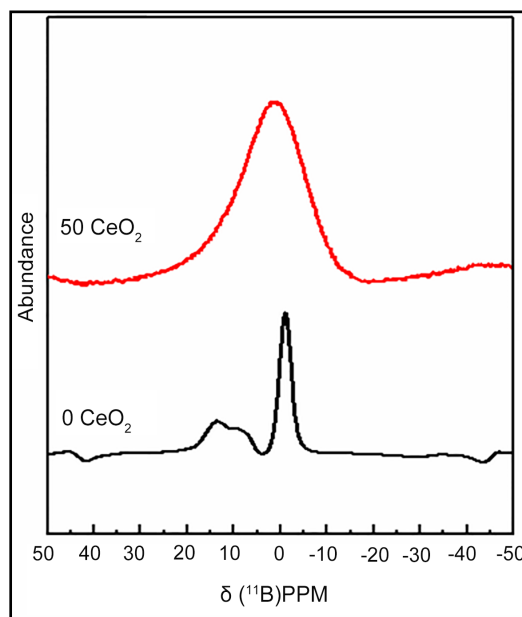


Figure 1. ^{11}B NMR spectra of cerium free (at the bottom) and of glass contains 50 mol% CeO_2 .

clearly distinguished. The fraction of boron tetrahedral units is ~ 0.53 which means that 53% from the total boron is found in its tetrahedral coordination with oxygen atoms. This suggests that the majority of PbO is consumed as a glass modifier. It converts two BO_3 units to two BO_4 groups. On the other hand, broader and anti-symmetric NMR band of CeO_2 - B_2O_3 glass are clearly evidenced by the effect of CeO_2 . It can be seen from the ^{11}B spectrum of the glass that the bands characterizing BO_3 is diluted by CeO_2 . As a result, a wide spectrum containing overlapped peaks characterizing BO_3 and BO_4 is obtained, see **Figure 1**. The fraction of tetrahedral boron is much lower than that of lead borate glass, since the determined value of $B_4 = 0.34$.

Similar observation can be also found in FTIR absorbance spectra of the two glasses, see **Figure 2**. It can be seen from the spectrum of cerium free glass that individual resonances representing BO_3 and BO_4 are markedly distinguished. Higher CeO_2 concentration (50 mol%) leads to appearing of broader and anti-symmetric FTIR resonance band. This wide band is assigned to mixed $\text{Ce}_4\text{-O}$, $\text{B}_4\text{-O}$ and $\text{B}_3\text{-O}$ stretching vibration mode.

3.2. Ternary Cerium Lead Borate Glasses

There are two main spectral regions which characterize the NMR resonance modes of the ternary glass network. The first is dominant in glass of $0 \leq \text{CeO}_2 \leq 10$ mol%, since both resonance spectra characterizing separated BO_3 and BO_4 groups are clearly appeared [12]-[15] (**Figure 3**). The wide spectral band of chemical shift exists between 11 - 20 ppm is attributed to BO_3 (both in ring and nonring) groups [12] [13]. The second appears at 0 ppm which is due to tetrahedral BO_4 units. An extra increase in CeO_2 at expense of PbO concentration will result in overlapping resonance spectra characteriz-

ing both BO_3 and BO_4 groups. This may reflect change in structure role of cerium oxide in this composition region, since it acts as a glass former [1] [13] [16] [17]. As a direct result, tetrahedral CeO_4 species are suggested to be formed upon a frequent replacement of CeO_2 with PbO . Increasing concentration of CeO_4 groups is accompanied with a decrease in the fraction of BO_4 units. This is because part of modifier oxide is consumed to modify CeO_2 network. The same feature is reported in detail in our previous work [18] on the same glasses investigated by FTIR spectroscopy.

Figure 4 represents the changes of B_4 and N_4 fractions with CeO_2 concentration. The B_4 can be showed to change with different rates upon addition of CeO_2 concentration.

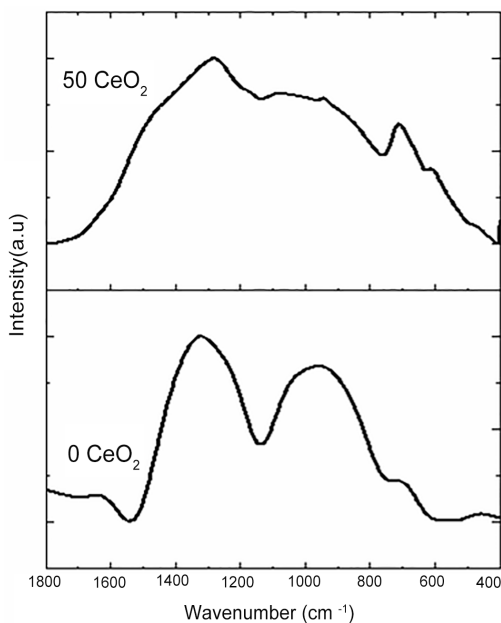


Figure 2. FTIR absorbance spectra of cerium free (at the bottom) and of glass contains 50 mol% CeO_2 .

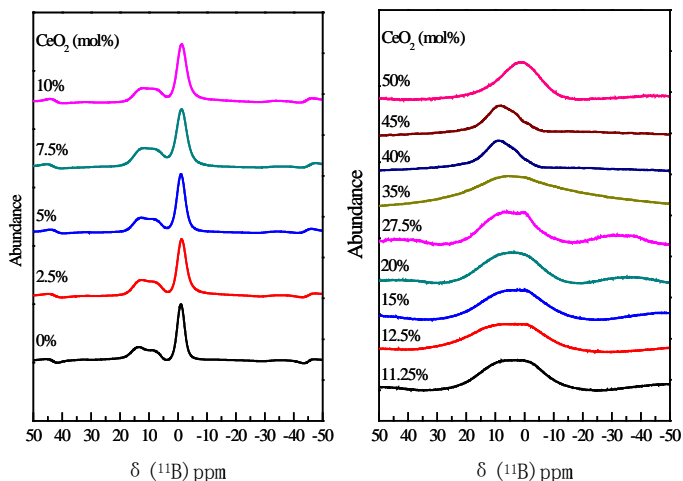


Figure 3. ^{11}B spectra for CeO_2 - PbO - B_2O_3 glasses at different CeO_2 concentrations.

First, both B_4 and N_4 value in both cases changes slightly around fixed value with introducing CeO_2 up to ~ 10 mol%. This little difference between the two fraction (B_4 and N_4) may be considered due to the same role of both lead and cerium as glass modifier, since substitution of PbO by CeO_2 hasn't remarkable effect on both values. Further substitution of PbO by CeO_2 (in the region >10 mol %) will result in decreasing in both B_4 and N_4 with different rates. Moreover, the differences between them increase with increasing CeO_2 contents. Increasing differences between B_4 and N_4 may lead to conclusion that the ability of CeO_2 to act as a glass former is increased with its content. Thus the formation of CeO_4 groups as the most dominate species in this region is considered as the main reason of reduction in the tetrahedral (BO_4) groups in the glass network. As a direct effect, B_4 is abruptly decreased upon more addition of CeO_2 (see **Figure 4**). The difference between B_4 and N_4 for each composition gives a quantitative concentration of CeO_4 fraction as a glass former. **Figure 5** presents the change of CeO_4 .

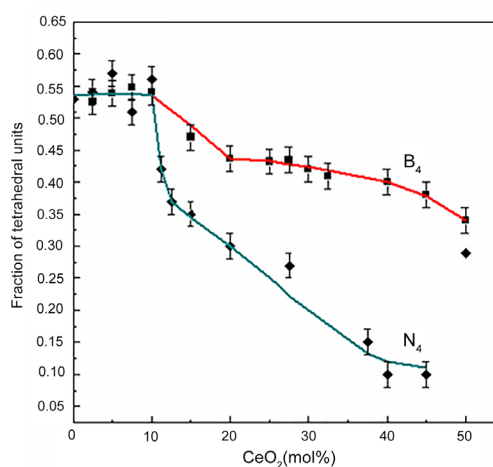


Figure 4. Changes of B_4 and N_4 fraction as function of CeO_2 concentration.

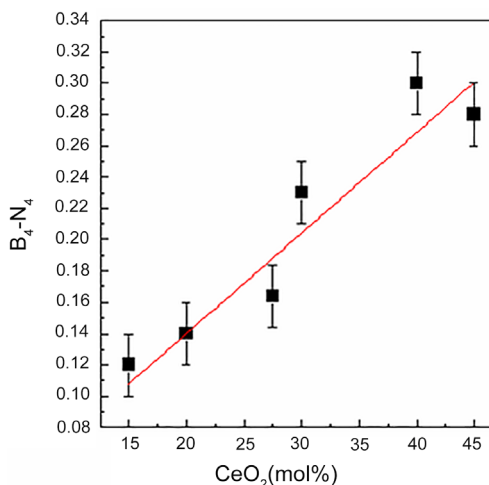


Figure 5. Changes of Ce_4 fraction as function of CeO_2 concentration.

fraction with CeO₂ contents. Ce₄ is observed to increase linearly with increasing CeO₂ concentration. The linear correlation between Ce₄ and CeO₂ concentration leads to confirm that most of all CeO₂ enters the glass network as a strong glass former.

Based upon the above considerations, we suggest that Ce (in high CeO₂) glasses has strong ability to form its own structural units and preferentially bridge to BO₃ rather than increasing number of tetrahedral BO₄ groups. For this reason both B₄ and N₄ values are continuously decreased with increasing CeO₂ contents.

4. Conclusion

Glasses in system of xCeO₂·(50 – x)PbO·50B₂O₃ with 0 ≤ x ≤ 50 mol% have been investigated, for the first time, by ¹¹B NMR structural technique. It is evidenced that cerium and lead ions play a dual role in the studied system. In low CeO₂ content, ≤10 mol, CeO₂ plays a modifier role. The structure role of CeO₂ is changed from modifier to a glass former at higher content. The fraction of the tetrahedral cerium (Ce₄) as a former species is determined from a suggested approach which is based on correlation between structural feature obtained from both NMR and FTIR analysis. Accordingly, Ce₄ fraction is determined from the differences between values of B₄ and N₄.

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