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Impedance spectroscopy in soda-lime glasses with and without Ag ion exchange and subsequent thermal treatment

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The influence of silver on the electrical conductivity of some soda-lime-silica glasses was studied. Glasses with composition (mol%) $22\text{Na}_2\text{O} \cdot 8\text{CaO} \cdot 65\text{SiO}_2 \cdot 5\text{MO}_2$ ($M = \text{Si, Ti, Ge, Zr, Sn, Ce}$) were prepared. Silver was introduced in the glasses by Ag^+/Na^+ ion exchange at 350 °C for 1 h. The ion exchanged samples were further submitted to a thermal treatment at 500 °C for 24 h. The electrical measurements were performed with a Solartron impedance analyzer. Z'' vs. Z' and conductivity vs. f plots for several temperatures were obtained to determine the activation energy for electrical conductivity, E_a , at the low frequency limit, by two different ways. After $\ln \sigma_{dc}$ vs. T^{-1} plots we calculated $0.72 < E_a < 0.83$ eV. These values are in agreement with those found in the literature for soda-lime-silica glasses. The conductivity values obtained for the ion exchanged samples show a small increase comparing to the pristine glass samples, probably due to the increasing number of charge carriers, mainly Ag^+ ions, in the glass matrix. The thermal treatment reduces the conductivity of the samples which can be attributed to a higher polymerization degree of the glass structure due to the formation of metallic silver nanoparticles in the glass matrix or to the blocking effect related to these particles, that obstruct the Na^+ ion displacement. The presence of the nanoparticles was confirmed by the UV-visible optical absorption spectra which present an absorption band with maximum at ~ 420 nm. The shape of this band enables to calculate the size of the nanoparticles. The decrease in electrical conductivity was different for each glass composition submitted to ion exchange and subsequent thermal treatment. The electrical conductivity of the Ce-containing glass was less affected by both ion exchange and thermal treatment. The profile of Ag in this glass, obtained by energy dispersive X-ray spectroscopy (EDS), show that the silver remain in the vicinity of the surfaces even after the thermal treatment, which leads to conclude that the Ce^{4+} in the glass presents a similar behavior like Ca^{2+} , in the sense that both, as modifying oxides, block the diffusion of Na^+ and Ag^+ during the nanoparticle growth as well as during the conductivity measurements. Financial support: FAPESP (Grant nº 2008/07304-7)