

The effect of the iron redox on aluminoborate glasses: from nano to macroscopic scale

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The structure and properties of glasses in the CaO-Al₂O₃-B₂O₃ (CAB) system play an important role in materials sciences. Small amounts of boron can significantly modify the structure of these glasses. However, additional complexity arises from the introduction of iron which may be in two different oxidation states. The aim of our study is to investigate the structural effect of the iron redox on CAB glasses prepared by classical quenching. The CAB35.02 glass (CABX.Y where X= %mol of Al₂O₃, Y= %mol of B₂O₃ and 100-(X+Y)=%mol of CaO) was modified by adding different amounts of Fe₂O₃ ranging from 4% to 16% mol. Fe³⁺ and Fe²⁺ are mainly in tetrahedral and octahedral coordination, respectively, although other coordination states exist for both cations. As a first approximation, Fe²⁺ is a network-modifier cation and Fe³⁺ a network former, sometimes playing the role of a charge compensator with the presence of alkali and alkaline earth elements. The oxidation state of iron in Al₂O₃-CaO-B₂O₃-Fe₂O₃ system has been determined by X-ray absorption near edge structure (XANES) and Raman spectroscopies. Both techniques agree with the wet chemical analysis and confirm the presence of iron mostly in (+3). Moreover, an unusual band appears in Raman spectra around 700cm⁻¹, in aluminoborate glasses, attributed to Fe³⁺ whereas the trivalent iron common band is generally ~980cm⁻¹ in silicate glasses. Besides the structural changes, the presence of iron has an impact on the macroscopic properties of the glasses. Glass transition temperature, T_g , decreases with the addition of iron and a drastic change in viscosity values is observed.