Tungsten Glass Ceramics as Conductive Solid Electrolytes

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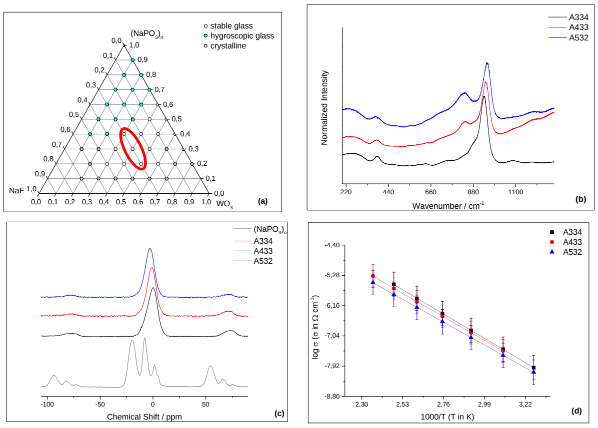
Introduction

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

The vitreous samples were synthesized in the WO_3-$(NaPO_3)_n$-NaF system. The glass ceramics were produced by heating the glasses 50 ºC above Tg for 0.5 h. The code for the samples is AXY(1-X-Y), with A being the system, X the percentage of WO_3, Y the percentage of $(NaPO_3)_n$ and (1-X-Y) the percentage of NaF. All three values were multiplied by 10 for convenience.
The ternary diagram, Fig. 1a, shows that glasses in this system, white dots, have good thermic stability, with Tx-Tg~100 °C. In this work, the compositions A334, A433 and A532, red circle, were selected to study the thermal, structural, optical and ionic conductivity properties.
DSC analysis indicates that the Tg values decreases with higher NaF content, which implies in a break of the WO_6 units. RAMAN spectra, Fig. 1b, shows that increasing NaF content leads to depolymerization of WO_6 units, what is characterized by the decreasing in intensity of W-O-W bonds, ~885 cm^{-1}, and increasing of W-O^-, ~945 cm^{-1}, bonds ^{31}P NMR spectra, Fig. 1c, sugests only the presence of PQ_3 units, i.e. the phosphate units must be intercalated to the WO_6 units. In addition, the increase of NaF into the samples displaces the chemical shift to positive values. This is due to the deshielding effect of the F^- ions, decreasing the electron density around the protons of the P atoms. This effect is stronger at higher amount of NaF, suggesting that F^- are replacing O atoms in the phosphate.
Impedance Spectroscopy, Fig. 1d, shows that increasing NaF, leads to higher ionic conductivity.

Figure 1 – Ternary diagram of the glass system (a), RAMAN Spectroscopy (b), ^{31}P NMR (c) and Impedance Spectroscopy (d) of the samples A334, A433 and A532.



Source: Elaborated by the authors (2015).

Conclusions

We believe that the higher the quantity of NaF in the glass ceramics, more W-O^- bonds are formatted, which favors the mobility of Na^+ and F^- ions through the structure, rising the ionic conductivity of the material.

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