CONDUCTIVE PROPERTIES OF ALIOVALENT-SUBSTITUTED KTP-ANALOGUES $KM^{II}_{0.333}Nb_{0.667}OPO_4$ (M^{II} – Mn, Co, Ni)

A.A. Babaryk[1], I.V. Zatovsky[1], R.N. Kuzmin[1], N.S. Slobodyanik[1], V.N. Baumer[2]

[1] Taras Shevchenko Kyiv National University, Kyiv, Ukraine
[2] STC Institute for Single Crystal "NAS" of Ukraine, Kharkiv, Ukraine
E-mail: babaryk@bigmir.net

Complex phosphates with $KTiOPO_4$ (KTP) structure are well-known ferroelectric materials for optoelectronics, mainly due to the special domain organization. Here we report the structure, single crystal growth and conductive properties study of aliovalent-substituted KTP analogues $KM^{II}_{0.33}Nb_{0.67}OPO_4$ (M^{II} – Mn, Co, Ni). Electrophysical properties of crystalline and glassy samples were studied using the impedance spectroscopy method. The direct oscillography technique was applied to measure the magnitude (Z) and the phase shift (φ) of impedance. Frequency and temperature ranges were extended from $f_{min} = 0.1$ Hz to 30 MHz and from 293 K to 803 K, correspondingly. The amplitude of the probing sinusoidal alternating voltage was chosen from issue to obtain the linear response. All data were corrected on the LRC properties of extrinsic measurement circuit. On the basis of experimental data the real, Z' and imaginary, Z'' components of samples impedance were calculated. These values are used to construct the complex impedance spectra (Cole-Cole plots for impedance) by non-linear least square fitting. At all temperatures these plots can be represented by parallel connection of resistor R_{dc} and constant phase element Q. We consider the resistor R_{dc}, as the ideal bulk resistance of the sample and use it to determine the own conductivity of the material. It was found that dc-conductivity is increasing with temperature growth. This fact is due to increase in the thermally activated drift mobility of ions according to the hopping conduction mechanism [1]. The complex electric conductivity $\sigma(\omega) = \sigma'(\omega) + j\sigma''(\omega) = (L/S) Z^{*-1}$, where $\omega = 2\pi f$, L is a distance between electrodes and S - electrode area. The frequency dependence of complex conductivity is well described by known power law for the model of hopping relaxation $\sigma(\omega) = \sigma_{dc} [1 + (\omega/\omega_h)^n]$, where ω_h corresponds to the average frequency of ions hopping – ν_h. The latter value can be determined under the condition $\sigma(\nu_h) = 2\sigma_{dc}$. The temperature dependence of ions hopping frequency shows the activation behavior and obeys to the equation of Arrhenius type – $\nu_h = \nu_0 \exp(-\Delta H_h /kT)$, where ΔH_h represents the enthalpy of hopping frequency activation. The $Z''(\omega)$ dependency shows maxima, frequency of which dependents on temperature. The value, that is inversed to frequency of maxima $-\tau = 2\pi/\omega$, has the physical meaning of time. The straight-line behavior of τ versus $1000/T$ shows the Debye-like centers responsible for Z'' behavior. It is believed that Debye-like centers correspond to dipole-dipole interactions related to either induced type of dipoles or the second-order Janh-Teller effect of d^0(Nb)-p_π(O) conjugated system.

References
[1]   D.P. Almond, C.C. Hunter, A.R. West. *J. Mater. Sci.* (1984). 19, 3236-3248.