

Synthesis and characterization of zinc phosphates doped with samarium and manganese

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Samarium and manganese doped zinc phosphate compositions were prepared by high-temperature ceramic synthesis where ZnO, NH₄H₂PO₄ and Sm₂O₃ (or MnO) of pre-determined ratios were powdered, mixed and placed in alumina crucibles. The synthesis was performed at 950 °C for 3 hours in a muffle furnace. Samples were quenched out of the melt to room temperatures and after that annealed at 250 °C for 2 hours. Sm₂O₃ and MnO doping varied between 0.03 and 0.28 mol percentage.

Using powder X-ray diffraction, we have found that the observed fundamental crystalline phase is iso-structural with α -Zn₂P₂O₇, where samarium and manganese ions most probably substitute for Zn²⁺. This is supported by the obtained photoluminescence spectra. The lattice parameters obtained from the Le Bail calculations for the doped zinc phosphate crystalline phase are very similar to the lattice parameters of α -Zn₂P₂O₇. Deviation of lattice parameters is associated with different ionic radius of dopant Sm³⁺ and Mn²⁺.

Key words: doped zinc phosphates, samarium, manganese, crystal structure, photoluminescence.

INTRODUCTION

Recently there has been significant interest in materials based on phosphates (P₂O₅), doped with rare earths and others elements (such as transition elements) due to their unique optical and electrical properties and related photo-, electro-, luminescent effects and others. These materials have potential applications in advanced devices such as laser sources, sensors, photodiodes, X-ray imaging plates, anti-counterfeit printing additives etc.

These compositions, stoichiometric or alloys, have been synthesized by different methods – sintering, melting, sol – gel and others. They may have polycrystalline, amorphous or amorphous-crystalline mixed phase composition. The amorphous state provides technological and functional advantage in many cases. Attention is directed to changing their optical, mechanical and thermal properties for different ratio of ZnO and P₂O₅ and different contents of doped elements [1–4].

Our research on samarium and manganese doped zinc phosphates has demonstrated that UV

and X-ray excited photo-luminescence in the visible spectra and glass ceramics materials are formed in the ZnO – rich compositions. We believe the strong photoluminescence is due to the stabilisation of samarium and manganese ions within both the glass matrix and within the crystalline phases dispersed into these scintillating materials. It is of particular interest to investigate crystalline phases in this glassy matrix and to study their structures, in order to understand their relationship with the photo-luminescence properties.

In our work we present synthesis and characterisation studies of samarium and manganese doped ZnO-rich zinc phosphate material of composition $yM - (72-y)ZnO - 28P_2O_5$ where: M = Sm₂O₃ or MnO, y varied between 0.03 and 0.28 mol%. We examine the difference between the two dopant structures, and we correlate them to the observed photo-luminescence properties.

EXPERIMENTAL

Sample preparation

All samples were prepared by high-temperature ceramic methods using NH₄H₂PO₄, ZnO and Sm₂O₃ (or MnO) as starting materials. The reagents were

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thoroughly mixed, placed in alumina crucibles and heated at 950 °C for 3 hours in a muffle furnace. The obtained homogeneous melts were then poured onto a graphite plate and annealed at 250 °C for two hours. The obtained materials are easily reproducible. Synthesis of the doped zinc phosphate samples (samarium or manganese) is schematically presented on Fig. 1. Sm₂O₃ or MnO doping varied between 0.03 and 0.28 mol percentage.

Density measurements

Density measurements were carried out according to the Archimedes method using deionised water of density 1g/cm³ as an immersion liquid.

Photoluminescence measurements

The photoluminescence spectra were measured by optical CCD Aventes spectrometer Ave-Spec 2048, operating at 25 MW in the range 250–1100 nm at room temperature. Two light sources were used: 405 nm laser diode and 365 nm light emitting diode.

Powder X-ray diffraction analysis

Powder X-ray diffraction data were collected on TUR M62 diffractometer operating with a Cu K α radiation source ($\lambda = 0.15405$ nm), in steps of 0.04° over the range of 10–60° 2 θ , with a time per step of 2.8 sec.

Modelling of the powder X-ray diffraction patterns was carried out using Powder Cell software [5]. The Le Bail method [6] implemented within the

General Structure Analysis Software (GSAS) [7] was used to extract structure factors and refine the cell parameters. The Le Bail refinements were carried out based on the reported crystal structure of α -Zn₂P₂O₇ [8, 9, 10].

RESULTS AND DISCUSSION

Lists of the samples and the data obtained from density measurements of the same are presented in Table 1 and Table 2. There are some variations in the density as a function of Sm₂O₃ or MnO doping. This may be related to the changes in atomic masses, ionic size, cross-linking densities and occupied positions of the constituent dopant elements in glass-ceramics [11]. A somewhat similar trend was observed by Eraiah *et al.* [1] who found that the density of samarium doped zinc phosphate glasses reached a minimum at Sm₂O₃ doping level of 0.03 mol %. This trend is explained by the fact that Sm₂O₃ acts as

Table 1. List of samarium doped zinc phosphate samples

№	Composition			Density (ρ), g/cm ³
	Sm ₂ O ₃ , mol %	ZnO, mol %	P ₂ O ₅ , mol %	
1	0.03	72.28	27.69	4.60
2	0.09	72.17	27.74	4.46
3	0.14	72.06	27.80	4.26
4	0.28	71.79	27.93	4.74

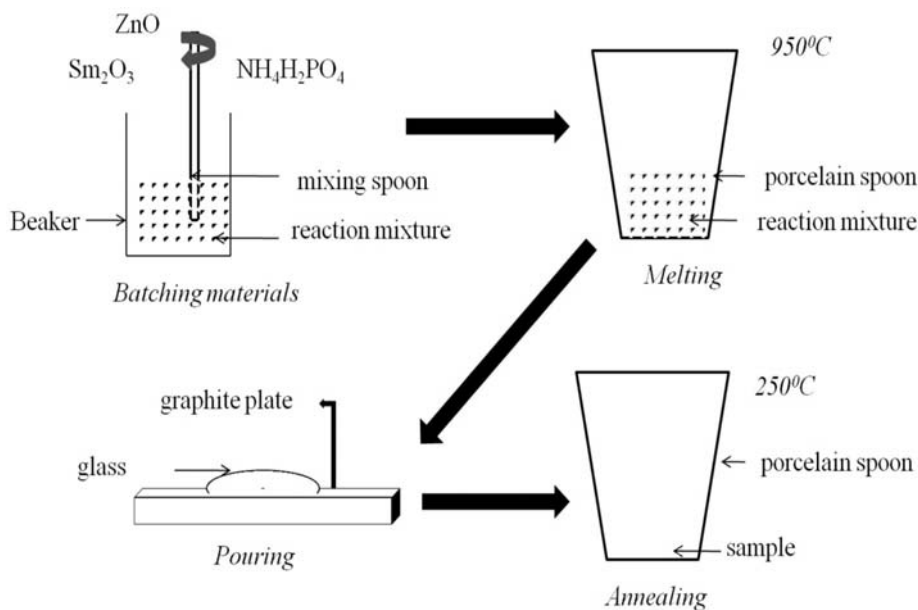


Fig. 1. Preparation of the samarium and manganese doped zinc phosphate samples

Table 2. List of manganese doped zinc phosphate samples

№	Composition			Density (ρ), g/cm ³
	MnO, mol %	ZnO, mol %	P ₂ O ₅ , mol %	
5	0.03	72.28	27.69	3.95
6	0.09	72.17	27.74	3.89
7	0.14	72.06	27.80	3.68
8	0.17	72.01	27.82	3.25
9	0.23	71.90	27.87	3.68
10	0.28	71.79	27.93	3.76

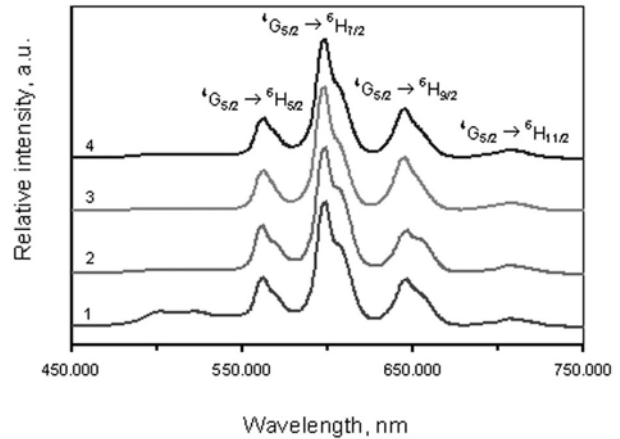


Fig. 2. Photoluminescence spectra of samples 1–4 at excitation wavelength 405 nm

a glass modifier that increases the fraction of non-bridging oxygen atoms and leads to increased porosity and reduced density of the glass.

The densities of the samples in our work are higher than the densities reported for samarium doped zinc phosphate glasses by Eraiah *et al.* [1]. This could be expected, given the higher molar fraction of ZnO in our material (70%), compared to the

glasses studied by Eraiah *et al.* [1] where the molar fraction of ZnO was 60%.

All synthesized materials display photoluminescence. Representative emission spectra for samples 1–4 are illustrated in Figure 2 and reveal four emission bands in the wavelength range be-

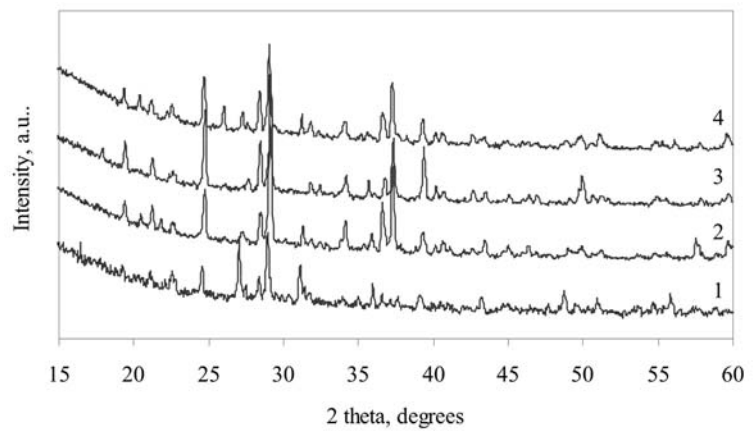


Fig. 3a

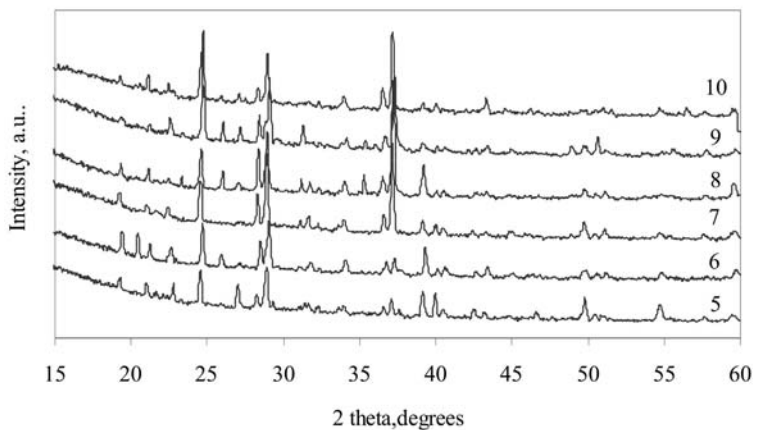


Fig. 3b

Fig. 3. Powder X-ray diffraction patterns for samarium (Fig. 3a) and manganese (Fig. 3b) doped zinc phosphate samples: No1 (0.03 mol% Sm₂O₃), No2 (0.09 mol% Sm₂O₃), No3 (0.14 mol% Sm₂O₃), No4 (0.28 mol% Sm₂O₃), No5 (0.03 mol% MnO), No6 (0.09 mol% MnO), No7 (0.14 mol% MnO), No8 (0.17 mol% MnO), No9 (0.23 mol% MnO), No10 (0.28 mol% MnO)

tween 450 and 750 nm, namely 564 nm, 600 nm, 645 nm and 710 nm. The band at 600 nm which corresponds to orange emission is the most intense. As shown in Figure 2, the emission bands can be assigned to the $4f-4f$ transitions from the excited ${}^4G_{5/2}$ level to the ground state ${}^6H_{5/2}$ and higher levels 6H_J ($J > 5/2$) of the trivalent Sm^{3+} ions which have $4f^5$ configuration. The spectra indicate that the luminescence reddish colour of UV irradiated (LED 365 and 405 nm) Zn-phosphate materials are due to Sm^{3+} ions only (no Sm^{2+} ions present) [12, 13].

Powder X-ray diffraction was used to identify the crystalline phases present in the obtained samples. The X-ray diffraction patterns, presented in Figure 3, confirm that all samples contain one or more crystalline phases. However, the poorly defined peak shapes and the presence of a high background, which is attributable to an amorphous phase, indicate the formation of mixed amorphous-crystalline (glass ceramic like) material.

Inspection of the powder patterns using Powder Cell software shows that the observed crystalline phases are iso-structural with $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$ [8, 9, 10], illustrated in Figure 4, where samarium and man-

ganese ions most likely substitute for Zn^{2+} . The material crystallises with monoclinic symmetry in space group $I2/c$ with unit cell parameters $a = 20.068(15)$ Å, $b = 8.259(6)$ Å, $c = 9.099(8)$ Å, $\beta = 106.35(5)^\circ$. Some of Zn^{2+} sites in the structure are 5-coordinated and others are 6-coordinated. The structure is composed of layers of PO_4 tetrahedra alternating with layers of Zn atoms. The suggestion that the Sm and Mn dopant ions substitute for the Zn sites in the structure is in agreement with the observed photo-luminescence spectra that confirm that all samarium ions are present in 3^+ -valence state, as shown in Figure 2.

In order to further investigate the crystalline phase that was present in all samples, the Le Bail method was used to compare the calculated powder X-ray diffraction pattern of $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$ against the experimental pattern of sample 2 and sample 8. The resulting fit is shown in Figure 5 and the lattice parameters obtained from the Le Bail calculations for sample 2 and sample 8 are listed in Table 3. It is evident that they are very similar to the lattice parameters of $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$, but slightly increased because of the Sm^{3+} and Mn^{2+} doping. Deviation of lattice parameters is associated with different ionic radius of Sm^{3+} and Mn^{2+} .

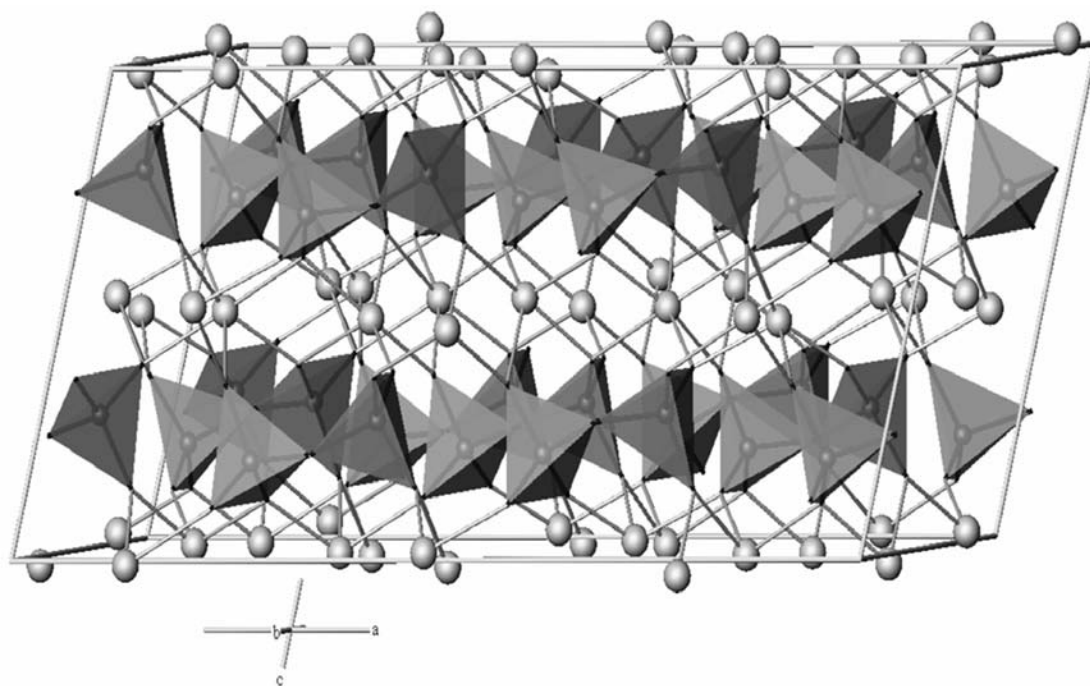
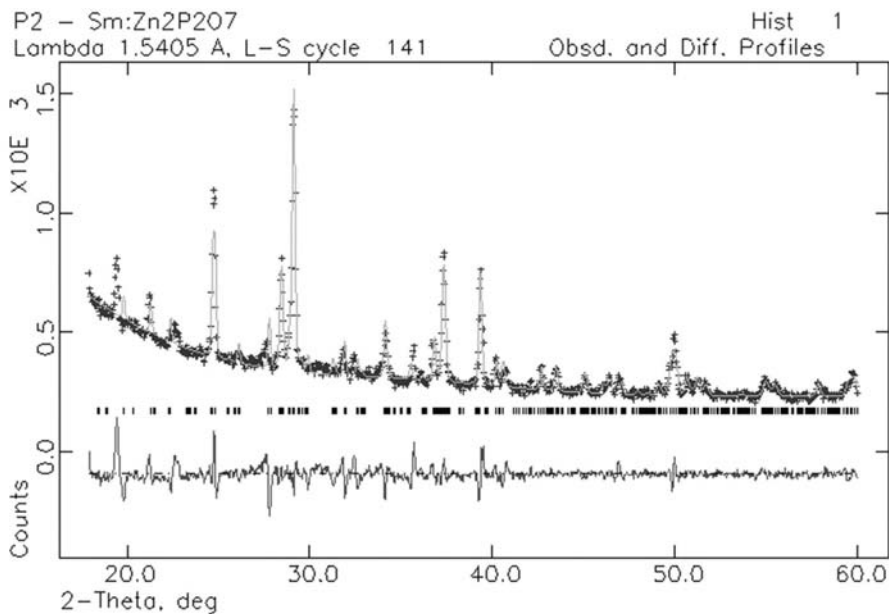


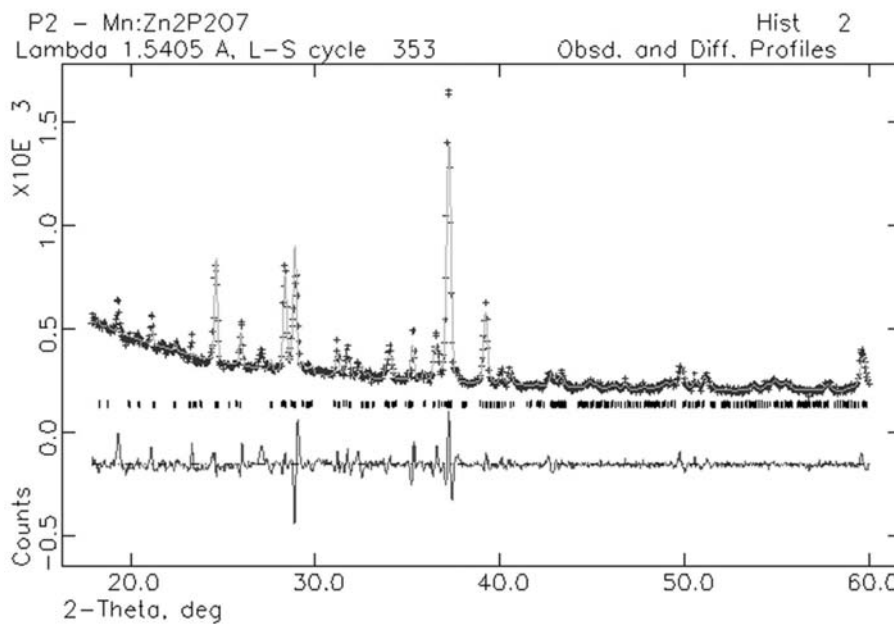
Fig. 4. Crystal structure of $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$ according to Robertson *et al* [8]

The picture shows the content of a single unit cell. The phosphorous atoms are shown by small circles that are located inside corner-sharing PO_4 tetrahedra, shown in grey. The zinc atoms, presented by light grey circles, occupy two different sites in the structure

Fig. 5. Le Bail calculations for sample 2 and sample 8. Grey crosses show the observed data points, solid grey line represents the calculated diffraction pattern and difference profile is shown at the bottom of the plot. Black vertical marks represent the calculated reflection positions.



Sample 2



Sample 8

Table 3. Lattice parameters for the crystalline phase in samples 2 and 8

Lattice parameters of Sm^{3+} doped $\text{Zn}_2\text{P}_2\text{O}_7$ (sample 2)	Lattice parameters of Mn^{2+} doped $\text{Zn}_2\text{P}_2\text{O}_7$ (sample 6)	Lattice parameters of $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$ from reference [4]
space group I2/c	space group I2/c	space group I2/c
$a = 20.071(2) \text{ \AA}$	$a = 20.126(3) \text{ \AA}$	$a = 20.068(15) \text{ \AA}$
$b = 8.261(9) \text{ \AA}$	$b = 8.328(2) \text{ \AA}$	$b = 8.259(6) \text{ \AA}$
$c = 9.101(2) \text{ \AA}$	$c = 9.015(2) \text{ \AA}$	$c = 9.099(8) \text{ \AA}$
$\beta = 106.42(1)^\circ$	$\beta = 106.07(1)^\circ$	$\beta = 106.35(5)^\circ$
$V = 1447.3(3) \text{ \AA}^3$	$V = 1451.8(3) \text{ \AA}^3$	$V = 1447.1 \text{ \AA}^3$

CONCLUSIONS

In our work, we present synthesis and characterisation studies of samarium and manganese doped zinc phosphate materials, we examine the difference between the two doped structures, and we correlate them to the observed photo-luminescence properties.

X-ray diffraction studies of the crystalline phases shows that they are iso-structural with $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$, where samarium and manganese ions most likely substitute for Zn^{2+} . The lattice parameters obtained from the Le Bail calculations for doped zinc phosphate materials are very similar to the lattice parameters of $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$. Deviation of lattice parameters is associated with different ionic radius of Sm^{3+} and Mn^{2+} .

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СИНТЕЗ И ХАРАКТЕРИСТИКА НА ЦИНКОВИ ФОСФАТИ, ДОТИРАНИ СЪС САМАРИЙ И МАНГАН

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(Резюме)

Дотираните със самарий и манган цинк фосфатни композиции са получени чрез високотемпературен синтез от ZnO , $\text{NH}_4\text{H}_2\text{PO}_4$ и Sm_2O_3 (или MnO) в определено съотношение. Изходните реагенти са стрити, смесени и сместа е поставена в керамичен тигел. Синтезът е извършен при температура от 950 °C за 3 часа в муфелна пещ. Пробите са охладени до стайна температура и след това темперирани при 250 °C за 2 часа. Дотирането със самарий и манган варира между 0,03 и 0,28 mol%.

Извършен е рентгеноструктурен анализ, който показва че получената основна кристална фаза е изоструктурна с $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$, в която самариевите и манганови йони най-вероятно заместват частично Zn^{2+} . Това се потвърждава от получените фотолуминесцентни спектри. Определените в резултат на изчислителния метод на Le Bail параметри на кристалната решетка на дотираната цинк фосфатна кристална фаза са много близки до тези на $\alpha\text{-Zn}_2\text{P}_2\text{O}_7$. Тази разлика в параметрите на кристалната решетка се свързва с различния йонен радиус на дотиращите йони Sm^{3+} и Mn^{2+} .