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Effect of Composition and Synthesis Route on Structure and Luminescence of $NaBaPO_4:Eu^{2+}$ and $ZnAl_2O_4:Eu^{3+}$

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$NaBaPO_4:Eu^{2+}$ and $ZnAl_2O_4:Eu^{3+}$ phosphors with different dopant content were prepared by solution-combustion (SC) and sol-gel (SG) method. SC route gives samples with high crystallinity, that does not always leads to increase in luminescent properties due to formation of admixture phases. In $NaBaPO_4$ phosphor series, crystallite size reversly depends on admixture $Ba_3(PO_4)_2$ phase content. Increase in europium concentration up to 10% lead to decrease of crystallite size in samples prepared by SC method, but increase of crystallite size in samples prepared by SG method. For $ZnAl_2O_4:Eu^{3+}$, prepared by sol-gel technique, increase in Eu^{3+} concentration leads to amorphization of structure.

1. Introduction

Inorganic phosphors are widely used in modern life in a number of different applications such as light sources, lasers, electronic devices, medicine etc. Phosphor's luminescent properties determines their quality and applications. Luminescence depend on a number of factors, such as chemical composition, crystal structure, dopants, etc., and can be controlled using various synthetic technique and treatments [1-4]. It is well known, that for the efficient luminescence, especially cathodoluminescence, crystallite size is very important, since boundaries between crystallites play role of non-radiative recombination sites [3]. Influence of synthesis temperature, time on crystallite size was extensively studied for many phosphors, however effect of activator content on crystallite size is not a well known subject [4,5]. For example, effect of Eu^{3+} concentration on crystal structure of Y_2O_3 phosphors, prepared by Pechini and solution-combustion methods were described [4,5]. It was shown that increase of dopant concentration leads to increase of crystallite size of Y_2O_3: Eu^{3+} phosphor prepared by sol-gel method that was explained by acceleration the phenomenon of nucleation of crystals in the presence of impurities. However it is also known that increase of impurities concentration leads to increase in a number of nucleation centers and therefore decrease of crystallite size. In this work synthetic route influence on effect of dopant concentration on crystal structure and luminescent properties of phosphors prepared via different synthetic methods was studied.

There were chosen sol-gel (SG) method, as one of the most well-known and widely used synthetic route, which however consists of several steps and is time consuming, and solution-combustion (SC) method, as fast and energy efficient technique.

Zinc aluminate spinel and mixed sodium-barium phosphate were used as a host material with europium in three- and divalent states as dopant. $NaBaPO_4:Eu^{2+}$ phosphor is known as chemically stable and promising material for W-LED application. $ZnAl_2O_4$ may be used as UV emitting

cathode-ray phosphor for pulsed UV sources without further dopation, Eu^{3+} activation makes it a source of red component in field emission displays or light bulbs. Europium ion emission is highly affected by ion position in lattice, crystal field and coordination, thus it can be used as indicator for structure analysis [4-8].

2. Experimental

Two types of materials were obtained by two synthetic routes that gives four series of phosphors with different concentration of activator in each. All chemicals were analytical grade. For prepared samples X-ray diffraction (XRD) spectra were measured using Difray X-ray diffractometer, photoluminescence (PL) spectra on "Avaspec-3648" spectrofluorimeter and brightness using IL-1700 brightness meter.

2.1 Synthesis of $NaBaPO_4:Eu^{2+}$ via solution-combustion method

$NaBaPO_4:Eu^{2+}$ phosphor was synthesized by solution-combustion method using b-alanine as fuel. The starting materials were $Ba(NO_3)_2$, NaH_2PO_4, Eu_2O_3, HNO_3, NH_4NO_3 and b-alanine. Firstly, Eu_2O_3 was placed in thin wall quartz beaker and dissolved in concentrated nitric acid to form nitrate solution. Then solution of $Ba(NO_3)_2$, NaH_2PO_4, NH_4NO_3 and b-alanine in small amount of distilled water was added. The amount of b-alanine was doubled from stoichiometric and NH_4NO_3 was used to increase temperature of reaction. The precursor solution was placed on a hot plate to evaporate water and form viscous mass that self ignites and burns producing large amount of gases and forms white sponge like product. To produce $NaBaPO_4:Eu^{2+}$ phosphor, product was milled in mortar and placed in corundum boats and introduced in tube furnace for annealing under reductive atmosphere ($5\%H_2 + 95\% N_2$) at 1050^0C for two hours.

2.2 Synthesis of $NaBaPO_4:Eu^{2+}$ via sol-gel method

Required amount of europium oxide was placed in beaker and dissolved in 35% nitric acid on magnetic stirrer to form nitrate solution. Barium nitrate solution was mixed in the beaker with europium nitrate and sodium phosphate solution was added dropwise to form translucent sol. Product was filtered and washed with distilled water on Buchner funnel and dried at 120^0C in vacuum drying cabinet. The xerogel was milled in mortar, placed in corundum crucible and introduced in muffle furnace for two hours at 600^0C. Then reduction annealing was done as described above.

2.3 Synthesis of $ZnAl_2O_4:Eu^{3+}$ via solution-combustion method

ZnO, Eu_2O_3, $Al(NO_3)_3*9H_2O$, HNO_3 and urea were used as starting materials. Oxides were placed in quartz beaker and dissolved in concentrated nitric acid to form clear solution. Aluminum nitrate and urea were dissolved in minimum amount of distilled water and added to beaker. The precursor solution was placed on a hotplate to remove water and then introduced in preheated furnace at 600^0C to start reaction with formation of porous white product with foam structure. Foam was annealed at 800^0C for two hours and milled.

2.4 Synthesis of $ZnAl_2O_4:Eu^{3+}$ via sol-gel method

Synthesis starts from preparing nitrate solution by dissolving required amounts of europium and zinc oxides in nitric acid in borosilicate glass beaker under magnetic stirring. Aluminum nitrate and 5 wt% solution of PEG-4000 were added to resulting solution. The $ZnAl_2O_4$ sol was formed caused by an addition of ammonia solution until pH reached a value 6-7. Product was filtered on Buchner funnel, dried at 120^0C, milled and annealed in furnace at 800^0C for two hours.

3. Results and discussion

3.1 $NaBaPO_4:Eu^{2+}$ phosphors

Figure 1 shows XRD data of $NaBaPO_4$ samples. Using Sharer formula crystallite sizes were calculated, results are shown in the Table I. Samples prepared using solution-combustion rout Fig. 1(a), 1(b) and 1(c) represents $NaBaPO_4$ with lower content of admixture phase, in contrast to samples prepared by sol-gel method Fig. 1(d), 1(e) and 1(f) that contain $Ba_3(PO_4)_2$ and $Ba_2P_2O_7$ phases. It can be easily seen, that crystallite size has opposite correlation to $Ba_3(PO_4)_2$ phase content since formation of admixture phase prevents crystallite growth. Crystallites of samples prepared by SC method with increase of dopant concentration decrease in size and for those prepared via SG increase in size with europium concentration increase up to 10%, this is similar to what was observed in works [4,5] for Y_2O_3 phosphors.

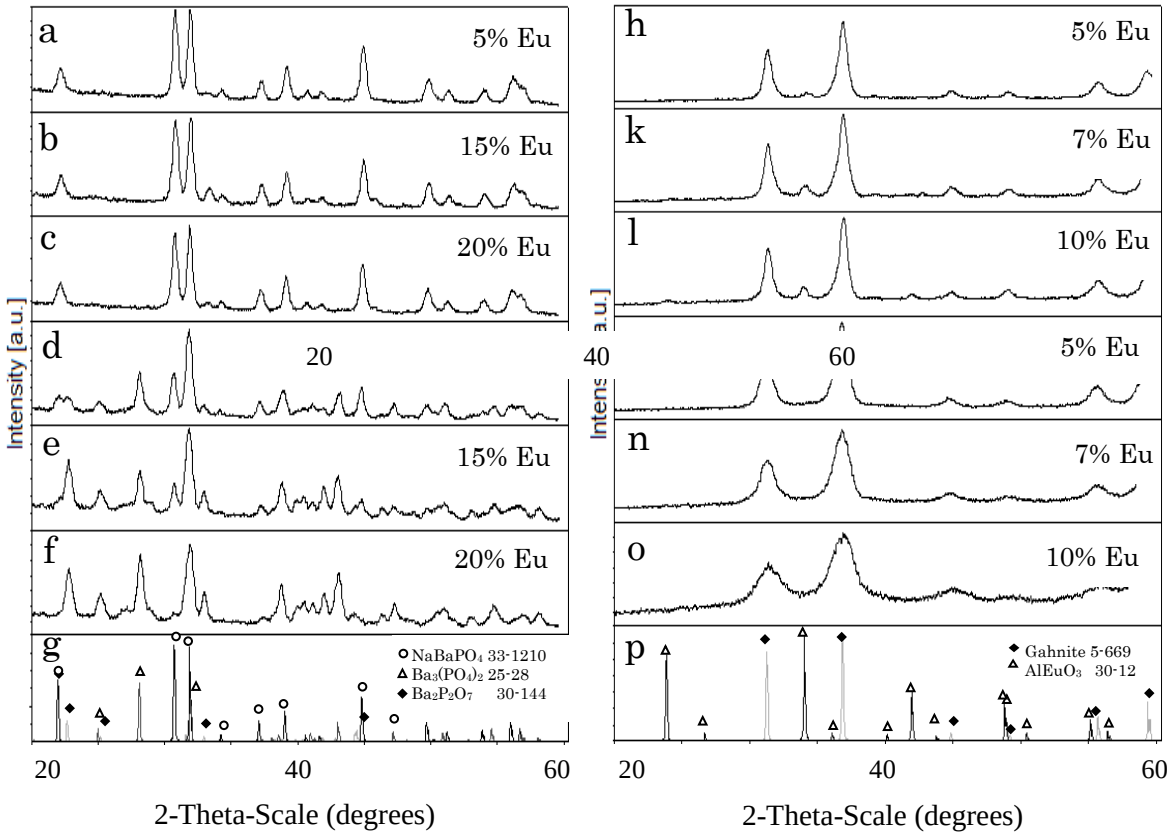

Fig. 1. XRD patterns of $NaBaPO_4$ phosphors prepared by SC (a,b,c) and SG method (d,e,f) and $ZnAl_2O_4$ phosphors prepared by SC (h,k,l) and SG method (m,n,o); (g,p)-PDF data.

Table I. Crystall properties of mixed sodium-barium phosphate phosphors.

Synthetic route	Parameter	Europium concentration, %				
		5	7	10	15	20
Solution-combustion	Crystallite size, nm	20.6	20.1	18.2	18.9	19.0
	$Ba_3(PO_4)_2$ phase content, %	0	13	35	14	7
Sol-gel	Crystallite size, nm	15.6	15.9	17.0	13.9	12.4
	$Ba_3(PO_4)_2$ phase content, %	49	46	38	58	100

Photoluminescence spectra of samples are shown on the Fig. 2, their shape weakly depends on dopant concentration but much stronger depends on synthetic route. The given spectra were decomposed into a Gaussian bands. Bands with maximums at 420, 450 and 480 nm are the most intense ones. According to literature data, 450 and 480 nm bands belong to Eu^{2+} in 12 (EuII) and 10 (EuIII) coordinated states that corresponds to Ba^{2+} and Na^{+}/Ba^{2+} sites in $NaBaPO_4$ matrix and 420 nm (EuI) to Eu^{2+} in Ba^{2+} sites of $Ba_3(PO_4)_2$ matrix [9, 10]. It can be seen that peaks of 12-coordinated europium ions decreasing with increase of doping content. Peak at 420 nm that belongs to Eu^{2+} in $Ba_3(PO_4)_2$ has no correlation to europium concentration, that can be caused by nonuniform distribution of dopant between phases. For sodium-barium phosphate phosphor series, europium concentration varies from 5 to 20%. Fig. 3 shows brightness depending on Eu^{2+} content, it can be easily seen, that optimum concentration does not depend on synthesis rout and correspond to 10%, however samples prepared by solution-combustion method brighter then those made by sol-gel due to presence of admixture phases, since luminescence of $Ba_3(PO_4)_2$:Eu^{2+} is in shorter wavelength region than those of $NaBaPO_4$.

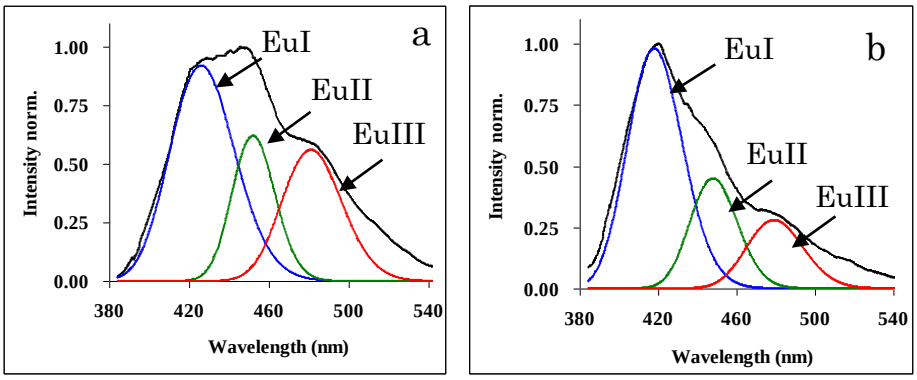

Fig. 2. Photoluminescence spectra of $NaBaPO_4$ based phosphors prepared by solution-combustion (a) and sol-gel method (b) with 15 % Eu^{2+} concentration.

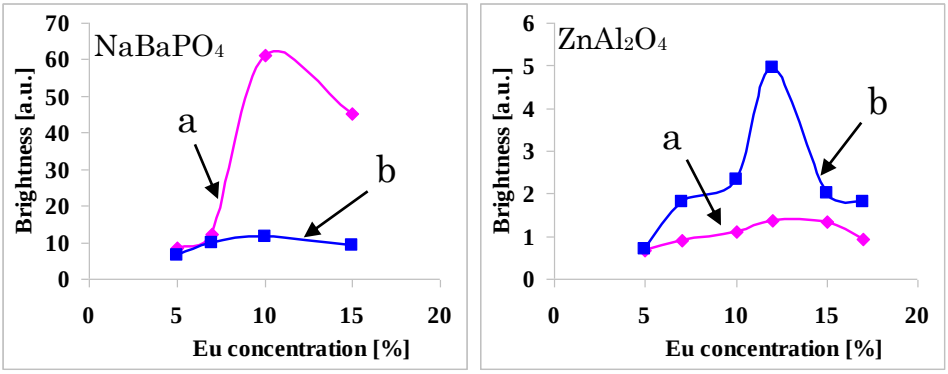

Fig. 3. Brightness depending on Eu content in $NaBaPO_4$ and $ZnAl_2O_4$ phosphors prepared by solution-combustion (a) and sol-gel method (b).

3.2 $ZnAl_2O_4$:Eu^{3+} phosphors

Zinc aluminate spinel XRD patterns are shown on the Fig. 1, according to them $ZnAl_2O_4$:Eu^{3+} phosphors produced by sol-gel route, have stronger influence of Eu^{3+} ions concentration on crystal structure. Namely, increase of europium concentration leads to amorphization, that can bee seen in broadening of XRD peaks, with increasing of doping level. Samples prepared by solution-

combustion method have higher crystallinity, due to high reaction temperature, it can be seen by narrow peaks on XRD patterns. Using Sharer formula crystallite sizes were calculated, Table II, it can be seen that increase in dopant concentration leads to change in crystallite size that has different tendency depending on synthetic rout, similar behavior for Y_2O_3:Eu^{3+} phosphor was observed in our previous work [4] and also described above for $NaBaPO_4$. Europium ions may substitute Zn^{2+} or Al^{3+} sites in spinel matrix or locate on surfaces of nanoparticles due to their porosity. Because of Eu^{3+} ions radii (0.95 Å) noticeably larger than that of Zn^{2+} (0.68 Å) or Al^{3+} (0.54 Å), surface localization is more probable.

Table II. Crystall properties of $ZnAl_2O_4$ phosphors.

Synthetic route	Parameter	Europium concentration, %		
		5	7	10
Solution-combustion	Crystallite size, nm	12.2	12.4	13.3
	$EuAlO_3$ phase content, %	10	17	20
Sol-gel	Crystallite size, nm	9.0	7.3	4.9
	$EuAlO_3$ phase content, %	<1	<1	<1

From luminescence spectra shown on the Fig. 4 it can be seen that 620 peak is the most intense for sol-gel prepared samples, it corresponds to $^5D_0 \rightarrow {}^7F_2$ electric-dipole transition of Eu^{3+} and is sensitive to the site symmetry, it is allowed when europium ions occupies sites without an inversion symmetry [11]. Due to amorphous matrix Eu^{3+} ions occupies low symmetry sites that intensifies band at 620 nm, thereby it confirms XRD data that increase of Eu^{3+} concentration results in decrease of crystallite size and amorphization that is similar to YAG samples described in [4] and it is important that $ZnAl_2O_4$ and $Y_3Al_5O_{12}$ may be classified as double oxide system. However, for samples prepared by SC, europium concentration does not noticeably affect crystallinity, that also shown by low intensity of 620 nm peak and intense 610 nm peak that belongs to $^5D_0 \rightarrow {}^7F_1$ magnet-dipole transition that is low sensitive to symmetry.

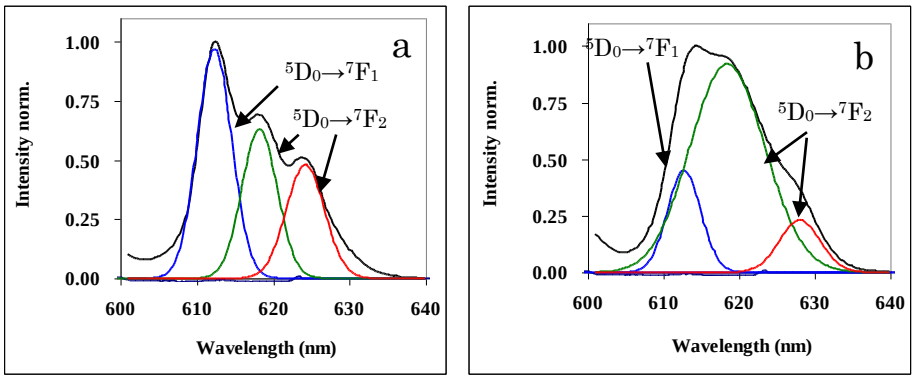

Fig. 4. Photoluminescence spectra of $ZnAl_2O_4$ based phosphors prepared by solution-combustion (a) and sol-gel method (b) with 7 % Eu^{2+} concentration.

Figure 3 shows brightness depending on Eu^{3+} content, it can be seen that samples prepared by SG has higher brightness then SC prepared, even thou the former one has lower crystallinity. That can be explained by presence of $EuAlO_3$ perovskite phase Fig. 1(h), 1(k) and 1(l), that's formed in samples prepared by SC route an its content increases proportionally to europium concentration, this results in europium ion consumption, so there is small amount of luminescent centers left in the spinel matrix. The presence of the perovskite phase in SC samples can be explained by the highly non-equilibrium conditions of process due to short reaction time and large exothermic effect.

On the other hand, SG process occurs at a low speed in solvent medium that provides conditions close to equilibrium in that case the formation of solid solution is more likely.

3. Conclusion

$NaBaPO_4:Eu^{2+}$ and $ZnAl_2O_4:Eu^{3+}$ phosphors with different dopant content were prepared by solution-combustion and sol-gel method. Solution-combustion route gives samples with higher crystallinity, which does not always leads to increase of luminescent properties due to formation of admixture phases. In $NaBaPO_4$ phosphor series, crystallite size reversely depends on admixture $Ba_3(PO_4)_2$ phase content. Below 10% increase in europium concentration lead to decrease of crystallite size in samples prepared by SC method, but increase of crystallite size in samples prepared by SG method. For $ZnAl_2O_4:Eu^{3+}$, prepared by sol-gel technique, increase in Eu^{3+} concentration leads to amorphization of structure, same effect observed in YAG samples, moreover this two host materials can be classified as double oxide systems. For $ZnAl_2O_4:Eu^{3+}$ prepared by SC increase in Eu concentration does not significantly affect crystallinity and leads to formation of admixture $EuAlO_3$ phase that results in lower brightness.
Thus doping allow to control crystallite size, that is important in phosphor, ceramic, and electronics technologies.

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