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Dielectric relaxation and electronic spectroscopy of double potassium yttrium tetraoxophosphate(V) $K_3Y(PO_4)_2$ doped by neodymium and europium ions

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ABSTRACT

The paper presents the results of our investigation on electric properties of double potassium yttrium tetraoxophosphate(V) doped by lanthanide ions $K_3Y_{(1-x)}Ln_x(PO_4)_2$ ($x = 0.01$, 0.05, Ln = Eu^{3+}, Nd^{3+}). Electric permittivity and dielectric loss measurements have been performed on polycrystalline samples in the temperature range −50 °C to +120 °C and frequency range 1 kHz–1 MHz by means of HP 4282A impedance meter. The frequency and temperature dependence of electric properties were analyzed by theoretical models of dielectric relaxation in order to obtain information abut molecular dynamic of our solids in external electric field.

1. Introduction

We would like to present the final part of our work concerning on dielectric properties in triple potassium yttrium lanthanide tetraoxophosphates(V) $K_3Y_{(1-x)}Ln_x(PO_4)_2$ ($x = 0.01$, 0.05) where Ln = Nd^{3+} and Eu^{3+}. The structural and spectroscopic properties of the Nd^{3+} and Eu^{3+} doped alkaline metal yttrium double tetraoxophosphate(V) with general formula $M_3Y_{(1-x)}Ln_x(PO_4)_2$ (M = Na, Rb, K: $x = 0.01$–0.3) were investigated by several authors [1–10]. In the recent years, the trivalent ions Eu^{3+} and Nd^{3+}, particularly YAG:Nd^{3+}, have acquired a prominent role in the laser technology. The structure of $K_3Y(PO_4)_2$ presented by Ushakov and Navrotsky [9] and Komissarova et al. [10] is describing as a monoclinic system with space group $P2_1/m$, with the cell parameters: $a = 7.358$, $b = 5.613$, $c = 9.349$ Å, $\beta = 90°.92'$ and $Z = 2$. This structure reminds a distortion of glaserite structure called the arcanite-type of $K_3Na(SO_4)_2$. Where the main subunit of octahedron [LnO_6] is connecting with alternately arranged up and down [PO_4] groups in its five vertices. The one tetrahedron group divides one of its edge with a polyhedron containing Ln. So, the number of coordination of Ln^{III} rises into 7 and symmetry of space group decreases from hexagonal to monoclinic. The potassium ions are situated along c axis among layer formed by tetrahedron and octahedron.

Trivalent lanthanide ions doped inorganic materials have received much attention because of their potential applications in variety of devices as optical switches for infrared and visible radiation, laser, optical detectors, sensors etc. Luminescence properties depend strongly on the crystal structure of the host materials. Eu^{3+} has such particular properties that it is considered the best choice to act as a probe to investigate the local structure in solid state materials. The luminescence electric dipole $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions are parity-forbidden. The intensity of these transitions depends strongly on the site symmetry in a matrix. Europium can be in crystalline hosts simultaneously in the form Eu^{3+} and Eu^{2+} that lead to formation of oxygen vacancies. Among the lanthanides, Nd^{3+} is recognized as one of the most efficient ions for solid-state laser materials due to its luminescence transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ with maximum of emission at about 1064 nm. The luminescence properties of Eu and Nd-doped $K_3Y(PO_4)_2$ crystalline samples and the excited state dynamics of the emitting levels have been reported in this paper.

The lanthanides usually occur as trivalent ions, although europium readily forms divalent compounds. Therefore, in order to confirm the oxidation states of ions other than 3+, the emission and absorption spectra in the ultraviolet and near infrared were carried out. Optical studies were complement to the dielectric responses and have helped in the interpretation of results of the molecular dynamics obtained by the methods of dielectric relaxation.

For data obtained in system where amount of doped material is 1% of Nd^{3+} and for the higher range for temperature of 5% Eu^{3+} the

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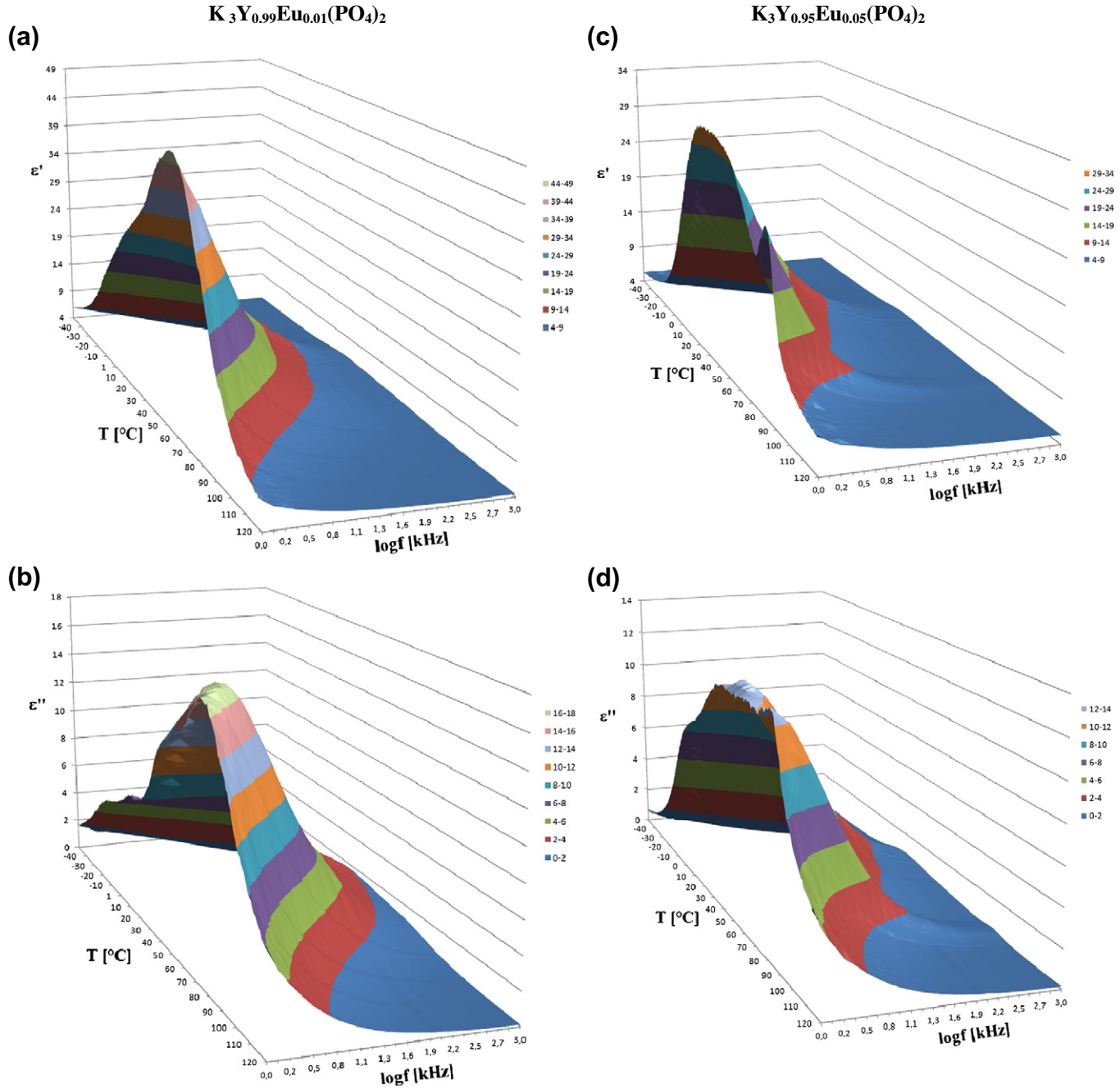

Fig. 1. The real and imaginary part of electric permittivity versus temperature and frequency for $K_3Y_{0.99}Eu_{0.01}(PO_4)_2$ and $K_3Y_{0.95}Eu_{0.05}(PO_4)_2$.

dielectric relaxation can be described by two-parametric dielectric response function of the Havriliak–Negami (HN) [11] (Eq. (1)).

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (i\omega\tau)^{1-\alpha})^\beta} \quad (1)$$

In the case of 1% and 5% Eu^{3+} and 5% Nd^{3+} our analysis has proved that one-parametric dielectric response function of the Cole and Cole [12] better describes the dependence of complex permittivity (Eq. (2)).

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (2)$$

where ε_s and ε_∞ are the static and optical permittivity respectively, α and β are the empirical coefficients ($0 \leqslant \alpha, \beta \leqslant 1$) and ω is the frequency of the relaxation process. The average values of relaxation times ($\tau = 1/\omega$) were obtained from the fitting of Havriliak–Negami and Cole–Cole equations in whole range of frequencies. Unfortunately, experimental points are located in high frequency region of the spectrum what results in large uncertainty of the fitted parameters. Matching mentioned models indicates the polydispersive nature of the studied systems. We are proposing the model of Dissado and Hill [13,14] based on Jonscher's theory [15–18] to explain the complex characteristic of dielectric response.

2. Experimental

Electric properties were investigated in double potassium yttrium tetraoxophosphates(V) $K_3Y_{(1-x)}Ln_x(PO_4)_2$ ($x = 0.01$, 0.05,