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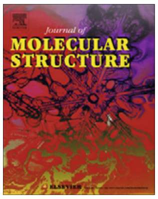

Dielectric relaxation in double potassium yttrium orthophosphate $K_3Y(PO_4)_2$ doped by praseodymium and dysprosium ions

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ABSTRACT

We report the paper presents the results of electric properties of double potassium yttrium orthophosphates doped by lanthanide ions $K_3Y_{(1-x)}Ln_x(PO_4)_2$ ($x = 0.01, 0.05$, Ln = Pr^{3+}, Dy^{3+}). Electric permittivity and dielectric loss measurements have been performed on polycrystalline samples in the temperature range −50–120 °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

In the previous report was presented dielectric properties in double potassium yttrium orthophosphates $K_3Y_{(1-x)}Yb_x(PO_4)_2$ ($x = 0.01, 0.05$) [1]. This paper is the second part of our investigation on double potassium yttrium orthophosphates doped by lanthanide ions. In this part general formula of our samples is $K_3Y_{(1-x)}Ln_x(PO_4)_2$ ($x = 0.01, 0.05$), where Ln = Pr^{3+} and Dy^{3+}. The structure data of $K_3Y(PO_4)_2$ was presented by Ushakov [2] and Komissarova et al. [3]. The authors reported a monoclinic system with space group $P2_1/m$ with the cell parameters: $a = 7.358$ (Å), $b = 5.613$ (Å), $c = 9.349$ (Å), $\beta = 90.92°$ and $Z = 2$. This structure can be described as a distortion of glaserite structure, where structural subunit is formed by octahedron $[LnO_6]$. Alternately arranged up and down $[PO_4]$ groups are connected with octahedron in its five vertices but one tetrahedron group divided one of its edge with a polyhedron containing Ln. In this way the number of coordination of Ln^{III} rises into 7 and symmetry of space group decreases from the hexagonal to the monoclinic. The potassium ions are situated along c axis among layer formed by a tetrahedron and a octahedron. This monoclinic distortion of the glaserite structure reminds the arcanite – type $K_3Na(SO_4)_2$ (Fig. 1). The spectroscopic properties of double alkali metal yttrium orthophosphates, with formula $M_3Y(PO_4)_2$, where the molar ratio of YPO_4:M_3PO_4 is 1:1 (M = Rb, Na, Lu) doped with Pr^{3+}, Dy^{3+} have been studied by several authors [4,5]. However, there is a few information about the dielectric properties of $M_3Y(PO_4)_2$ doped with the lanthanide ions.

The crystal structures of the obtained compounds were confirmed by X-ray diffraction using a diffractometer Siemens D 5000th. The resulting diffraction patterns were compared with the crystallographic data sheet number 049-0497 double potassium yttrium orthophosphate – $K_3Y(PO_4)_2$ in a crystal base ICCD PDF – 4+. The X-ray diagrams received for non-doped materials and with admixture depict that peaks derived from doped samples by lanthanide ions coincide with the peaks originating from pure $K_3Y(PO_4)_2$ (Fig. 2). It was found that the process of doping material and the fusion did not cause any changes in the crystalline structure of the compounds.

So far, we obtained in the system where amount of doped material is 1% of Dy^{3+} and Pr^{3+} the dielectric relaxation can be described by two-parametric dielectric response function of the Havriliak–Negami (HN) [6]. The real and imaginary part of permittivity were calculated using the following equations:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)\cos\left(\frac{\beta\cdot a\tan\left[\left(\frac{f}{f_c}\right)^{1-\alpha}\cos(\alpha\cdot 2\pi)/1-\left(\frac{f}{f_c}\right)^{1-\alpha}\sin(\alpha\cdot 2\pi)\right]}{\left[\left(1+\left(\frac{f}{f_c}\right)^{1-\alpha}\sin(\alpha\cdot 2\pi)\right)^2+\left(\left(\frac{f}{f_c}\right)^{1-\alpha}\cos(\alpha\cdot 2\pi)\right)^2\right]^{\beta/2}}\right)$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)\sin\left(\frac{\beta\cdot a\tan\left[\left(\frac{f}{f_c}\right)^{1-\alpha}\cos(\alpha\cdot 2\pi)/1-\left(\frac{f}{f_c}\right)^{1-\alpha}\sin(\alpha\cdot 2\pi)\right]}{\left[\left(1+\left(\frac{f}{f_c}\right)^{1-\alpha}\sin(\alpha\cdot 2\pi)\right)^2+\left(\left(\frac{f}{f_c}\right)^{1-\alpha}\cos(\alpha\cdot 2\pi)\right)^2\right]^{\beta/2}}\right) \quad (1)$$

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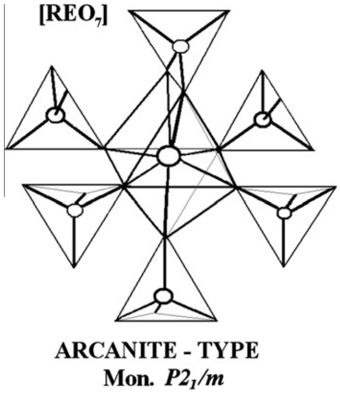

Fig. 1. Projection of the arcanite-type structure of $K_3Y(PO_4)_2$.

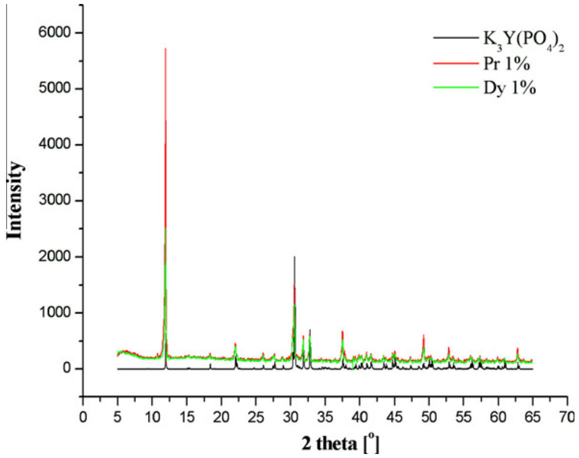

Fig. 2. The X-ray diagrams for $K_3Y(PO_4)_2$ (black), $K_3Y_{0.99}Pr_{0.01}(PO_4)_2$ (red) and $K_3Y_{0.99}Dy_{0.01}(PO_4)_2$ (green line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In the case 5% Pr^{3+} and Dy^{3+} our analysis prove that one-parametric dielectric response function of the Cole–Cole [7] better describe the dependence of complex permittivity in whole temperature range.

$$\begin{aligned}\frac{\varepsilon'-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty}&=\frac{1+(f/f_c)^{(1-\alpha)}\sin(\alpha\pi/2)}{1+(f/f_c)^{2(1-\alpha)}+2(f/f_c)^{(1-\alpha)}\sin(\alpha\pi/2)}\\ \frac{\varepsilon''}{\varepsilon_s-\varepsilon_\infty}&=\frac{(f/f_c)^{(1-\alpha)}\cos(\alpha\pi/2)}{1+(f/f_c)^{2(1-\alpha)}+2(f/f_c)^{(1-\alpha)}\sin(\alpha\pi/2)}\end{aligned}\tag{2}$$

where ε_s and ε_∞ is the static and optical permittivity, α and β are the empirical coefficients ($0 \leqslant \alpha,\ \beta \leqslant 1$) and f_c is the frequency of the relaxation process. The average values of relaxation times ($\tau = 1/2\pi f_c$) were obtained from the fitting of the Havriliak–Negami equation (for 1% Dy^{3+} and Pr^{3+}) (e.g. 1) and Cole–Cole equation (e.g. 2, 5% of impurity of Ln) in the whole range of frequencies. Unfortunately, experimental points are located in a high frequency region of the spectrum what results in large uncertainty of the fitted parameters.

All the tested compounds have a complex dielectric characteristics. The diagrams of the real and imaginary part of the permittivity as a function of temperature are in the form of broad bands, generated by the partial overlapping of several smaller components. Matching models Cole–Cole and Havriliak–Negami also indicates the polydispersive nature of the studied systems. In order to analyse the dielectric loss line shape the model of Dissado–Hill [8,9] based on Jonscher's theory [10–13] was used. The application of recalled models on double potassium yttrium orthophosphates doped by lanthanide ions was presented in previous part of this work [1].

2. Experimental

Electric properties were investigated in double potassium yttrium orthophosphates $K_3Y_{(1-x)}Ln_x(PO_4)_2$ ($x = 0.01.\ 0.05$, Ln = Pr, Dy). All compounds were synthesized by means of solid phase reaction by sintering a stoichiometric mixture of the initial orthophosphates of YPO_4, K_3PO_4 and Ln_2O_3 at 1200C for 4 h. The obtained orthophosphate were melted in closed platinum–rhodium tube in the argon atmosphere at 1440 °C [14].

Complex electric permittivity has been performed, as was written previously [1], on polycrystalline samples in the temperature range from −50 °C to +120 °C and frequency range 1 kHz–1 MHz by means of HP 4282A impedance meter. Samples were made as pellets 10 mm in diameter and about 1–2 mm thick. Copper-foil electrodes were affixed to the prepared pellets. Before experiment samples were annealed at a temperature of 170 °C in vacuum in order to decrease the amount of water absorbed from the air thus a number of electric charges is also reduced rather substantially. All measurements were carried out in a dry nitrogen atmosphere. The shape of measurements configuration was described previously [15].

3. Results

3.1. $K_3Y_{(1-x)}Pr_x(PO_4)_2$. *(x = 0.01, 0.05)*

Fig. 3 presents temperature dependence of the real and imaginary part of electric permittivity in materials doped by 1% and 5% praseodymium. Below −40 °C no dispersion and absorption is observed, this situation is similar for both ions. In discussed temperature range relaxation process is retarded because of the rigidity of crystallographic lattice. In a higher range of temperature (−20 °C to +100 °C) a dielectric dispersion and absorption is significantly illustrated. The dielectric response for a material doped by 1% of Pr, presented in the Fig. 3a, depicts one broad peak with a maximum at 24 °C. The absorption curve (ε'') at the frequency below 4.5 kHz two separated bands are clearly indicated. When the frequency increasing the maxima approaching and one broad peak is appeared, with maximum value at 24 °C. For temperature lower than 20 °C absorption maxima shift towards higher frequencies with temperature (color violet in the Fig. 4a), for the temperatures from 20 °C to 30 °C the maximum band does not change the position (Fig. 4a color red). With a further increasing of temperature the decreasing of the value of critical frequency is observed (Fig. 4a color green). In the Fig. 3c, for dependency of real part of permittivity, two peaks are observed, but the absorption diagram is more complex (Fig. 3d). First of all, it is noticeable that the broad absorption band is due to the imposition of three narrower bands. Beside, at the $T = 80$ °C the addition peak also appears. For the temperature lower then 10 °C maxima of the band are not clear separated, due to the appearance of a new band. Although the trend is visible of shifting the maxima with temperature towards to higher frequency (color violet in Fig. 4b). For the band in the range of temperature 15–20 °C characteristic is that the absorption reaches the highest value at temperature about 25 °C (color red Fig. 4b) independently apart from the frequency. The third maximum of the band shifts towards lower frequency with the increasing of the temperature (in the Fig. 4b color green).

The dielectric response data obtained for the material doped by 1% Pr in whole range of the temperature were evaluated by the Havriliak–Negami model. In compounds with 5% of Pr the