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On the Mixed Alkali Effect in the 0.17[xLi2O(1-x)Na2O]•0.33CaO•0.50SiO2 Glass System

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The well known mixed alkali effect remains one of the challenging open questions to be solved with respect to ionic conduction in glasses. In fact, when one alkali ion is progressively substituted by another, several examples reveal a drop of up to 2-3 orders of magnitude in electrical conductivity, at room temperature. It has also been observed that this decrease in electrical conductivity is followed by an increase in the activation energy, Ea. However, little, if any, attention has focused on the pre-exponential term A of the Arrhenius expression: ST=Aexp(-Ea/kT) Using impedance spectroscopy, we have measured the electrical conductivity of glass samples of the 0.17[xLi2O(1-x)Na2O]•0.33CaO•0.50SiO2 system (where x=0.0, 0.1, 0.2, 0.3, 0.5, 0.7, 1.0). This glass system was chosen due to parallel crystallization studies. The mixed alkali effect is observed, with electrical conductivity presenting a minimum for the x=0.5 composition, while the activation energy and the pre-exponential term of the Arrhenius equation present a maximum for the same composition. This work discusses the influence of the pre-exponential term on the value of electrical conductivity, and makes an exploratory analysis of this pre-exponential term based on microscopic and thermodynamic characteristics. Samples of 0.17Na2O•0.33CaO•0.50SiO2 glass with the addition of up to 7.5-mol % of Li2O are also investigated. In this case, a weak but well defined decrease in the electrical conductivity is observed with the addition of up to 3 mol% of Li2O. A further increase in Li2O content leads to an increase in electrical conductivity. The slight decrease in electrical conductivity and the shift of the minimum to a smaller amount of Li2O content indicate a competitive effect between the increase in alkali content and the mixed alkali effect.