Phosphate Glass and Glass Ceramics as Conductive Solid Electrolytes

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Introduction

Glass ceramics are polycrystalline materials produced from the controlled crystallization of glasses. Thus, the glass ceramics combine important features of glassy and crystalline materials, such as, for example, ion conductivity[1]. This characteristic is interesting since it makes possible to investigate the use of glass ceramics as energy storage systems enabling their use as secondary batteries, which are rechargeable batteries.[2]

It is well known that the interaction of alkali metals with transition metals may lead to formation of structures like bronzes, which may present values of conductivity.[3,4] This new structure has regions constructed from the glass former, with covalent bonds, and inter-network regions made up from the transition metals, ionic or non-bridging bonds. Therefore, the ionic transport will be most easily supported via the modified regions.[5] Hereby, it is interesting to investigate glass ceramics capability as ionic conductors and its use as energy storage systems.

Results and Discussion

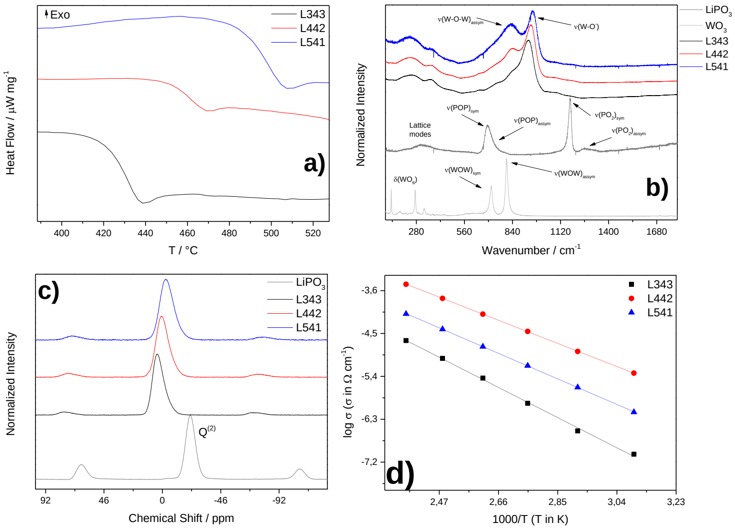
Vitreous samples were synthesized in the WO_3-$(LiPO_3)_n$-Li_2O system. Glass ceramics were produced by heating the glasses 50 ºC above Tg for 0 - 24 h. The code for the samples is LXY(1-X-Y), with L being the system, X the percentage of WO_3, Y the percentage of $(LiPO_3)_n$ and (1-X-Y) the percentage of Li_2O. All three values were multiplied by 10 for convenience.

DSC analysis, Fig. 1a, shows that Tg values increases with higher WO_3 content, leading to the depolymerization of P-O-P chains in these glasses.

RAMAN spectra, Fig. 1b, exhibits an increase of intensity of W-O-W bonds, ~830 cm^{-1}, and decrease of W-O^-, ~947 cm^{-1}, bonds due to higher incorporation of WO_6 units into the glasses structures. ^{31}P MAS-NMR spectra, Fig. 1c, sugest only the presence of PQ_2 units, i.e. O-P-O chains in the structure. In addition, the increases of WO_3 into the samples displaces the chemical shift to negative values, due to the electropositivity of W atoms, decreasing the electron density surround of the P atoms. This suggests the replacement of O-P-O bonds for W-P-O bonds in the glass structure.

Impedance Spectroscopy, Fig. 1d, for these glasses shows that incorporation of WO_3, leads to lower ionic conductivity, due to the formation of cluster of WO_6 units in the structure. Although, its activation energy for ionic conduction is lowered at the same time.

Figure 1 – DSC analysis (a), RAMAN Spectroscopy (b), ^{31}P MAS-NMR (c) and Impedance Spectroscopy (d) of the samples L343, L442 and L541.



Conclusions

We believe that are some equilibrium point between the amount of WO_3 incorporated and maximum ionic conductivity in the samples. The formation of glass ceramics with thermic treatment and its influence on ionic conductivity is, currently, being investigated.

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