Structural and electrical characterization of $K_{(1-x)}(NH_4)_xH_2PO_4$ mixed crystal.

F. M. Souza[a], C. J. Franco[b] and R. F. Bianchi[b]

[c]*Departamento de Engenharia Metalúrgica e Materiais, Escola Politécnica, Universidade de São Paulo, São Paulo, Brasil.*
[b]*Departamento de Física, Universidade Federal de Ouro Preto, Ouro Preto, Brasil.*

$K_{1-x}(NH_4)_xH_2PO_4$ - $KADP_x$, 0.0<x<1.0 mixed crystals exhibit different physical properties, piezoelectric, antiferroelectric, ferroelectric, nonlinear optical are currently found in this compounds depending of the x value.

The structural and electrical characterization of $K_{1-x}(NH_4)_xH_2PO_4$ - $KADP_x$ mixed crystals grown by the method of solvent evaporation at 40ºC and with x = 0.076, 0.118, 0.357, 0.857 and 0.942 was carried out.

Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) was performed in order to determinate x for each mixed crystal and thermogravimetric analysis (TGA) and X-ray diffraction (XRD) measurements have been carried out on $KADP_x$ in the temperature range of 30ºC - 450°C.

Our results show that, in the decomposition process, the shifts in the mixed crystals TGA curves are dependent on x in mixed crystals.

As compared with the TGA, the direct reflection of the exchange of constituent cations (NH_4^+ and K^+) increases with the addition ammonium and this conjecture concerning the matching of the exchange agrees with the increase of lattice parameters of crystals observed by XRD results.

The measured ac impedance data are analyzed as a function of frequency in the temperature range between 20ºC and 160°C. An equivalent circuit model based on two parallel G–C circuits was adopted to describe the impedance relaxational behavior observed in the crystals.

The conduction is attributed to the hopping of proton among hydrogen vacancies, however additional defects can be created by breaking the hydrogen bond of the ammonium groups.

Migrations of H_2O molecules due to the presence of inclusions in the mixed crystals, as well as potassium and ammonium ions are suggested to have the contribution to the electrical conduction at high temperatures.

The activation energies of migration were obtained in different temperature ranges. In the mixed crystals in ADP-rich (x = 0.942 and 0.857) and in KDP-rich (x = 0.076) the obtained dc conductivity is improved. Moreover, the microscopic environment around ammonium is more conducting than the environment around potassium in the $KADP_x$ crystals.

References:
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