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Ionic conductivity and mixed ion effect in metaphosphate glasses.

The study of phosphate glass structures has basic and technological interest for applications in optics, biomaterials and glass to metal seals, due to the close correlation of the macroscopic properties desired in mentioned applications and the structure of the vitreous network of those glasses. The mixed ion effect (MIE) is the non-linear variation of some properties of a glass (e.g., viscosity, conductivity, density) when an cation specie is substituted by a homologue, at constant total cation concentration. Several theories have been proposed trying to elucidate this effect based on dynamical or structural particulars of the cation insertion and diffusion in the glass matrix. Some structural aspects, such as the occurrence of uniform cation dispersion or cation clustering, are indispensable to develop and test models, and are the center of attention in simulations and other experimental studies. Mixed alkali metaphosphate glasses $A_{(1-x)}B_xPO_3$ (0 ≤ x ≤ 1) show cation size mismatch between the two mobile species resulting in mixed-ion effects (MIE) in the dc conductivities and glass transition temperatures. In this work, mixed alkali metaphosphate glasses based on K-Na, Rb-Na, Rb-Li, Cs-Na and Cs–Li combinations were studied by impedance spectroscopy, differential scanning calorimetry (DSC) and Raman spectroscopy. The dc conductivity and the activation energy for conduction show a strong mixed-ion effect decreasing by more than six orders of magnitude. The results show that the mixed-ion effect on the dc conductivity decreases as the temperature is increased. The mixed-ion effect was observed on glass transition and melting temperatures, T_g and T_m respectively. The present study confirms that the mixed-ion effect of the dc conductivity could be explained as a natural consequence of random ion mixing, considering that ion transport is favored between well-matched sites and impeded by the structural mismatch between neighboring sites for dissimilar ions.

Tipo de Apresentação

Poster

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