SYNTHESIS, STRUCTURE AND OPTICAL PROPERTIES OF COMPLEXIS PHOSPHATE- VANADATES OF K- LN (LN= Y, LA, EU, GD).

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Abstract Influence of Eu^{3+} introduction on structure and properties of $\text{K}_3\text{Ln}(\text{PO}_4)_x(\text{VO}_4)_{2-x}$ ($\text{Ln} = \text{Y, La, Gd}$) is investigated. Samples of $\text{K}_3\text{Ln}_{1-y}\text{Eu}_y(\text{PO}_4)_x(\text{VO}_4)_{2-x}$ ($\text{Ln} = \text{Y, La, Gd}$; $0 \leq x \leq 2$) were received by solid state method by multistep annealing from 70 to 750 $^{\circ}\text{C}$ with use of Ln_2O_3 ($\text{Ln} = \text{Y, La, Eu, Gd}$), KH_2PO_4 , NH_4VO_3 and K_2CO_3 . There are restrict or wide solid solution range is observed in systems under investigation.

INTRODUCTION

Information about double phosphates and vanadates of K- rare earth elements mainly concerns structure characteristic and luminophores synthesis. It has been reported that $\text{K}_3\text{Eu}(\text{PO}_4)_2$ is perspective cathodoluminophor in devices with high current density.¹ Good laser characteristics were obtained for $\text{K}_3\text{Nd}_x\text{La}_{1-x}(\text{PO}_4)_2$ crystals with x of about 0.2 – 0.4.² In this report influence of Eu^{3+} introduction on structure and properties of $\text{K}_3\text{Ln}(\text{PO}_4)_x(\text{VO}_4)_{2-x}$ ($\text{Ln} = \text{Y, La, Gd}$) will be discussed.

EXPERIMENTAL PROCEDURE

Samples of $\text{K}_3\text{Ln}_{1-y}\text{Eu}_y(\text{PO}_4)_x(\text{VO}_4)_{2-x}$ ($\text{Ln} = \text{Y, La, Gd}$; $0 \leq x \leq 2$) were received by solid state method by multistep annealing from 70 to 750 $^{\circ}\text{C}$ with use Ln_2O_3 ($\text{Ln} = \text{Y, La, Eu, Gd}$), KH_2PO_4 , NH_4VO_3 and K_2CO_3 . Polycrystals $\text{K}_3\text{Ln}_{1-y}\text{Eu}_y(\text{PO}_4)_x(\text{VO}_4)_{2-x}$ were identified by X – ray diffraction analysis with X – ray diffractometer DRON – 3M

(Cu_{Kα} - radiation, $\lambda=1.5418$ Å) performance. Luminescence investigation was carried out from spectrophotometer SDL – 1 with UV - laser excitation.

It was calculated crystal parameters for all samples under investigation.

RESULTS AND DISCUSSION

Substitution of Ln³⁺ - cation by Eu³⁺ - cation in K₃Ln_{1-y}Eu_y(PO₄)_x(VO₄)_{2-x} (Ln= La, Gd) such as in K₃Y_{1-y}Eu_y(PO₄)_x(VO₄)_{2-x} ($y = 0.4 - 2$) in broad range of concentration Eu³⁺ - (more then 50 mol.%) is bring to lattice parameter change. The dependencies of crystal lattice parameters of solid solutions and their volumes from a ratio PO₄³⁻/VO₄³⁻ have linear character.

Introduction of Eu³⁺ - cation in K₃Y_{1-y}Eu_y(PO₄)_x(VO₄)_{2-x} ($y= 0- 50$; $x= 0- 2$) result to widening of arcanite - type solid solution range. In this case introduction so insignificant amount of europium (5 mol.%) into glazerit – like K₃Y(PO₄)_{0.3}(VO₄)_{1.7} lead to arcanite - type solid solution formation. Addition of Eu³⁺ - cation into glazerit – like K₃Y(VO₄)₂ in concentration more then 15 mol.% (from 15 up to 60 mol.%) is lead to byphase area formation. When concentration of Eu³⁺ - cation reach more then 70 mol.%, formation of arcanite – like solid solution is observed.

Spectra luminescence of K₃Ln_{1-y}Eu_y(PO₄)_x(VO₄)_{2-x} (Ln = Y, La, Gd) was received. The nature of spectra suggests that ion Eu³⁺ replacing Y³⁺ forms one active centre of symmetry not above C_{2v}. Some features of spectra were observed:

1. presence of narrow lines in 570 – 630 nm field;
2. presence of broad band in 430 – 550 nm;
3. absence of full concentration quenching;
4. sharply luminescence intensity reducing under cooling at 77 K.

Presence of broad band is connected with electron transition in anions.³ The lines narrow is caused by electron transitions ⁵D₀ – ⁷F₀, ⁵D₀ – ⁷F₁, ⁵D₀ – ⁷F₂ in Eu³⁺ - cations.³ Absence of full concentration quenching is due to dipole – dipole interaction of Eu³⁺ absence because of screening of them by anion layers.¹

Transitions in field 590 – 620 nm for samples under investigation produce “red” cathodoluminescence. Moreover, analysis spectrum in this area permits to determine the site - symmetry of Eu³⁺ as stoichiometric peculiarities of Eu³⁺ entering in K₃Ln(PO₄)_x(VO₄)_{2-x} matrix.

Spectra luminescence of $K_3Ln_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ ($Ln = La, Gd$) is present at fig. 1 on instance of $K_3Gd_{0.9}Eu_{0.1}(PO_4)_{0.3}(VO_4)_{1.7}$. Analysis of spectra showed that Eu^{3+} concentration increase by their introduction in solid solutions $K_3Ln(PO_4)_x(VO_4)_{2-x}$ ($Ln = La, Gd$; $x = 0 - 2$) and $K_3Y(PO_4)_x(VO_4)_{2-x}$ ($x = 0.3 - 2$) results to irregular broadening of Eu^{3+} luminescence lines. New lines haven't been observed. It means negligible distortion of crystal field when concentration of Eu^{3+} varying.

Anion substitution of PO_4^{3-} by VO_4^{3-} leads to intensity of luminescence lines alteration. In this case formation of another centre of luminescence isn't observed. Similarity of spectra for $K_3Ln_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ ($Ln = La, Gd$; $x = 0 - 2$) and $K_3Y_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ ($x = 0.3 - 2$) demonstrates the structure identity of these solid solutions. Indeed, these compositions are crystallised in arkanite – like structure.

Introduction of Eu^{3+} in $K_3Y(VO_4)_2$ up to 10 mol.% doesn't alter character of spectra. Increasing of Eu^{3+} concentration above 15 mol.% bring to new lines appearing. This lines are due to presence of two types of luminescence centres (fig. 2). It conforms byphase samples formation.

Distinctions among spectrum of $K_3Y_{1-y}Eu_y(VO_4)_2$ ($y = 0.05, 0.1$) -and $K_3Y_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ ($x = 0.3 - 2$) conforms different structural types of this solid solutions.

It is established that intensity of luminescence of $K_3Ln_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ depends on material of matrix, concentration of Eu^{3+} , ratio PO_4^{3-}/VO_4^{3-} .

The samples with higher contents of groups VO_4^{3-} have bright - red luminescence. The increase of group PO_4^{3-} contents up to $x = 0.3$ slightly reduces luminescence intensity. Further increasing of PO_4^{3-} contents leads to sharply reducing of luminescence intensity.

Increasing of Eu^{3+} concentration up to 30 mol.% leads to luminescence intensity increasing.

Solid solutions $K_3Ln_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ ($Ln = Y, Gd$) posses more bright luminescence intensity than $K_3La_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$. It is associated with different cation radii of Ln ($Ln = Y, La, Gd$) and those of Eu .

FIGURE 1. Spectra luminescence of $\text{K}_3\text{Gd}_{0.9}\text{Eu}_{0.1}(\text{VO}_4)_2$ at 77 K (1) and 300 K (2).

FIGURE 2. Spectra luminescence of $\text{K}_3\text{Y}_{0.9}\text{Eu}_{0.1}(\text{VO}_4)_2$ (1) $\text{K}_3\text{Y}_{0.9}\text{Eu}_{0.1}(\text{PO}_4)_{0.3}(\text{VO}_4)_{1.7}$ (2) and $\text{K}_3\text{Y}_{0.5}\text{Eu}_{0.5}(\text{VO}_4)_2$ (3) at 300 K.

SUMMARY

In this work we prepared solid solution $K_3Ln_{1-y}Eu_y(PO_4)_x(VO_4)_{2-x}$ ($Ln = Y, La, Gd$) with arcanite- or glazerite – like structure. It is expected that these compositions are available as “red” cathodoluminophors.

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REFERENCES

1. Zorina L. N., Eszova Z. A., Orlovsky V. P., Koval E. M., Sochin N. P. Neorg. Mat., 15, № 6, 1116 (1979).
2. Hong H. Y.-P., Chinn S. R. Mater. Res. Bull., 11, 421 (1976).
3. Fotiev A. A., Shulgin B. V., Moskvina A. S., Gavrilov F. F. Vanadium crystallophosphores. Moscow, 205 p. (1976).