

# Structure and Properties of Mixed Former Aluminum Borate Glasses Modified With Silver Oxide

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## Research Article

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# Abstract

The current study focuses on glass preparation and characterization in the  $x\text{Al}_2\text{O}_3$  (35-x)  $\text{Ag}_2\text{O} \cdot 0.65\text{B}_2\text{O}_3$  system ( $0 \leq x \leq 35$  mol%), where  $\text{Ag}_2\text{O}$  is replaced with  $\text{Al}_2\text{O}_3$ . To examine a wide range of both structure and morphology of the produced glasses, nuclear magnetic resonance (NMR) of  $^{27}\text{Al}$  nuclei, X-ray diffraction (XRD) spectroscopy, and transmission electron microscopy (TEM) are used. Changing the  $\text{Al}_2\text{O}_3$  and  $\text{Ag}_2\text{O}$  molar ratios reveals a substantial change in material structure. In  $\text{Al}_2\text{O}_3$ -rich glass, the well-formed  $\text{AlO}_6$ ,  $\text{AlO}_5$ , and  $\text{AlO}_4$  structured groups are the well-formed units. In samples of (20 and 30 mol %  $\text{Al}_2\text{O}_3$ ), tetrahedral  $\text{AlO}_4$  and traces from  $\text{AlO}_6$  units may be detected. At lower concentrations of  $\text{Al}_2\text{O}_3$  (10 mol%), the dominant unit is only  $\text{AlO}_4$  groups containing non-bridging oxygen bonds (NBO). The XRD and EDP spectra confirm the amorphous nature of the glasses of  $\text{Al}_2\text{O}_3 \leq 20$  mol%. Glasses of higher  $\text{Al}_2\text{O}_3$  concentrations contain crystalline  $\text{Ag}_2\text{Al}_2\text{B}_2\text{O}_7$  which are formed due to the higher oxygen packaging of the mixed  $\text{AlO}_5$  and  $\text{AlO}_4$  compared with that of glasses containing only  $\text{AlO}_4$  species. The amount of higher coordinated Al species  $\text{AlO}_5$  and  $\text{AlO}_6$  are gradually increased in response to an increase in the ratios of  $\text{Al}_2\text{O}_3/\text{Ag}_2\text{O}$ . The morphology of crystalline units is confirmed from TEM to differ from that of an amorphous composition. The conductivity decreases and the activation energy for ionic conduction increase with increasing  $\text{Al}_2\text{O}_3$ . The hardness number of the studied glasses is highly increased with increasing  $\text{Al}_2\text{O}_3$  content. The increase of activation energy and the hardness number of the glasses led to an increase in the durability of the investigated glasses.

## 1. Introduction

In recent decades, glass or glass-ceramics containing  $\text{Al}_2\text{O}_3$ , such as  $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-SiO}_2$ , or  $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ , and  $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$  systems, have gotten a lot of attention [1- 4]. This is because the presence of  $\text{Al}_2\text{O}_3$  in glass systems improves chemical stability [5] and leads to good mechanical properties [6, 7]. Physical characteristics of  $\text{Al}_2\text{O}_3$ -containing glasses, such as micro-hardness, conductivity, and chemical durability, are strongly linked to their Al coordination, which shifts from six ( $\text{AlO}_6$ ) to five ( $\text{AlO}_5$ ) to four ( $\text{AlO}_4$ ) coordination [7–10]. Then, for adjustments of the structure to get appropriate physical properties, it is important to control both the boron and aluminum coordination in the investigated glasses.

The relation between adding network modifiers and changing in both boron and aluminum coordination had been documented in earlier reports [9, 11]. Increasing the molar ratio of modifier oxide to aluminum oxide should lower or suppress the concentration of higher coordinated Al species such as  $\text{AlO}_6$  and  $\text{AlO}_5$  in glasses. Reverse behavior was identified with increasing  $\text{Al}_2\text{O}_3$  concentration in the glass network since higher-coordinated  $\text{AlO}_6$  and  $\text{AlO}_5$  can simply be formed because their cationic field strength is sufficiently large.

Recently, there are some available researches on alumina-based glasses and glass ceramics but little research attention has been paid to crystalline  $\text{Ag}_2\text{O- Al}_2\text{O}_3\text{-B}_2\text{O}_3$  nano-composites. Studies concerning

this issue are our main aim. The addition of  $\text{Ag}_2\text{O}$  to aluminum borate glasses can expand the glass formation region and generate the intended amounts of  $\text{AlO}_6$  beside  $\text{AlO}_5$ , proportional to the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{Ag}_2\text{O}$ . In addition, at high  $\text{Al}_2\text{O}_3/\text{Ag}_2\text{O}_3$  ratios, crystalline structural units can be formed in the range of nanoscale.  $\text{Al}_2\text{O}_3$  oxide reinforced crystallized glasses [12–15] give the material a good advantage to be used as compatible dental fillers to enhance the hardness and other mechanical properties of dental material [12–14].

Borate glasses containing silver, strontium, zinc, and/or cerium oxides can simply exhibit good compatibility with tissues and support cell proliferation [15–17]. But there is a problem in the case of releasing a high amount of boron ions during the dissolution process which may become toxic. To solve such a problem, mixing of  $\text{B}_2\text{O}_3$  with an additional glass former such as  $\text{P}_2\text{O}_5$ ,  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  can regulate the process of ion release in the solution and prevent the toxicity to be performed. The mixed ion effect can also optimize the dissolution and boron release rate. Therefore, our aim in this work is to study the effect of mixing specific concentrations from  $\text{Al}_2\text{O}_3$  with  $\text{B}_2\text{O}_3$  in silver borate glasses. The  $\text{Al}_2\text{O}_3$  can enhance the hardness and toughness of the glass and makes the material durable against corrosions. The Ag, as well as Cu ions, are known to promote the proliferation of endothelial cells, which are important processes for wound healing. In addition,  $\text{Ag}^+$  ions in glasses have a good ability to be used as antibacterial agents giving the mixed former glasses more advantages toward biomedical applications [18].

## 2. Experimental Work

### 2.1. Preparation of Glasses

The chemically pure  $\text{AgNO}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{Al}_2\text{O}_3$  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 1340-1450°C. Subsequently, melts were quenched on a metal plate that was pre-heated to 350°C to avoid cracking progress. The resulting glasses had formulations of  $x\text{Al}_2\text{O}_3 \cdot (35-x) \text{Ag}_2\text{O} \cdot 65 \text{B}_2\text{O}_3$  ( $x= 0-35$  mol%).

### 2.2. Measurements

X-ray diffraction measurements are carried out with Shimadzu X-ray diffract meter (Dx-30, Metallurgy institute, El Tebbin-Cairo). The peak position and intensity values used to identify the type of material phases were compared with patterns in the international powder diffraction file (PDF) database compiled by the joint committee for powder diffraction standards (JCPDS). NMR measurements were carried out at ambient temperature on a JEOL RESONANCE GSX-500 spectrometer operating at a high external magnetic field (11.747 T).  $^{27}\text{Al}$  NMR spectra were measured at the resonance frequency of 130.2 MHz, using a 3.2 mm MAS NMR probe operated at a rotor frequency of 15 kHz. Typical pulse lengths were 2.5  $\mu\text{s}$  and 60 seconds delay time was sufficient to enable relaxation. Spectra are referenced to  $\text{Al}(\text{NO}_3)_3$  (0

ppm)...  $^{27}\text{Al}$  spectra were fit with Delta NMR software, version 5.04 (Japan) has been used for NMR analysis, simulation, and integration of the area under each species peak.

### 3. Results And Discussion

#### 3.1 XRD and TEM-EDP

The formation of the crystalline aluminum-borate structure in some of the investigating compositions is very important in the broad field of applications. The ordered species from  $\text{Ag}_2\text{Al}_2\text{B}_2\text{O}_7$  [18] would play a good role in the improvement of hardness and compactness of the material network and consequently enhance its corrosion resistance. In addition, both boron and silver ions impeded in these crystalline phases play the role of antibacterial species. The formation of different types of B-O-Al, Al-O-Al bonds in the network plays role in the enhancement of material properties. The bond types and their concentration in different phases can be documented utilizing both XRD and NMR spectroscopy.

XRD spectra (figure 1) showed a structural change when  $\text{Al}_2\text{O}_3$  is added to the  $\text{Ag}_2\text{O}$ - $\text{B}_2\text{O}_3$  network. The amorphous structure is dominant in the composition of up to 20 mol%  $\text{Al}_2\text{O}_3$ . The formation of crystalline  $\text{Ag}_2\text{Al}_2\text{B}_2\text{O}_7$  phases is confirmed upon more additions of  $\text{Al}_2\text{O}_3$ . Increasing crystallinity of the  $\text{Al}_2\text{O}_3$  rich glasses is accompanied by decreasing the rate of transformation of  $\text{BO}_3$  units to  $\text{BO}_4$  groups that lead to a decrease in the fraction of tetrahedral boron (N4)[19]. Besides, most  $\text{Ag}_2\text{O}$  are consumed firstly to modify  $\text{Al}_2\text{O}_3$  forming  $\text{AlO}_4$  groups and the rest are used to modify  $\text{B}_2\text{O}_3$  to form  $\text{BO}_4$  tetrahedral units. The shortage in  $\text{Ag}_2\text{O}$  concentration upon  $\text{Al}_2\text{O}_3$  replacement forces some of  $\text{Al}_2\text{O}_3$  to enter as  $\text{AlO}_6$  to compensate for the electronegativity around the well-formed structural units. Thus the introduction of  $\text{Al}_2\text{O}_3$  into the borate matrix produces not only Al-O-Al-O-B bonds but also gives rise to an increase in the tendency to crystallization as is shown in Figure (1).

This result of XRD is agreed to some extent with the TEM results presented by Figures (2 and 3). As is shown from the figures, different species of different morphologies are simply shown. The electron diffraction pattern of this composition confirms the formation of the crystalline structure of the distributed species. On the other hand, the homogenous morphology with amorphous EDP is seen for a glass of lower  $\text{Al}_2\text{O}_3$  concentration.

#### 3.2. Electrical Conductivity

It is also important in this work to study the electrical properties of the investigated glasses. This is because to apply such material in the field of bio applications, its ability to conduct or resist current should be determined. The trial will be done to correlate the changes of both conductivity and activation energy for conduction with the structural changes detected by NMR spectroscopy upon replacing  $\text{Ag}_2\text{O}$  with  $\text{Al}_2\text{O}_3$ . At first, it can be assumed that  $\text{Ag}^+$  ions related to the borate matrix are the predominant contributor to the conduction mechanism [20]

The studied glasses show a linear dependence of the logarithm of conductivity ( $\log \sigma_{200}$ ) with reciprocal of absolute temperature ( $1/T$ ), Figure 4. This behavior is a feature of the ionic conduction process that can be described by the Arrhenius relation. Figure (5) shows that there is a fast change in both  $\log \sigma_{200}$  and  $E$  with increasing  $\text{Al}_2\text{O}_3$  contents. The result reveals that conductivity decreases by about six orders of magnitude upon replacing 30 mol%  $\text{Ag}_2\text{O}$  with  $\text{Al}_2\text{O}_3$ . The remarkable change in conductivity is accompanied by an increase of  $E$  from 1.2 eV to 0.51 eV.

The change of the Vickers hardness ( $H_v$ ) with the  $\text{Al}_2\text{O}_3$  content is shown in Figure 6. It can be seen that the hardness number increases with increasing  $\text{Al}_2\text{O}_3$  content and there is a large increase in hardness value of the investigated system from about 2.3 to 4 GP as aluminum oxide content increases from 0 to 30 mo%. It is known that the increase in hardness is related to the increase in the rigidity of glass [21, 22]. These results are consistent with the increase in activation energy for conduction (figure 5), the increase of both  $H_v$  and  $E_a$  indicated that the addition of  $\text{Al}_2\text{O}_3$  created some units from five and six coordinated aluminum species. In addition, the relative concentration of three coordinated boron is also increased at expense of the four coordinated one. The presence of such units plays the role of strengthening the glass which may be reflected from the increasing behavior between the hardness number and  $\text{Al}_2\text{O}_3$  content.

### 3.3. $^{27}\text{Al}$ NMR investigation

To understand the changes in the NMR spectra of the aluminate structural species, the role of  $\text{Al}_2\text{O}_3$  must be firstly determined. For instance, the addition of  $\text{Al}_2\text{O}_3$  to silicate or borosilicate glasses requires charge compensation which can be achieved by either depolymerization of the silicate network or formation of  $\text{AlO}_6$ . At a high Al/Si ratio (greater than 1), the tetrahedral ( $\text{AlO}_{4/2}$ ) are avoided to linked together [23, 24] and as a result  $\text{AlO}_6$  octahedral must be present in the form  $(\text{AlO}_{6/2})^{3-}$ . The situation is different to a great extend in  $\text{Al}_2\text{O}_3$  borate glasses. since most of  $\text{Al}_2\text{O}_3$  would suppress the continued formation of  $\text{BO}_4$  [25]. This is because  $\text{Al}_2\text{O}_3$  enters as a glass former ( $\text{AlO}_4$ ) which is compensated with a modifier or with octahedral aluminum. Then not all the modifiers can consume in boron transformation but the main portion from  $\text{Ag}_2\text{O}$  can be used to form  $\text{AlO}_4$  units as network former species.

**Figure (7)** represents  $^{27}\text{Al}$  NMR spectra of three different compositions of the studied glasses. An intense  $^{27}\text{Al}$  NMR resonance of chemical shift at about 55, 51, and 44 ppm arising from Al(4) was seen for glasses containing 10, 20, and 30 mol%  $\text{Al}_2\text{O}_3$  respectively. This figure demonstrates that in every composition the main portion of the aluminum is acting principally as a network former ( $\text{AlO}_4$ ) species. Indeed there was a broad spectral peak which evidenced that a little of  $\text{Al}_2\text{O}_3$  enters as Al(6) (small peak at about 16 ppm) in glasses of 20 and 30 mol%  $\text{Al}_2\text{O}_3$ . Similarly, the appearance of the Al(5) resonance only as a shoulder indicates a rather low concentration of this structural type within the glass. The distortions of the peak that represents  $\text{AlO}_4$  resonance may be considered due to the effect of second-order quadrupolar interactions due to the presence of even low concentrations from  $\text{AlO}_5$  structural units within the glass [26]. This consideration can be more evident from the analysis of the experimental spectra by deconvolution process Figures (8-10). The resonance was found to have a contribution as the

observed shoulder which can represent  $\text{AlO}_5$  at about 35 and 40 ppm, Figures (9 and 10). Accurate integration of the NMR spectrum to give precise information concerning the relative amount of these structural elements was possible owing to the separation of the spectra into its component bands. The analyzed broad peak around 16 ppm (figure 8 and 9) represents  $\text{AlO}_6$  octahedral units where such species ( $\text{AlO}_6$ ) is expected to be formed to avoid two  $\text{Al}(4)$  bonding [26, 27].

The NMR data therefore strongly suggest that adding  $\text{Al}_2\text{O}_3$  changes the microstructure of the glass network. For instance, in the high  $\text{Al}/\text{Ag}$  ratio ( $>1$ ), both  $\text{Al}(4)$  and  $\text{Al}(6)$  are significantly formed. But at lower  $\text{Al}/\text{Ag}$  ratios, only  $\text{AlO}_4$  units are considered the main structural species representing the aluminate structure. Given that the excess aluminum can be consumed in constructing a regular silver borate phase containing aluminate species. This would imply that the glass at high alumina content is not homogenous. This result is agreed to some extent with the TEM results presented in Figure 3. As is shown from this figure different species of different morphology are seen (The electron diffraction pattern of this composition confirms the formation of the crystalline structure of the distributed species. On the other hand, the homogenous morphology with amorphous EDP is seen for a glass of lower  $\text{Al}_2\text{O}_3$  concentration Figure (2).

## 4. Conclusion

The structure of silver aluminoborate (NAB) glasses containing a high concentration of  $\text{Al}_2\text{O}_3$  (30 mol%) were studied by X-Ray diffraction, TEM spectroscopy, and  $^{27}\text{Al}$  nuclear magnetic resonance (NMR) spectroscopy. The effects of replacing  $\text{Ag}_2\text{O}$  with  $\text{AlO}_3$  content on the structure of the NAB glasses were evaluated.  $\text{Al}^{3+}$  ion enters into the glass structure mainly in fourfold coordination, forming  $(\text{AlO}_{4/2})^-$  tetrahedral. A small amount of  $\text{Al}^{3+}$  is found in fivefold and sixfold coordination.  $\text{Al}_2\text{O}_3$  acts as network formers producing more bridging oxygen atoms with  $\text{BO}_3$  units. The exchange of  $\text{Ag}_2\text{O}$  with  $\text{Al}_2\text{O}_3$  decreases the conductivity and increases the activation energy for ionic conduction. The hardness of the studied glasses is improved with increasing  $\text{Al}_2\text{O}_3$  content.

## Declarations

### Data Availability

As authors, we are increasingly make our research data available and Data will be made available on request.

### Conflicts of Interest/Competing Interests

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

### Consent to Participate

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

## Consent for Publication

We all of listed authors agree to publish this work in Journal of " Journal of Inorganic and Organometallic Polymers and Materials and agree to all of the publication rights

## References

- [1] G. Okada, K. Shinozaki, T. Komatsu, N. Kawano, N. Kawaguchi, and T. Yanagida, "Tb<sup>3+</sup>-doped BaF<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> glass and glass-ceramic for radiation measurements," *J. Non. Cryst. Solids*, vol. 501, pp. 111–115, 2018.
- [2] A. Tarafder, A. R. Molla, S. Mukhopadhyay, and B. Karmakar, "Fabrication and enhanced photoluminescence properties of Sm<sup>3+</sup>-doped ZnO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass derived willemite glass-ceramic nanocomposites," *Opt. Mater. (Amst.)*, vol. 36, no. 9, pp. 1463–1470, 2014.
- [3] D. C. N. Fabris, M. B. Polla, J. Acordi, A. L. Luza, A. M. Bernardin, A. De Noni Jr, and O. R. K. Montedo, "Effect of MgO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> glass-ceramic as sintering aid on properties of alumina armors," *Mater. Sci. Eng. A*, vol. 781, p. 139237, 2020.
- [4] A. M. Abdelghany and Y. S. Rammah, "Transparent alumino lithium borate glass-ceramics: synthesis, structure and gamma-ray shielding attitude," *J. Inorg. Organomet. Polym. Mater.*, vol. 31, no. 6, pp. 2560–2568, 2021.
- [5] S. V Pershina, E. A. Il'ina, K. V Druzhinin, and A. S. Farlenkov, "Effect of Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> glass crystallization on stability versus molten lithium," *J. Non. Cryst. Solids*, vol. 527, p. 119708, 2020.
- [6] Y. Hou, J. Cheng, J. Kang, J. Yuan, and J. Cui, "Structure, glass stability and rheological properties of Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses doped with Y<sub>2</sub>O<sub>3</sub>," *Ceramics-Silikáty*, vol. 62, no. 2, pp. 173–180, 2018.
- [7] F. Z. Souissi, H. Ettoumi, M. Barré, and M. Toumi, "Preparation and electrical conductivity of potassium phosphate glasses containing Al<sub>2</sub>O<sub>3</sub>," *J. Non. Cryst. Solids*, vol. 481, pp. 585–589, 2018.
- [8] J. M. Delaye, A. Le Gac, S. Macaluso, F. Angeli, F. Lodesani, T. Charpentier, and S. Peugot, "Investigation of alumino-silicate glasses by coupling experiments and simulations: Part I-Structures," *J. Non. Cryst. Solids*, vol. 567, p. 120936, 2021.
- [9] R. Zhang, Z. Wang, Y. Meng, S. Jiao, J. Jia, Y. Min, Y., and C. Liu, "Quantitative insight into aluminum structures in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system via Raman and <sup>27</sup>Al MAS-NMR spectroscopies," *J. Non. Cryst. Solids*, vol. 573, p. 121116, 2021.

- [10] X. Feng, W. Yao, and J. Li, "Effect of  $B_2O_3$  on the structure of  $CaO-Al_2O_3-B_2O_3$  ternary melts: A molecular dynamics simulation," *J. Non. Cryst. Solids*, vol. 574, p. 121141, 2021.
- [11] H. Singh, Q. Shu, G. King, Z. Liang, Z. Wang, W. Cao, M. Huttula, and T. Fabritius, "Structure and viscosity of  $CaO-Al_2O_3-B_2O_3-BaO$  slags with varying mass ratio of  $BaO$  to  $CaO$ ," *J. Am. Ceram. Soc.*, 2021.
- [12] G. El-Damrawi, A. Hassan, and A. Shahboub, "Characteristic studies on  $Ag_2O-Al_2O_3-P_2O_5$  glasses and glass ceramics," *Mater. Sci. Eng. B*, vol. 264, p. 114957, 2021.
- [13] T. Kato, D. Shiratori, M. Iwao, H. Takase, D. Nakauchi, N. Kawaguchi, and T. Yanagida, "Ag Concentration Dependence of Build-up Effect of Radio-photoluminescence in Ag-doped  $P_2O_5-Al_2O_3-Na_2O-SiO_2$  Glasses," *Sensors Mater.*, vol. 33, no. 6, pp. 2163–2169, 2021.
- [14] K. Kato, T. Hayakawa, Y. Kasuya, and P. Thomas, "Influence of  $Al_2O_3$  incorporation on the third-order nonlinear optical properties of  $Ag_2O-TeO_2$  glasses," *J. Non. Cryst. Solids*, vol. 431, pp. 97–102, 2016.
- [15] X. Liu, Z. Xie, C. Zhang, H. Pan, M. N. Rahaman, X. Zhang, Q. Fu and W. Huang, "Bioactive borate glass scaffolds: in vitro and in vivo evaluation for use as a drug delivery system in the treatment of bone infection," *J. Mater. Sci. Mater. Med.*, vol. 21, no. 2, pp. 575–582, 2010.
- [16] A. M. Abdelghany, "Novel method for early investigation of bioactivity in different borate bio-glasses," *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 100, pp. 120–126, 2013.
- [17] A. M. Abdelghany, H. A. ElBatal, and F. M. EzzElDin, "Bone bonding ability behavior of some ternary borate glasses by immersion in sodium phosphate solution," *Ceram. Int.*, vol. 38, no. 2, pp. 1105–1113, 2012.
- [18] J. Hum and A. R. Boccaccini, "Bioactive glasses as carriers for bioactive molecules and therapeutic drugs: a review," *J. Mater. Sci. Mater. Med.*, vol. 23, no. 10, pp. 2317–2333, 2012.
- [19] S. Kurajica, J. Šipušić, M. Zupancic, I. Brautović, and M. Albrecht, "ZnO- $Al_2O_3-SiO_2$  glass ceramics: Influence of composition on crystal phases, crystallite size and appearance," *J. Non. Cryst. Solids*, vol. 553, p. 120481, 2021.
- [20] A. Okasha, S. Y. Marzouk, A. H. Hammad, and A. M. Abdelghany, "Optical character inquest of cobalt containing fluoroborate glass," *Opt. J. Light Electron Opt.*, vol. 142, pp. 125–133, 2017.
- [21] M. Bauchy, M. J. A. Qomi, C. Bichara, F.-J. Ulm, and R. J.-M. Pellenq, "Rigidity transition in materials: hardness is driven by weak atomic constraints," *Phys. Rev. Lett.*, vol. 114, no. 12, p. 125502, 2015.

- [22] P. Liu, K. Januchta, L. R. Jensen, M. Bauchy, and M. M. Smedskjaer, "Competitive effects of free volume, rigidity, and self-adaptivity on indentation response of silicoaluminoborate glasses," *J. Am. Ceram. Soc.*, vol. 103, no. 2, pp. 944–954, 2020.
- [23] A. Abd El-Moneim, I. M. Youssof, and L. Abd El-Latif, "Structural role of RO and Al<sub>2</sub>O<sub>3</sub> in borate glasses using an ultrasonic technique," *Acta Mater.*, vol. 54, no. 14, pp. 3811–3819, 2006.
- [24] S. Bruns, T. Uesbeck, D. Weil, D. Möncke, L. van Wüllen, K. Durst, and D. De Ligny, "Influence of Al<sub>2</sub>O<sub>3</sub> addition on structure and mechanical properties of borosilicate glasses," *Front. Mater.*, vol. 7, p. 189, 2020.
- [25] G. P. Singh, S. Kaur, P. Kaur, and D. P. Singh, "Modification in structural and optical properties of ZnO, CeO<sub>2</sub> doped Al<sub>2</sub>O<sub>3</sub>–PbO–B<sub>2</sub>O<sub>3</sub> glasses," *Phys. B Condens. Matter*, vol. 407, no. 8, pp. 1250–1255, 2012.
- [26] T. Schaller and J. F. Stebbins, "The structural role of lanthanum and yttrium in aluminosilicate glasses: A <sup>27</sup>Al and <sup>17</sup>O MAS NMR study," *J. Phys. Chem. B*, vol. 102, no. 52, pp. 10690–10697, 1998.
- [27] W. F. Du, K. Kuraoka, T. Akai, and T. Yazawa, "Study of Al<sub>2</sub>O<sub>3</sub> effect on structural change and phase separation in Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass by NMR," *J. Mater. Sci.*, vol. 35, no. 19, pp. 4865–4871, 2000.

## Figures

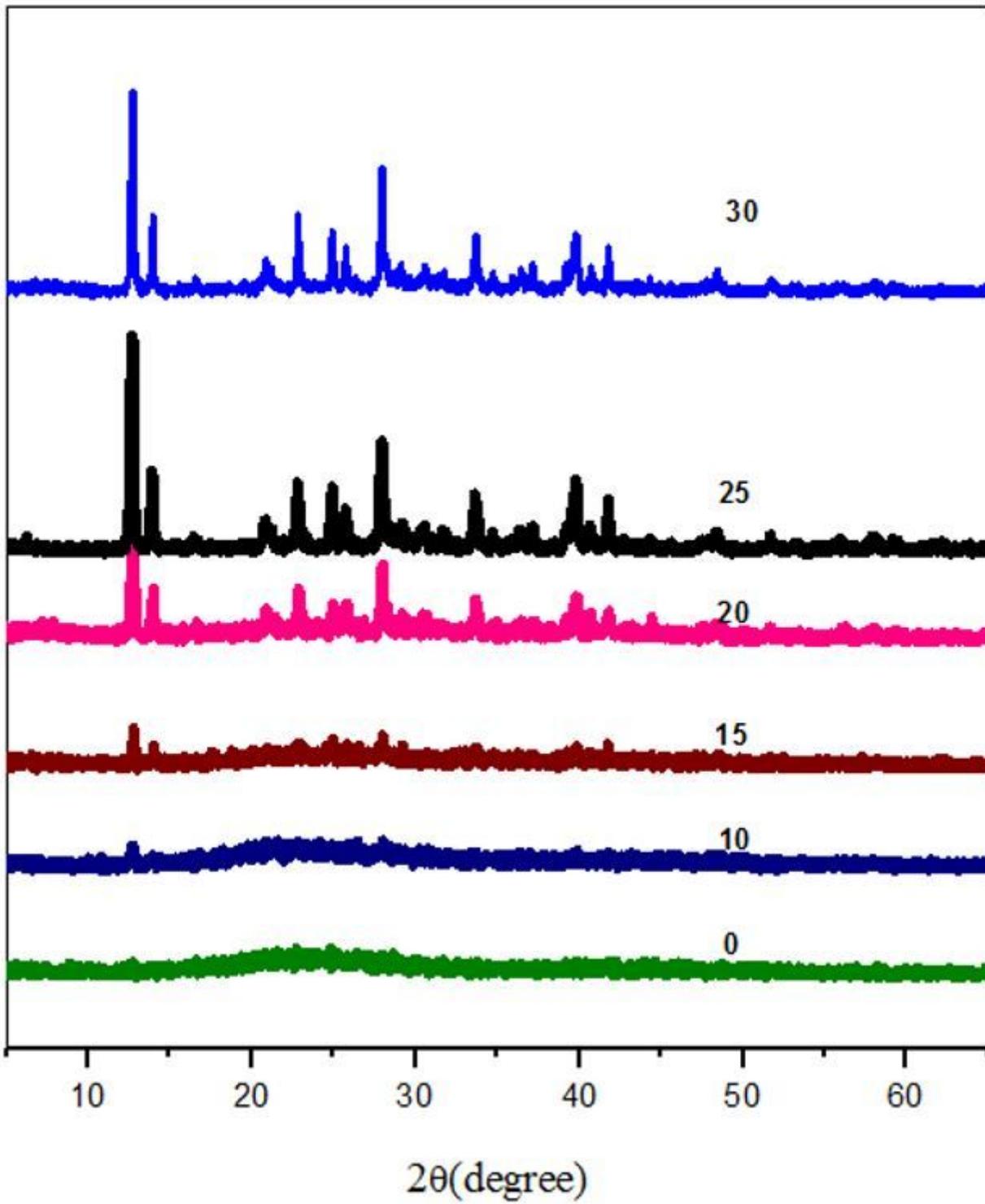


Figure 1

X-ray diffraction spectra of some glasses.

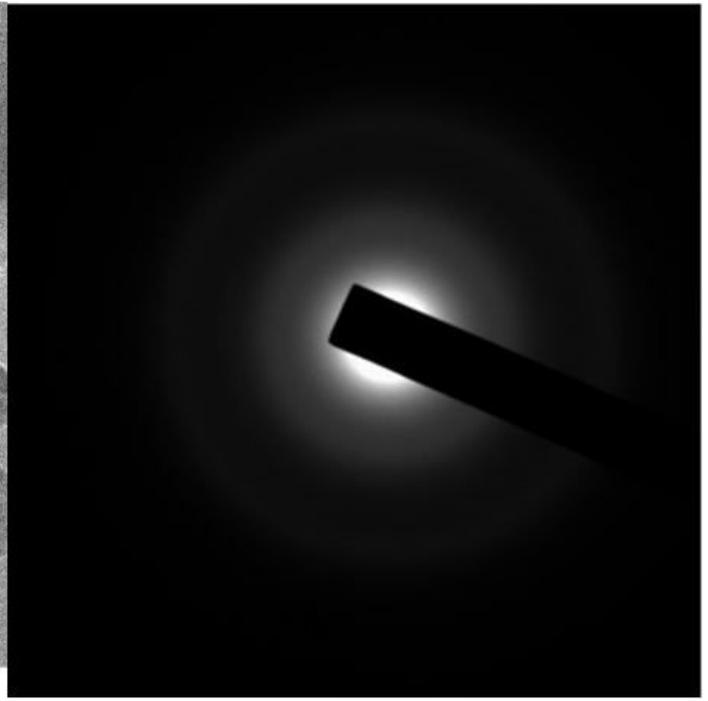
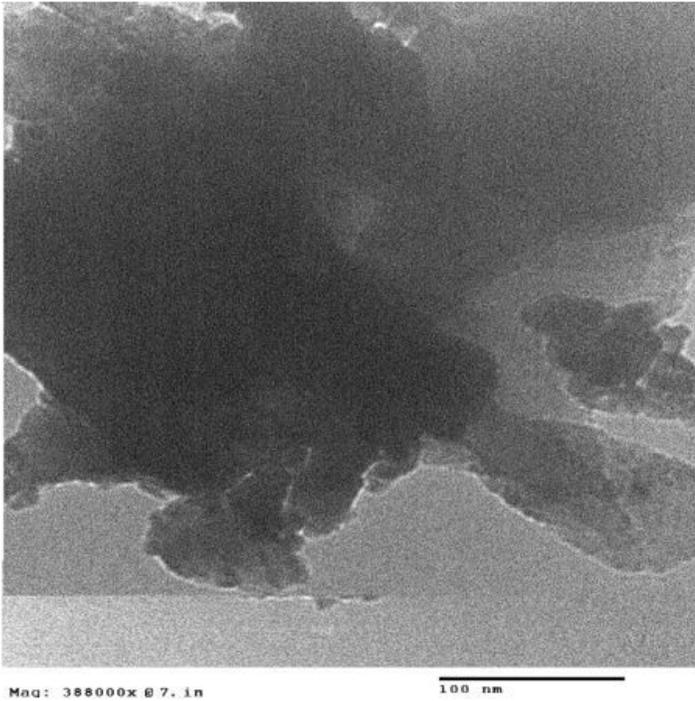


Figure 2

SEM -EDP for a glass containing 15 mol% Al<sub>2</sub>O<sub>3</sub>

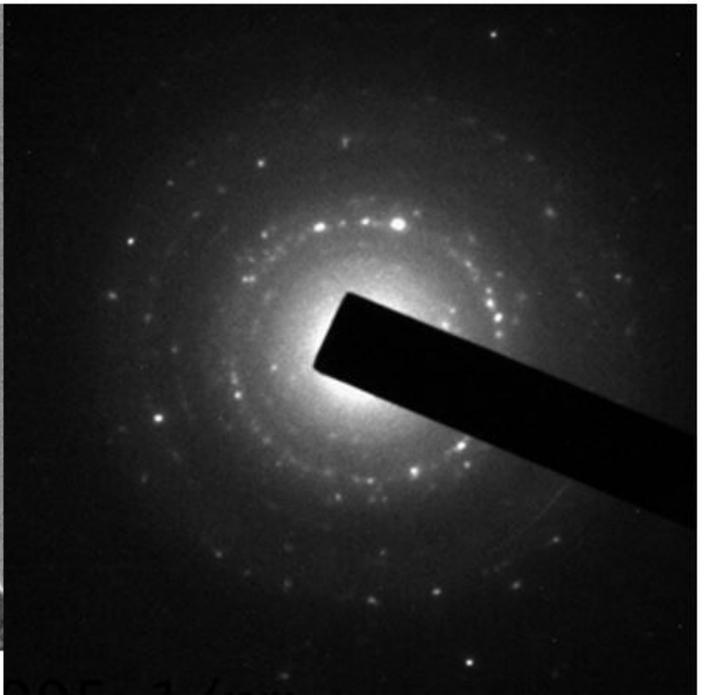
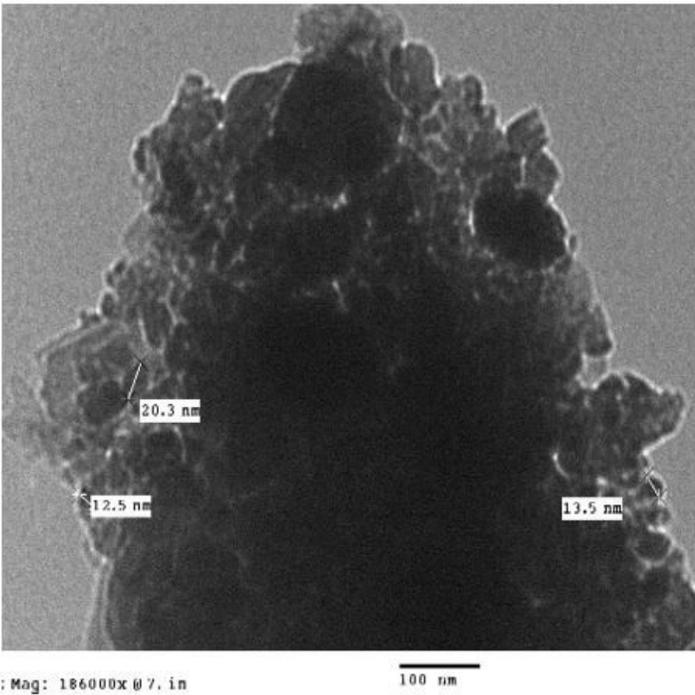


Figure 3

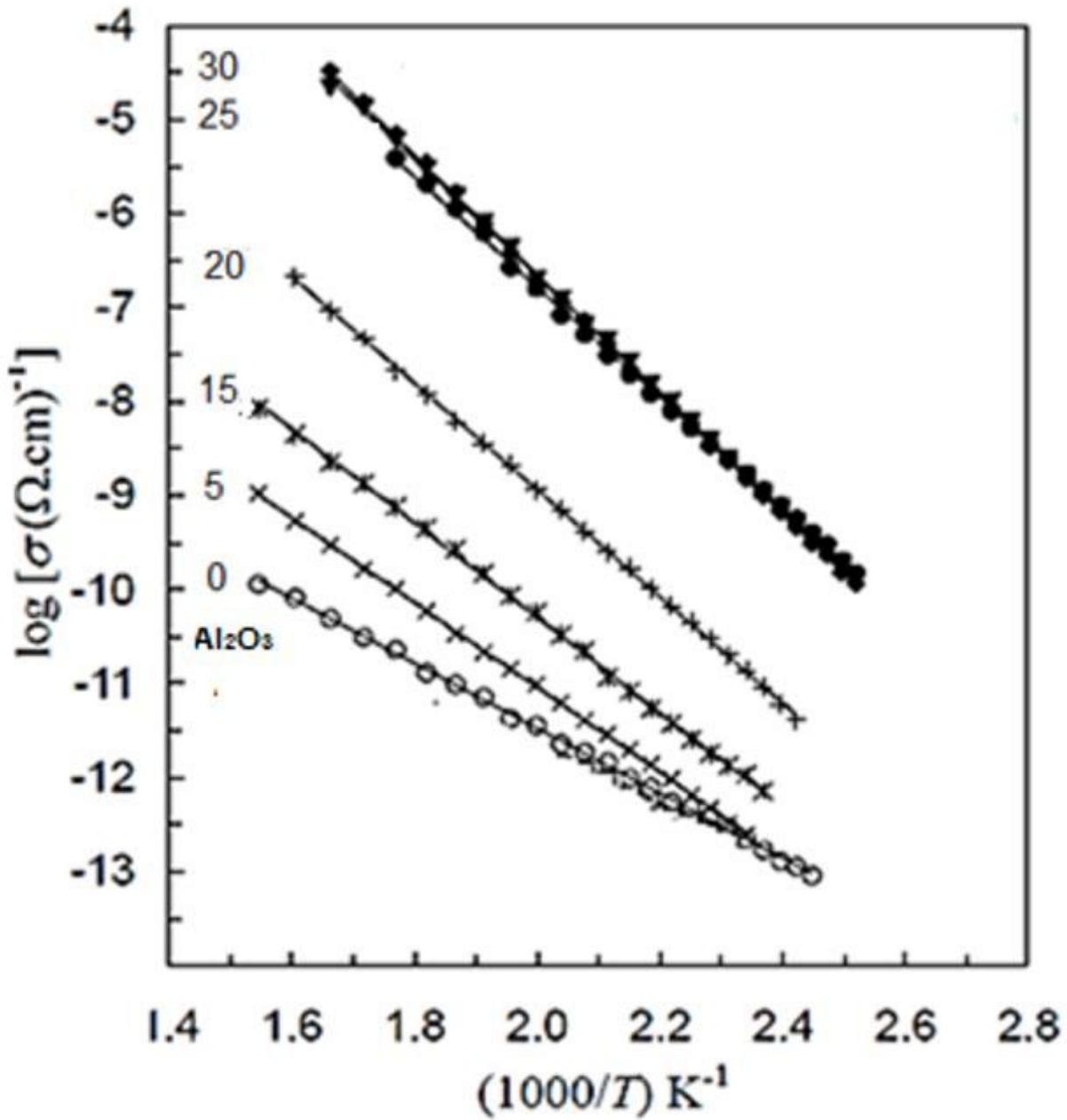
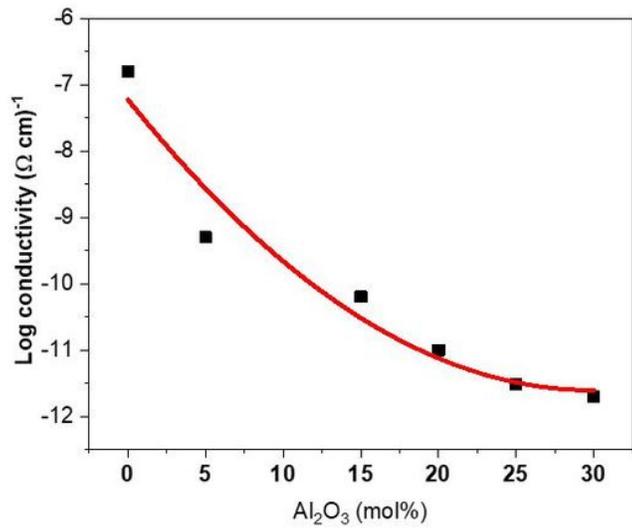
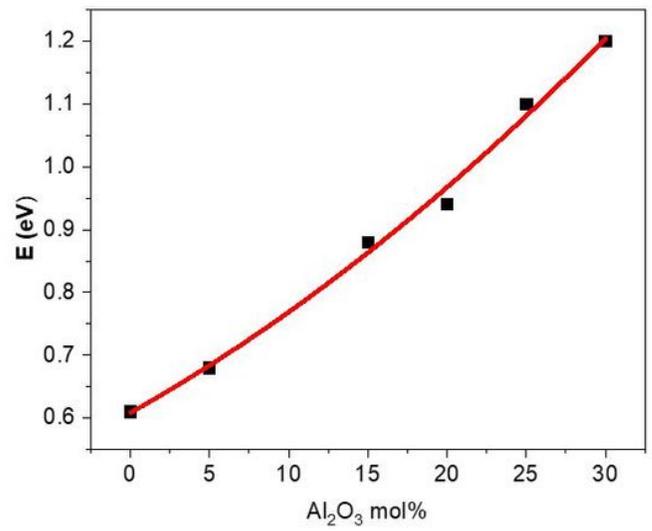


Figure 4

Logarithm of conductivity (log s) with reciprocal of absolute temperature (1000/T)



(a)



(b)

**Figure 5**

changes in log  $s_{200}$  and E with increasing Al<sub>2</sub>O<sub>3</sub> contents.

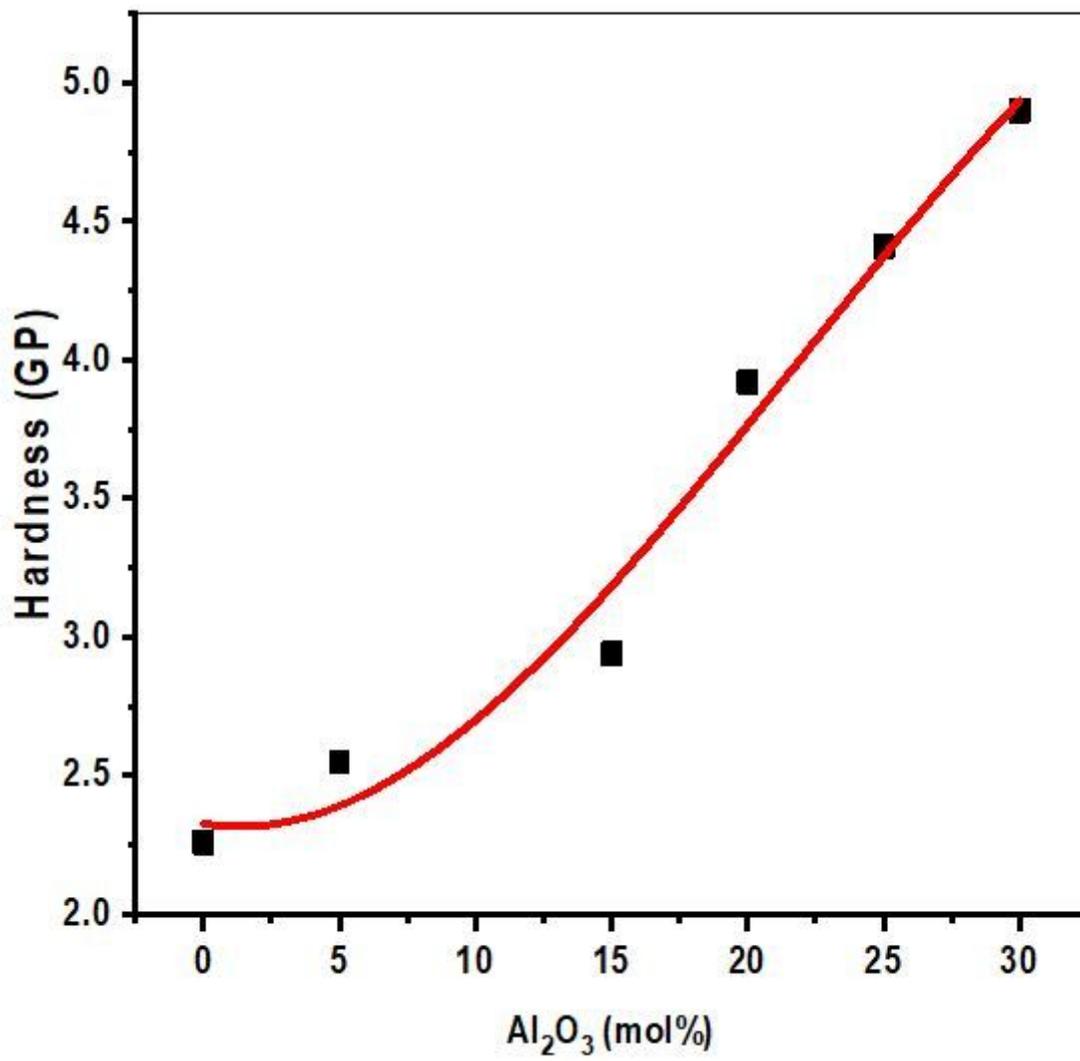


Figure 6

variation of Vickers Hardness number with increasing Al<sub>2</sub>O<sub>3</sub> content

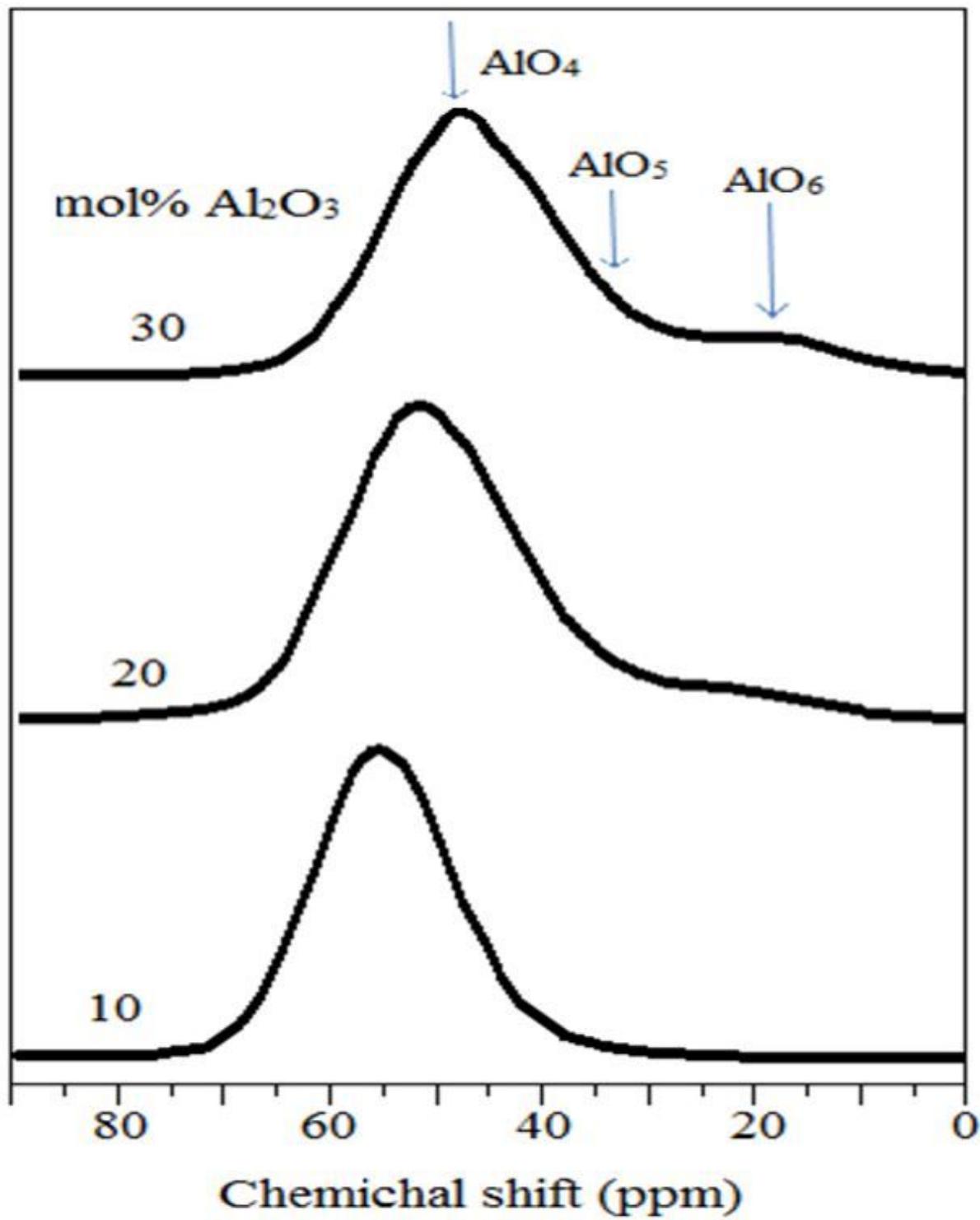


Figure 7

$^{27}\text{Al}$  MAS NMR spectra of sodium borate glass containing 10, 20, and 30 mol%  $\text{Al}_2\text{O}_3$

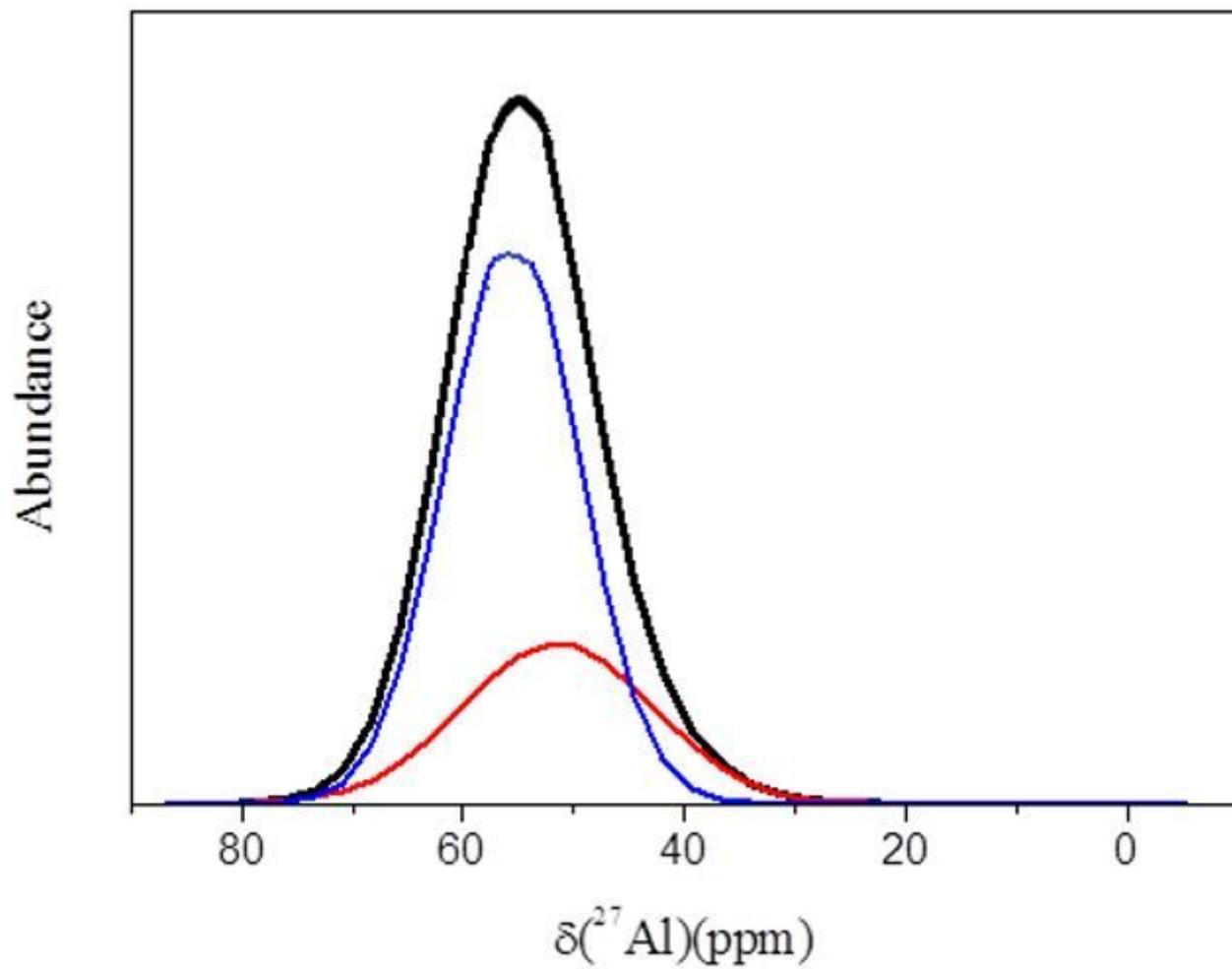


Figure 8

Peak separation and integration for a glass containing 10 mol%.

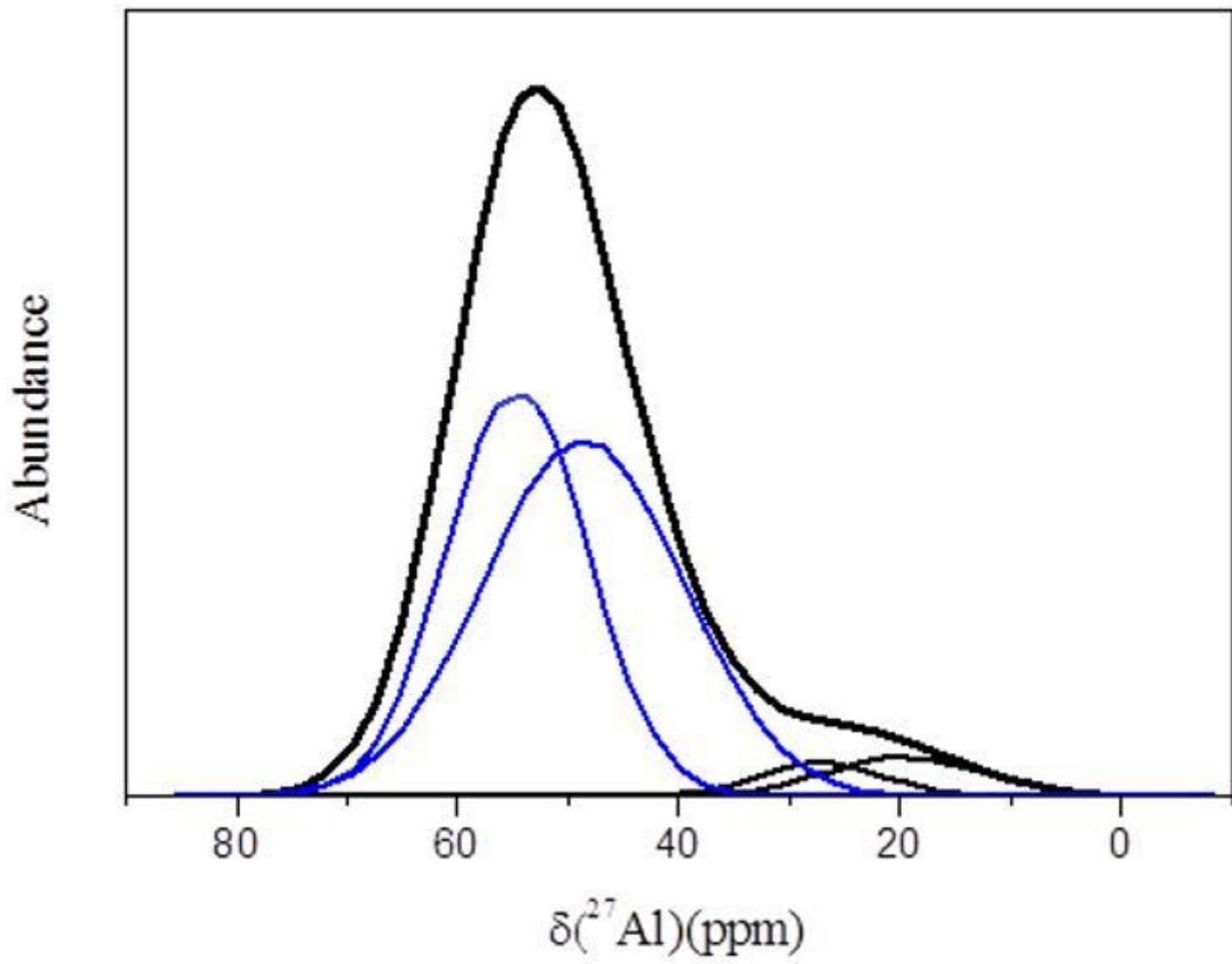


Figure 9

Peak separation and integration for a glass containing 20 mol%.

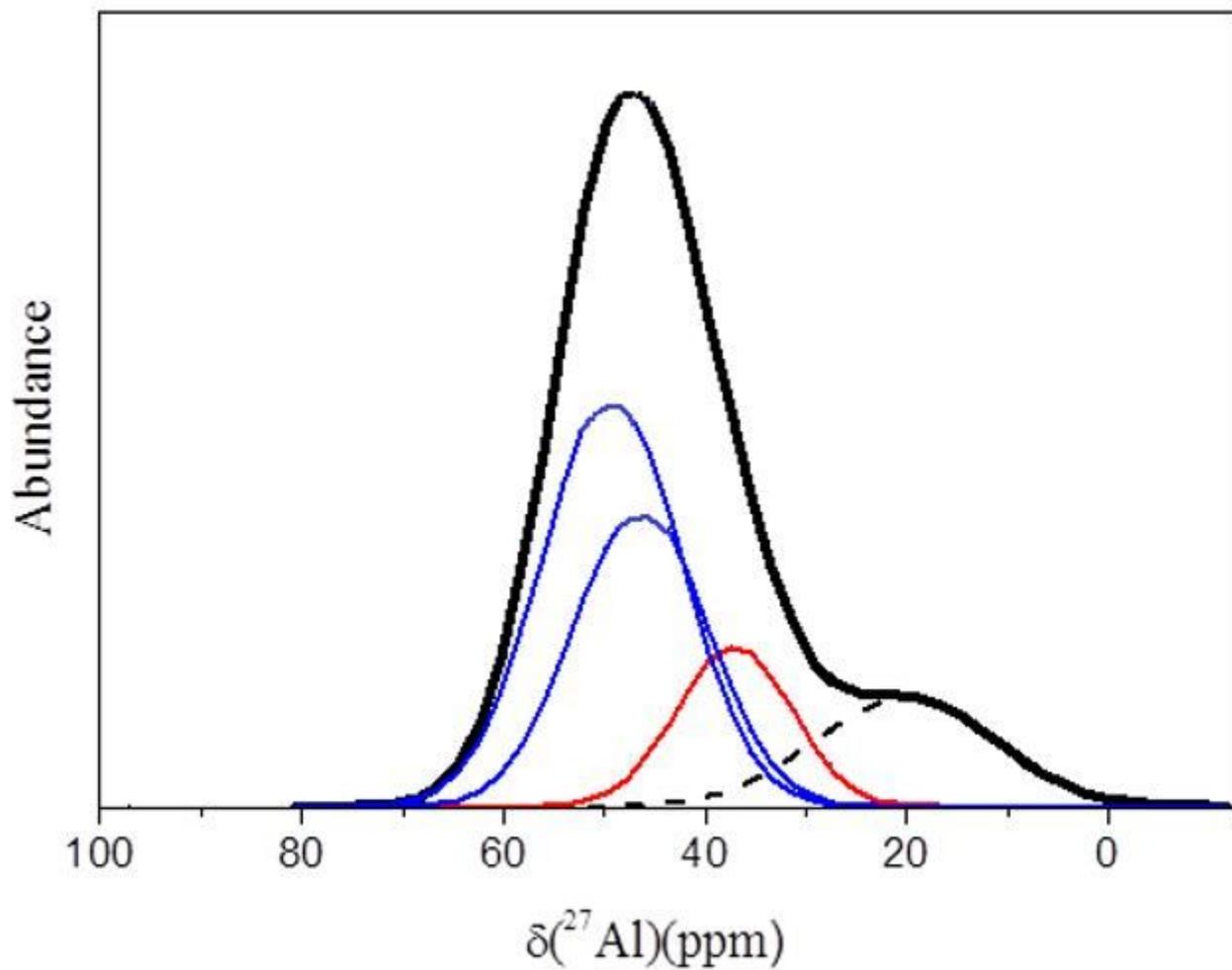


Figure 10

Peak separation and integration for a glass containing 30 mol