

INFLUENȚA CONDIȚIILOR DE PRECIPITARE ASUPRA CRISTALIZĂRII ȘI MORFOLOGIEI ORTOFOSFATULUI DE LANTAN DOPAT CU EUROPIU

INFLUENCE OF PRECIPITATION CONDITIONS ON THE CRYSTALLISATION AND MORPHOLOGY OF EUROPIUM-DOPED LANTHANUM ORTHOPHOSPHATE

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Eu-doped lanthanum orthophosphate samples were prepared by precipitation in aqueous solution of lanthanide ions using different precipitation agents or applying a hydrothermal treatment. The influence of the precipitation parameters on the structure and morphology of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ was studied analyzing the samples by XRD, FTIR and SEM. $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ synthesized by precipitation method presented rhabdophane structure, whereas the hydrothermal method leads to rhabdophane phase when H_3PO_4 was added in the synthesis and a mixture of rhabdophane and monazite phases when KH_2PO_4 or Na_2HPO_4 were used. The annealing step at $550^\circ\text{C}/1\text{h}$ led to the monazite phase stabilization. The luminescent properties of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ samples were investigated.

Probele de ortofosfat de lantan dopat cu europiu s-au preparat prin precipitarea ionilor de lantanide în soluție apoasă folosind diferiți agenți de precipitare sau prin aplicarea unui tratament hidrotermal. S-a studiat influența parametrilor de precipitare asupra structurii și morfologiei $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ analizând probele sintetizate prin XRD, FTIR și SEM. $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ sintetizat prin metoda precipitării a prezentat structură de tip rabdofan, în timp ce metoda hidrotermală a condus la obținerea fazei de tip rabdofan la adăugarea de H_3PO_4 la sinteză, respectiv un amestec de faze (rabdofan și monazite) la utilizarea KH_2PO_4 sau Na_2HPO_4 . Etapa de tratament termic la $550^\circ\text{C}/1\text{h}$ a condus la stabilizarea fazei monazit. S-au investigat proprietățile luminescente ale $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$.

Keywords: Eu-doped lanthanum orthophosphate, precipitation technique, hydrothermal treatment

1. Introduction

The structure and morphology, as well as surface properties of luminescent materials deeply influence their emission efficiency. Many efforts are focused in developing new biological labels that involve the obtaining new nanostructured luminescent materials with monodisperse particles and certain morphology [1]. Among the host lattice for different highly luminescent rare-earth ions are lanthanide orthophosphate, which can have rhabdophane structure with hexagonal symmetry or monoclinic monazite structure, respectively. Lanthanum orthophosphate can accommodate luminescent rare earth ions in its structure. Due to many well-defined transition modes involving the electrons from $4f$ orbitals of Eu^{3+} , as well as lanthanum orthophosphate properties, like, high refractive index, thermal and chemical stability, and its non-toxic nature, europium-doped lanthanum orthophosphate can be used in luminescent devices, moisture sensors, heat resistant materials, biological labels, laser hosts etc. [1-4] In monazite lanthanum orthophosphate, lanthanum ions are coordinated by nine oxygen atoms of phosphate

distorted tetrahedrons, while hexagonal lanthanum phosphate with the chemical formula $\text{LaPO}_4 \cdot 0.5\text{H}_2\text{O}$, has layered structure, in which La atoms are coordinated by eight oxygen atoms belonging to phosphate groups [5]. Buissette *et al.* [1] reported the synthesis of lanthanide phosphate colloids with rhabdophane structure and their luminescent properties and Ma *et al.* [3] described the obtaining of 1D nanostructured core-shell $\text{CePO}_4@/\text{LaPO}_4$ composites with improved luminescent properties.

The paper presents our studies on synthesis and characterization of Eu-doped lanthanum orthophosphate, $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, by two different techniques: precipitation in aqueous solution (*method A*) and hydrothermal method (*method B*) by using different precipitation agents, $\text{Na}_5\text{P}_3\text{O}_{10}$, KH_2PO_4 , NaH_2PO_4 and H_3PO_4 . We investigated the influence of synthesis parameters on the structure, morphology and luminescent properties of europium-doped lanthanum phosphate. The concentration of dopant ions was chosen 5% (mol.), which was found optimum for luminescence properties by other authors [2].

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2. Experimental

Two different methods were used to prepare europium-doped lanthanum orthophosphate, starting with corresponding metallic nitrates, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, >99%) and different precipitation agents, $\text{Na}_5\text{P}_3\text{O}_{10}$, KH_2PO_4 , NaH_2PO_4 and H_3PO_4 85% (aq) (Sigma, >98%), that were used as received.

Method A. The precipitation in aqueous solution was performed starting with 0.1M metallic nitrates aqueous solution, at which was drop wised 0.1M aqueous solution of precipitation agent ($\text{Na}_5\text{P}_3\text{O}_{10}$, KH_2PO_4 or H_3PO_4), at room temperature. The reaction mixture was kept at 90°C for 7h under refluxing and stirring.

Method B. The hydrothermal method consists in a reaction mixture of 0.1M lanthanum and europium nitrates aqueous solution in corresponding molar ratio and 0.1M aqueous solution of the precipitation agent (KH_2PO_4 , Na_2HPO_4 or H_3PO_4) obtained at room temperature, and hydrothermal treated at different temperature (140°, 160°, 200° or 250°C/24h), at autogenic pressure.

In both methods, the white precipitate of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$, named as-synthesized powder, was separated by centrifugation, washed with water and dried at 100°C. To obtain monazite phase, an annealing treatment at 550°C/1h was performed.

Eu-doped lanthanum phosphate samples were characterized by various techniques. The structure of the samples was analyzed by X-ray diffraction (XRD) performed on a Rigaku Miniflex II instrument with Ni filtered $\text{CuK}\alpha$ radiation and FTIR spectroscopy by using Bruker Tensor 27 spectrometer in order to evaluate the purity of synthesized orthophosphates. The morphology of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ was investigated by scanning electron microscopy (SEM) using Tescan Vega III microscope. The luminescence spectra of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ was excited with a ScienceTech Xe-Hg 350 W lamp with suitable filters selecting the radiation domain corresponding to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of the Eu^{3+} ions.

3. Results and discussion

To elucidate the structure of Eu-doped lanthanum orthophosphates, XRD analyses were performed. The as-synthesized powders obtained by *method A* using $\text{Na}_5\text{P}_3\text{O}_{10}$, KH_2PO_4 or H_3PO_4 have rhabdophane structure with hexagonal symmetry (Fig. 1a, b, c) and the phosphates annealed at 550°C have monazite structure with monoclinic symmetry (Fig. 1d). Orthophosphoric acid added to the reaction mixture led to a more crystalline Eu-doped orthophosphate with rhabdophane structure than the other samples prepared in the same conditions by using other

precipitation agents (Fig. 1). The crystallite size values of rhabdophane phase, calculated by using Rigaku PDXL software, from XRD peak (100) from $2\theta=14.45^\circ$, were different depending on the precipitation agent, 17 nm for H_3PO_4 , 8 nm for KH_2PO_4 , and 5 nm for $\text{Na}_5\text{P}_3\text{O}_{10}$, respectively.

When temperature of hydrothermal treatment (*method B*) increased, the equilibrium shifted towards the monazite $\text{LaPO}_4 \cdot \text{Eu}^{3+}$ (the phase more stable at high temperature). In 160° - 250°C temperature range, a mixture of rhabdophane and monazite was obtained (Fig. 2b,c,d) in agreement with other data reported in the literature [5,6]. When orthophosphoric acid is added to the reaction mixture and a hydrothermal treatment is applied at 140°C, single rhabdophane phase (Fig. 2a) was obtained with higher crystallinity than the other samples obtained by the same method. Similar to *method A*, the monazite structure was obtained by annealing of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ at 550°C as XRD confirmed (Fig. 2e). Lin *et al.* [6] reported their studies on synthesis of lanthanide phosphates by hydrothermal method using $\text{NH}_4\text{H}_2\text{PO}_4$ as precipitation compound. They stated that the temperature of hydrothermal treatment determined the structure of lanthanum phosphate, the rhabdophane structure was obtained at 150°C, while the temperature is increased to 180°C, monoclinic phase was isolated.

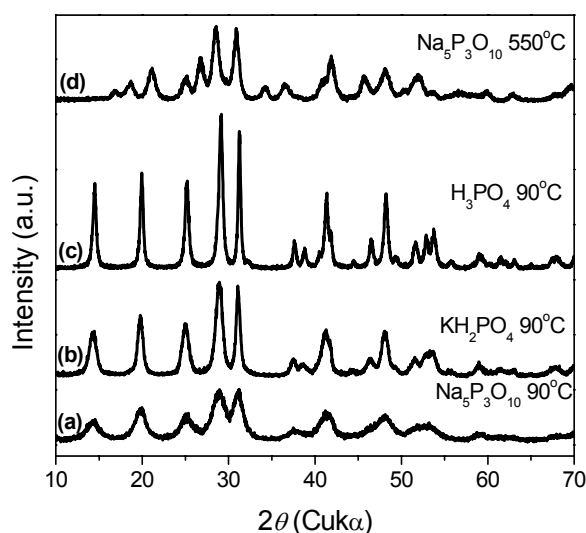


Fig. 1 - XRD data of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ obtained by *method A* using different precipitating agents: as-synthesized powder prepared in the presence of $\text{Na}_5\text{P}_3\text{O}_{10}$ (a), KH_2PO_4 (b), H_3PO_4 (c), sample prepared in the presence of $\text{Na}_5\text{P}_3\text{O}_{10}$ and annealed at 550°C/1h (d) / *Difracția de raze X pentru $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ obținut prin metoda A folosind diferiți agenți de precipitare: pulberea sintetizată în prezența $\text{Na}_5\text{P}_3\text{O}_{10}$ (a), KH_2PO_4 (b), H_3PO_4 (c), pulberea obținută în prezența $\text{Na}_5\text{P}_3\text{O}_{10}$ și calcinată la 550°C/1h (d).*

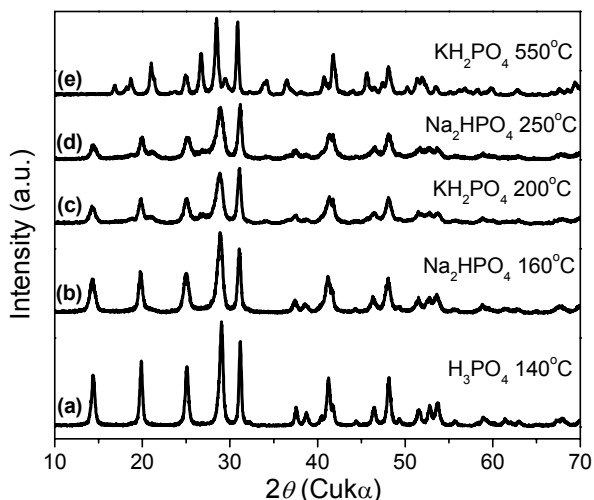


Fig. 2 - XRD data of $La_{0.95}Eu_{0.05}PO_4$ obtained by *method B* in different conditions / Difracția de raze X pentru $La_{0.95}Eu_{0.05}PO_4$ obținut prin metoda B în diferite condiții.

The samples were also analyzed by FTIR spectroscopy in order to evaluate their purity and to confirm the structure of the samples.

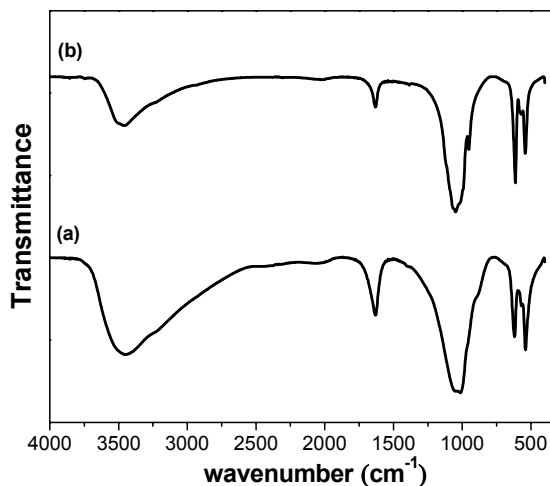


Fig. 3 - FTIR spectra of $La_{0.95}Eu_{0.05}PO_4$ obtained by: *method A* using $Na_5P_3O_{10}$ as precipitation agent (a); *method B* using KH_2PO_4 as precipitation agent, 200 °C/24h (b) / Spectrele FTIR pentru $La_{0.95}Eu_{0.05}PO_4$ obținut prin: metoda A folosind $Na_5P_3O_{10}$ ca agent de precipitare (a); metoda B folosind KH_2PO_4 ca agent de precipitare, 200 °C/24h (b).

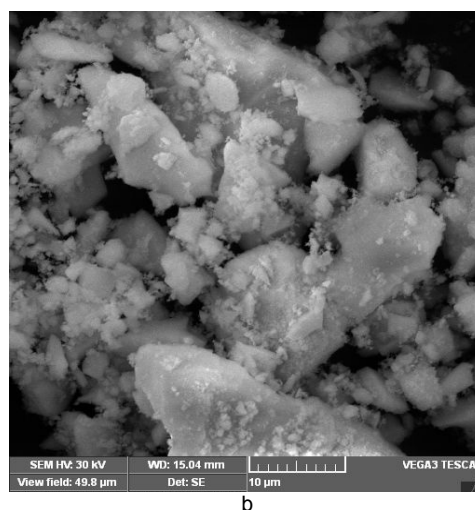
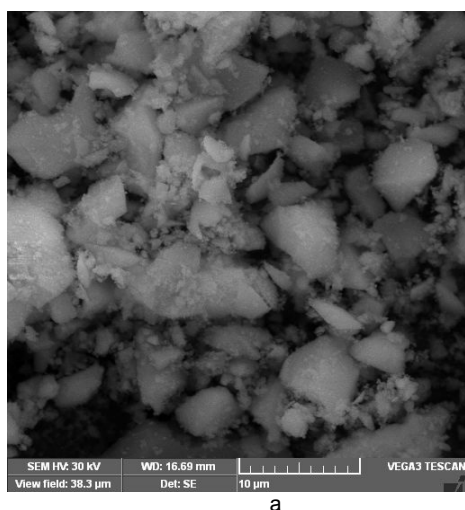


Fig. 4 - SEM micrographs of $La_{0.95}Eu_{0.05}PO_4$ obtained by *method A* using $Na_5P_3O_{10}$: as-synthesized powder (a); annealed sample at 550°C/1h (b) / Imagini SEM pentru $La_{0.95}Eu_{0.05}PO_4$ obținut prin metoda A folosind $Na_5P_3O_{10}$: pulberea sintetizată (a); proba tratată termic la 550°C/1h (b)

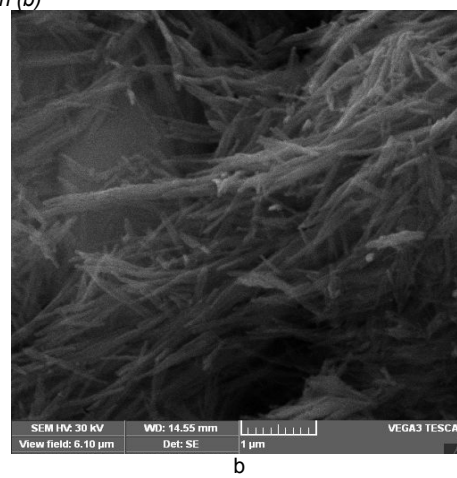


Fig. 5 - SEM micrographs of $La_{0.95}Eu_{0.05}PO_4$ obtained by *method B* using KH_2PO_4 : as-synthesized powder (a); annealed sample at 550°C/1h (b) / Imagini SEM pentru $La_{0.95}Eu_{0.05}PO_4$ obținut prin metoda B folosind KH_2PO_4 : pulberea sintetizată (a); proba tratată termic la 550°C/1h (b)

In figure 3 were presented the FTIR spectra of as-synthesized samples obtained by both methods. In both spectra, one can notice the characteristic stretching vibrations of P-O bond of phosphate groups, at 520 cm^{-1} and 600 cm^{-1} and the large, intense bands in the range of $950\text{--}1070\text{ cm}^{-1}$ assigned to bend vibrations of phosphate ions that are more split in the case of monoclinic phase. In the figure 3b, it can be observed the split of bend vibrations of phosphate group and less intense bands at 1630 cm^{-1} and $3400\text{--}3600\text{ cm}^{-1}$ attributed to hydration water from rhabdophane structure as a consequence of the existence of a mixture of both hexagonal and monoclinic phases in the as-prepared powder obtained by hydrothermal treatment at 200°C [7].

The morphology of the samples depends on the synthesis method and was investigated by SEM. Eu-doped lanthanum orthophosphates obtained by precipitation in aqueous solution have the tendency to form agglomerates with irregular shapes (Fig. 4a). No significant difference on the morphology of the samples prepared by method A was noticed after the annealing treatment (Fig. 4b). In the case of $\text{LaPO}_4\cdot\text{Eu}^{3+}$ obtained by hydrothermal method, SEM investigation revealed the nanowires formation, more evident for the annealed sample (Fig. 5b) than for as-prepared powder (Fig. 5a). Also, a higher degree of agglomeration of as-synthesized powder than for the thermal treated sample was noticed.

In the luminescence spectra of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ samples (Fig. 6, 7), one can observe the main electronic transitions originated from the $^5\text{D}_0$ level towards $^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) levels, as well as transitions from $^5\text{D}_1$ level to $^7\text{F}_1$ level ($\sim 545\text{ nm}$).

Due to the sensitivity of the luminescence of the europium ions ($4f^6$ electronic configuration) to the change of their neighborhoods. Eu^{3+} is used as structural probe for the estimation of the symmetry in crystals, thin films and glasses [8]. The resolved lines of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transitions (involving two non-degenerate levels) give the number of nonequivalent centers. The probability of the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), allowed by the parity rule (Laporte), is independent to the neighborhood in the host material and can be used as internal reference. The electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is hypersensitive and its intensity depends on the modifications of the europium ions surrounding. From the two electric dipole transitions, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$, only the second one is permitted. The asymmetry ratio, defined as the ratio between the areas of electric dipole ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and magnetic dipole ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) transitions is used to estimate the modification of the symmetry by deviation from the spatial inversion and/or covalency changes. Values higher than one for this ratio are known for hosts like Y_2O_3 or langasite [9, 10].

The luminescent spectra of the samples obtained by *method A*, using $\text{Na}_5\text{P}_3\text{O}_{10}$ as precipitation agent confirm the hexagonal (Fig. 6a) to monoclinic (Fig. 6b) polymorph transition proved by the XRD results. The weaker splitting of the lines belonging to the magnetic dipole transition for the annealed sample suggests a weaker crystalline field of the monoclinic phase [11, 12]. Narrow lines in the case of the monazite phase emphasize the improved crystallinity (possibly by larger particles). For similar systems of Eu^{3+} in LaPO_4 hosts with monoclinic or hexagonal-type phases, different shapes of luminescence spectra were observed [1-3, 13].

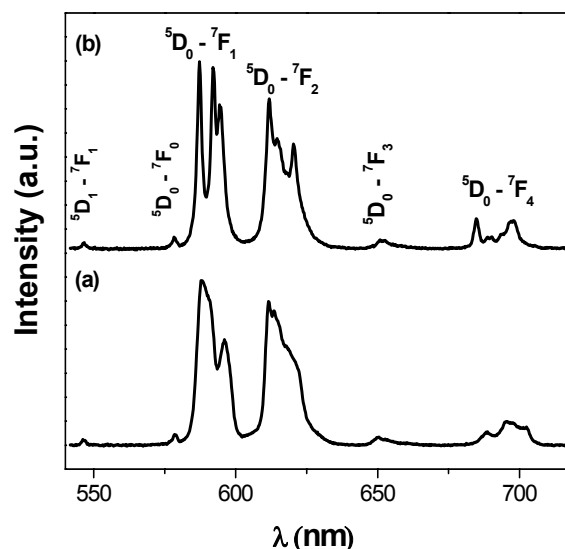


Fig. 6. PL spectra of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ obtained by *method A* by using $\text{Na}_5\text{P}_3\text{O}_{10}$ as precipitation agent: as-synthesized powder (a) and annealed sample at $550^\circ\text{C}/1\text{h}$ (b) / Spectrele de fotoluminescență ale $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ obținut prin metoda A folosind $\text{Na}_5\text{P}_3\text{O}_{10}$ ca agent de precipitare: pulberea sintetizată (a) și proba tratată termic la $550^\circ\text{C}/1\text{h}$ (b).

Using KH_2PO_4 as precipitation agent followed by a hydrothermal treatment ($200^\circ\text{C}/24\text{ h}$) led to a mixture of crystalline phases as XRD confirmed (Fig. 7a, b), the photoluminescence spectrum reflecting the coexistence of hexagonal and monoclinic phases. More than three lines could be noticed for the magnetic dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$), although the maximum degeneracy of this level is three. The transition was solved by Fityc software using Voigt functions (Fig. 7a,b inset). Contrary to the X-ray diffraction analysis that detected only the patterns of the monazite phase, in the luminescent spectrum of the annealed sample lines corresponding to a hexagonal impurity phase are noticed (insets Fig. 7b).

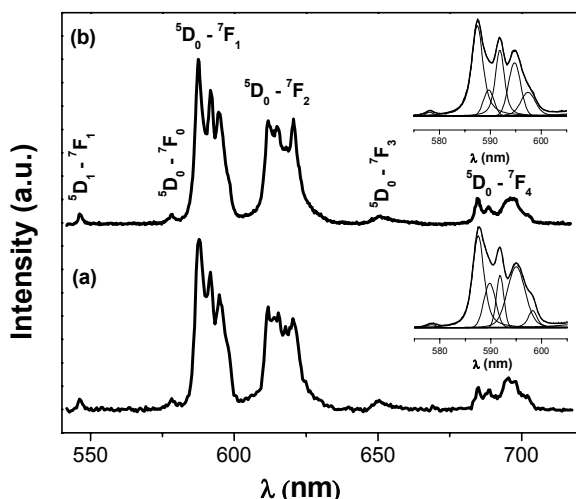


Fig. 7. PL spectra of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ obtained by *method B* by using KH_2PO_4 as precipitation agent: as-synthesized powder and hydrothermal treated at $200^\circ\text{C}/24\text{h}$ (a) and annealed sample at $550^\circ\text{C}/1\text{h}$ (b). Insets – the solving of the band ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ with Voigt functions / *Spectrele de fotoluminescență ale $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ obținut prin metoda B folosind KH_2PO_4 ca agent de precipitare: pulberea sintetizată și tratată hidrotermal la $200^\circ\text{C}/24\text{h}$ (a) și proba tratată termic la $550^\circ\text{C}/1\text{h}$ (b). Inserate – rezolvările benzilor ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ cu funcții Voigt.*

4. Conclusions

The structure and the morphology of $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ can be controlled by using different precipitation conditions. More crystalline samples were obtained when orthophosphoric acid was used as precipitation compound. By hydrothermal method, only at low temperature and using H_3PO_4 , the hexagonal rhabdophane phase was obtained, unlike the method A that lead to the hexagonal phase formation, irrespective to the precipitation agent added in the synthesis. Annealing the as-synthesized samples at 550°C , by both methods discussed in this paper, the monazite monoclinic $\text{La}_{0.95}\text{Eu}_{0.05}\text{PO}_4$ was formed. Depending on the synthesis conditions, different morphologies were obtained that affect the luminescent properties of the samples.

Acknowledgements

The authors thank to Dr. A.M. Voiculescu for performing the photoluminescence measurements.

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