DESIGN OF $\text{LaPO}_4\text{:Nd}^{3+}$ MATERIALS BY USING IONIC LIQUIDS

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Abstract

Monoclinic monazite-type Nd^{3+} -doped lanthanum orthophosphate ($\text{LaPO}_4\text{:Nd}^{3+}$) nanoparticles were prepared by microwave treatment of simple lanthanide precursors such as $\text{Nd}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$, OAc = acetate) with task-specific dihydrogen phosphate ionic liquids (ILs) 1-butyl-1-methylpyrrolidinium dihydrogenphosphate- $\text{BmPyrH}_2\text{PO}_4$ (IL 1) and 2-hydroxyethyl-N,N,N-trimethylammonium, $[\text{choline}][\text{H}_2\text{PO}_4]$ (IL2) as the reaction medium, reactant and in-situ nanoparticle stabilizer and templates at 140°C within 10 minutes. This synthesis route possesses many advantages as it is a fast and facile preparation method for the desired phosphate nanomaterials without the necessity for post-reaction heat treatment to obtain the anhydrous high temperature monazite phosphate phase.

The nano-sized phosphors $\text{Nd}^{3+}\text{:LaPO}_4$ were carefully analyzed by the powder X-ray diffraction, electron microscopy and spectroscopic techniques taking advantage of the Nd^{3+} spectroscopic probe to analyze in detail the structural properties. Applied high resolution low temperature absorption and emission techniques allowed to complete the structural information unavailable from the XRD powder patterns.

A clear influence of the used task-specific dihydrogen phosphate ILs on the structure, morphology, luminescence intensity and lifetimes of the obtained $\text{Nd}^{3+}\text{:LaPO}_4$ was found. It is worth noting that the Nd^{3+} luminescence in LaPO_4 has never been reported up to now.

Keywords: orthophosphates, ionic liquids assisted synthesis, neodymium doping, NIR emitting phosphors

1. Introduction

In the modern technology functional nanomaterials plays very important role, thus as the morphology – size and particles shape influence the physico-chemical properties of these materials, it is crucial to develop synthesis protocol which allows to obtain well reproducible particles. In materials with good optical properties, for transformation from bulk or crystals to the nanometric scale phosphors it is necessary to consider all the advances like for example reduced light scattering and avoiding unwanted drawbacks, such as a high surface defect concentration, which is likely to result in luminescence quenching. From a spectroscopic point of view the large surface of nanoparticles (NPs) is without a doubt critical, and fundamental luminescence properties such as decay times and non-radiative as well as radiative relaxation paths are strongly affected. For these reasons, extreme care must be taken in order to find ways to fabricate nanometer-scale phosphor materials with good optical properties. Among the techniques for phosphor materials, which was applied lately in different nanomaterials preparation, such as, fluorides, oxides, or phosphates, nanomaterials the synthesis with using Ionic Liquids (ILs) seems to be very promising one [1-5]. The advantages of ILs in nanoparticle synthesis in comparison with other methods of preparation of nanomaterials were presented in the detailed description in [6].

In this method ionic liquids can be not only reaction medium but also reactant [6-10]. From chemical point of view ILs are considered to be generally ionic organic compounds, with melting point below 100°C, many of them are even already liquid at room temperature (RTILs). The physicochemical properties of ILs as thermal stability, viscosity, density, melting temperature can be modify by selecting appropriate cations and anions. The extremely low vapor pressure and non-flammability of most ionic liquids makes them good candidates to replace some organic solvents. The number of potential cation/anion modification seems to be unlimited. This offers the possibility to design an IL with properties for a specific application (task-specific ionic liquids, *TSILs*). It is also possible to use these salts as a template for nano-particles synthesis, and by changing the cation or anionic part in ILs one can change size and shape of the synthesized nanomaterials. A strong influence on the size and morphology of the obtained particles can be expected, as ionic liquids can work as a template and in-situ stabilizing preventing the particles grow and agglomeration [6-8, 10,11]. Up to the date detailed studies of influence ILs composition on the optical properties of lanthanide doped fluorides and phosphates were reported [6-8, 10,11].

The orthophosphates doped with optically active lanthanides ions were studied over many years as these crystal lattices are matrices with high mechanical and chemical performances.

For the doping of trivalent rare earth ions no charge compensation is required. With relatively large band gap they open possibility to observe an efficient emission of optically centers in Vis and/or IR spectral ranges [12-15]. They are extensively studied as phosphors, scintillators and laser materials. The Nd^{3+} activated phosphates are very popular among researchers. As example we can mention the $\text{LuPO}_4\text{:Nd}$ and $\text{YPO}_4\text{:Nd}$ as new promising VUV scintillation materials [16] or neodymium ultra-phosphate (penta-and tetra phosphates) crystals, which belong to the group of high concentration neodymium stoichiometric laser materials, where weak concentration dependence of Nd^{3+} fluorescence is predominantly associated with a large distance (6.6 Å) between neighboring Nd^{3+} ions resulting in reduced concentration quenching [17-21].

Lately many studies were devoted to the orthophosphate materials in nanoscale as they can find many applications, also in bio imaging [22]. These materials doped with optically active lanthanide ions have properties as narrow emission bands, with submilliseconds lifetimes of the emitting metastable levels which make them good candidate for fluorescent agents. Very important requirement for this purpose is the location of excitation and emission bands, which should be in the spectral range 800-1300 nm, thus in the transparency window of biological tissues. It also prevents high autofluorescence of tissues. One of lanthanides ions, which fulfil this demand is Nd^{3+} ion, showing relatively efficient NIR luminescence. It is well known, because of nanoparticles big surface to volume ratio these materials show less intensive emission than the crystals, or bulk as the nonradiative processes of the deexcitation can be promoted by the water and other impurities bounds on the surface. In the case of the fluorescence in the UV region the contribution of the quenching caused by –OH groups to the overall relaxation rate is not so significant due to very high energy of optical transitions. However, this effect can play significant role especially in quenching emission in infrared range. This obstacle is a fundamental one, as most of the methods of synthesis of water dispersible nanoparticles are carried out either in water or in other –OH containing media. Later the molecules of water can be removed only by high temperature treatment accompanied by agglomeration of the NPs with an expected loss of dispersibility.

This is why we would like to perform the studies of Nd^{3+} activated LaPO_4 prepared by using earlier reported method of synthesis of nanoscale orthophosphate with ILs, which allow to synthesize anhydrous materials at relatively low temperature. The Eu^{3+} ions doped materials showed relatively high luminescence, and the impurity traces did not efficiently quench luminescence [6,11]. We applied above preparation protocol to synthesize $\text{LaPO}_4\text{:Nd}^{3+}$ materials, in aim to study the influence of ILs on the morphology of obtained

particles on their NIR emission performance. The Nd³⁺ luminescence in LaPO₄ has never been reported up to now.

2. Materials and characterizations

2.1. Synthesis of Nd³⁺-doped orthophosphates using ILs as reaction media

The studied nano-powdered samples were synthesized according the procedure described earlier in [6,11]. In this synthesis protocole lanthanides precursors, which are the simple lanthanide salts like nitrate or acetate hydrates are converted at relatively low temperature (~140°C) to anhydrous lanthanide phosphate. A phosphate ionic liquid is used as the reactant and phosphate group donor. By applying such a synthesis protocol it is possible to obtained relatively phosphate particles small (even below 10 nm) as ionic liquid (IL) also prevent the formed nanoparticles from agglomeration and coalescence to the bulk.

In order to obtain LaPO₄:Nd³⁺ nanomaterials the proper mixture of Ln(III) acetate hydrate and Nd(III) acetate hydrate was dissolved in small amount of ethylene glycol and then excess amount of ILs (1-butyl-1-methylpyrrolidinium dihydrogenphosphate, BmPyrH₂PO₄ (IL 1) and 2-hydroxyethyl-N,N,N-trimethylammonium dihydrogenphosphate, [choline][H₂PO₄] (IL2), see Fig. 1). Usually the reactant ratio was of 150 mg of lanthanide(III) acetate and 0.3 g of ILs. The reaction solution was stirred until homogeneity is reached and then placed in a 10 ml microwave reaction vessel. The reaction was carried out in two steps - first heating to 60°C for 10 minutes and then increasing the temperature to 140°C for another 10 minutes using a single mode microwave (CEM Discover, Kamp-Lintfurt, Germany) operating at 2455MHz. The post reaction colloidal solution was centrifuged and the powdered material was washed with ethanol and dichloromethane. The obtained powder was dried at 100°C for 12 hrs.

The preparation of samples under investigations can be described by the following equation:

Ln = lanthanide; OAc = acetate, [cat] – 1-butyl-1-methylpyrrolidinium dihydrogenphosphate-BmPyrH₂PO₄ (IL 1) and 2-hydroxyethyl-N,N,N-trimethylammonium, [choline][H₂PO₄] (IL2).

With these two ionic liquids anhydrous lanthanide phosphates LnPO₄ were obtained directly from the process even at low temperatures (T = 140°C/10 min) without the need for a post reaction heat treatment.

For LaPO_4 , two modifications are known in the bulk materials and crystals: the low temperature monoclinic phase of LaPO_4 (tysonite type of structure) with irreversibly undergoes a phase transformation to the monazite structure above 600°C . Using IL as reaction medium, in situ stabilizer and donor of phosphate group lead to high temperature phase already at 140°C .

2.2. Sample characterization

XRD phase analysis

The powder X-ray diffraction patterns were collected at room temperature by using a D8 Advance X-ray diffractometer (Bruker). The measurements were performed within the range $10 - 60^\circ 2\theta$ with a scan rate of 0.008° per step and a counting time of 5 s per step. For the experiments nickel-filtered CuK_α radiation ($K_{\alpha 1+2}$, $\lambda = 0.15418 \text{ nm}$) was used.

FT-IR measurements

FT-IR spectra of powdered samples in the $3800 - 300 \text{ cm}^{-1}$ spectral range were measured using at Specord-M-80 spectrometer (Carl Zeiss Jena). The powdered samples were mixed with Nujol oil (a mixture of liquid hydrocarbons). The spectral resolution of FT-IR measurement was 2 cm^{-1} .

Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM).

Scanning electron microscopy (SEM) studies were carried out on a Hitachi S-3400N equipped with an energy dispersive X-ray spectroscopy (EDX) EDAX analyser. The powders were coated with a thin gold alloy layer to facilitate conductivity.

Transmission electron microscopy (TEM) measurements were carried out on a Tecnai G2 20 X-Twin TEM (Fei, Hillsboro, USA) or a H-8100 TEM of the Hitachi company (Tokyo, Japan) equipped with a Penta FET EDX detector (Oxford Instruments, UK). An acceleration voltage of 200 kV was applied. To prepare the samples, a suspension of the sample in ethanol was dropped on a copper or gold grid coated with carbon and then dried in air.

Absorption measurements

Absorption spectra in the 200 - 2500 nm spectral range were recorded at 4 and 293 K with a Cary-Varian 5000 Scan spectrometer equipped with an Oxford CF 1204 helium flow cryostat. The pellets used for the absorption measurements were prepared under 20 MPa pressure during 5 minutes.

Luminescence decay measurements

The luminescence decay curves were recorded under pulsed laser excitation (OPO laser, EKSPLA NT342, 10Hz, 7 ns), the fluorescence intensity around $1 \mu\text{m}$ being detected with a

R1767 Hamamatsu photomultiplier through a HRS1 Jobin-Yvon monochromator equipped with a 1 μm blazed grating and coupled to a LECROY LT 342 digital oscilloscope. Both the luminescence emission spectra detected with the help of an IR Hamamatsu CCD camera and decay curves were recorded at room and liquid nitrogen temperature. As an excitation source also LED (λ_{ex} -590 nm) and Ar^+ laser have also been used.

3.Results and discussion

3.1. XRD analysis of phosphates nano-powders

Lanthanide (RE) orthophosphates are very well known, being stable materials. They can be found in nature as minerals existing in two common phases – monazite and xenotime. Depending on the ionic radius of the rare earth ion either the monazite or xenotime structure is the thermodynamically stable phase. In both types of structure the atomic arrangements is characterized by chains of interconnected phosphate tetrahedra and RE polyhedral. These are in case of the xenotime structure with is preferentially adopted by the smaller RE (Y, Tb-Lu) a REO_8 polyhedron (distorted square anti-prism) and REO_9 polyhedron (fairly distorted tricapped trigonal prism. In both structures the PO_4 are isolated, separated by LnO_x polyhedra [23-26]. Low temperature hydrated rhabdophane with a general formula $\text{REPO}_4 \cdot n\text{H}_2\text{O}$ (RE: La $\rightarrow$ Dy) has been considered to crystallize in the hexagonal [26] system. However, recent investigations show that the structure of this compounds is rather monoclinic than hexagonal and that it can be found for Ln = La-Dy [26]. It was found that this phase irreversibly transforms to monazite after heating to 600°C.

Fig. 2 presents the visualization of the polyhedral view of PO_4 tetrahedra and REO_9 polyhedra in the structures of monazite type LaPO_4 (Fig.2a) and PO_4 tetrahedra and REO_8 polyhedra (Fig.2b) in hexagonal rhabdophane type orthophosphates. This hexagonal structure is made of PO_4 tetrahedron and LaO_8 polyhedra linked together to form chains alternating PO_4 and LaO_8 polyhedron. The chains are linked together by P–O–La bonds leaving an open channel along the hexagonal axis. The open channel has a minimum diameter of 3.4 Å and can contain 0–1 mol of water molecules [27] The zeolitic water in the hexagonal rhabdophane type (for hydrated) evaporates between 180°C and 280°C. [24]

In Fig. 3 we present the X-ray powder diffraction pattern of Nd^{3+} -doped LaPO_4 obtained from (IL2) together with the simulated XRD patterns of monazite type LaPO_4 (ICSD#01-071-6745). The insert contains the simulated patterns (taken from the Database of Inorganic Crystal Structure XRD) of monazite and rhabdophane phases. It is presented to clearly point out on the difference in the localisation of the reflections of both phases. Thus for Nd^{3+} -doped LaPO_4 (IL2) sample the XRD patterns in the 2θ range of 15–60 corresponds very well to

monoclinic phase. Despite the large width of registered peaks all reflections fit perfectly to the pattern of monoclinic monazite phase. Fig. 4. displays an example of the XRD patterns recorded for the 5% -doped and stoichiometric materials obtained by using two different ILs. With increasing amounts of Nd^{3+} ions a shifting of all diffraction peaks towards higher 2θ angles is observed. For as-prepared with using IL2 raw materials the powder diffraction patterns show very good matching with the simulated patterns, what confirm that we obtained the monoclinic monazite phase. For IL1 the reflections are not formed well, the samples are amorphous and a clear assignment of the crystallographic structure is very difficult. For all compounds we observe a very broad reflections characteristic for nanomaterials. From this comparison one can conclude that the synthesis with using IL2 leads to a product better crystalized and of better quality.

3.2. Morphology and particle size by SEM and TEM analysis

The morphologies of nano-crystallites were analyzed with using a scanning electron microscopy (SEM) and a transmission electron microscopy (TEM).

Representative micrographs of $\text{LaPO}_4\text{:Nd}^{3+}$ nanoparticles obtained by using the two ILs IL1 and IL2 are presented in Fig. 5. The left part of the figure presents the nanoparticles obtained using $\text{BmPyrH}_2\text{PO}_4$ (IL1), on the right side we present the results obtained when using $[\text{choline}]\text{H}_2\text{PO}_4$ (IL2). The overview pictures reveal the presence of nanoparticles that are loosely aggregated. Especially in the case of the product obtained from IL 1, the relatively small nanoparticles form agglomerates creating balls of dimensions of about 700 nm (see Fig.5 left). The large magnification by using the TEM technique reveals that in the nanoparticles obtained from IL1 most probably we observe at segregation of the Nd^{3+} ion in the middle of the ball seen as the white areas in the middle of the sphere. As we see from the SEM micrographs the number of such spherical agglomerates are fairly big.

For Nd^{3+} -doped LaPO_4 obtained from IL 2 $[\text{choline}]\text{H}_2\text{PO}_4$ (Fig. 5, right) the images are somewhat different. Both in the TEM and SEM micrographs we observe not such an extremely strong agglomeration. Separate irregularly shaped nanoblocks can be made out. Similar morphology we have observed for the Eu^{3+} -doped samples of LaPO_4 prepared with $[\text{choline}]\text{H}_2\text{PO}_4$. [6]

The obtained results are very similar in two series of Nd^{3+} -doped lanthanum orthophosphates contained different concentrations of the activator according to the application of the different ionic liquids. The series from IL1 clearly shows the higher

agglomeration of the products which is in agreement with the XRD analysis, confirming that the product of better quality with using of IL2 ionic liquid was obtained.

3.2. FT-IR spectra

The infrared spectra recorded for both types of samples is given in Fig. 6. Most of the bands are characteristic of the vibrations of phosphate groups PO_4^{3-} . So the characteristics of monoclinic phase of four band, located at about 536, 563, 577 and 623 cm^{-1} , were clearly observed in the ν_4 region of PO_4 group's vibration (the bending vibrations). A massive band appears in the ν_3 (stretching vibrations) region between 900 and 1150 cm^{-1} . In comparison with the hexagonal structure, the presence of additional bands of phosphate vibrations is characteristic of the vibration of phosphate groups in the monoclinic structure of monazite-type LaPO_4 and results from the distortion of the tetrahedral phosphate groups in the nine-fold coordinated La atoms [23, 24].

Unexpectedly, we observe the broad bands between 3250 and 3750 cm^{-1} and 1250-1600 what confirm the presence of the molecules H_2O on the surface. The same low temperatures synthetic method applied for $\text{LaPO}_4\text{:Eu}^{3+}$ gives an access to anhydrous nanophosphates with excellent photophysical properties [6,11]. The absence of water and hydrous compounds was confirmed by IR spectroscopy. Also for $\text{GdPO}_4\text{:Eu}^{3+}$ only the characteristic asymmetric P-O modes in the 1250-750 cm^{-1} spectral range were observed. The broad intense O-H band usually located between 3350-3650 cm^{-1} was absent. In case of $\text{YPO}_4\text{:Eu}^{3+}$ traces of this band can be noticed. But as the intensity of observed O-H band is relatively low it could be due to the traces of surface bond water.

Because the measurements were performed in the nujol oil, the spectrum of this oil is presented in figure also. We can clearly see that the bands located at 721, 1377, 1460, 2 854 and 2 938 cm^{-1} overlap with bands observed for the samples under investigations.

In IR spectra for the samples activated with the Nd^{3+} ions the intensities of characteristic P-O modes both in the spectra range of 650 -500 cm^{-1} and 1250-750 cm^{-1} are higher for the sample obtained from IL2 (choline). Also at the same time for the sample the O-H modes in the 1250-1700 cm^{-1} spectral region are less intense. The obtained results allow to conclude that Nd^{3+} -doped samples have a higher affinity to keep the water on the surface than that activated with the Eu^{3+} ones. We should not forget that in the samples used for IR investigations the concentration of the Nd^{3+} ions was high (50%) which may also be important, as introducing into the crystal lattice cations with somehow different size (La^{3+} were replacing by Nd^{3+}) can cause some structural distortions. However, our results confirm

previous findings that choline dihydrogenphosphate is very efficient reactant allowing to stabilizing the obtained nanoparticles.

Investigations of the effect of Nd^{3+} ion concentration in LaPO_4 on the presence of molecules of water with using different ionic liquids, but the same method and conditions of synthesis will be the subject of our further work. Despite a large number of articles devoted to nanocrystalline LaPO_4 activated with different lanthanides and obtained by fast method the knowledge about the Nd^{3+} -doped lanthanum orthophosphates is still very limited.

3.3. Spectroscopic consideration

3.3.1. Energy level diagram of Nd^{3+}

The trivalent neodymium ion can be used to study the local environment structure in the host matrix.

Fig. 7 presents the energy level diagram for the Nd^{3+} ion with $4f^3$ configuration. Electronic transitions are located in a wide spectral region (V–UV, UV, NIR and IR). There are two important levels: the singlet of $^2P_{1/2}$ and the doublet of $^4F_{3/2}$, which can be useful for structural studies. On the basis of the number of components for these transitions observed in the absorption spectra at low temperature (4 K) one can conclude on the number of non-equivalent positions occupied by the Nd^{3+} ion in the host lattice.

3.3.2. Optical absorption spectra

As it was discussed above powder X-ray diffraction and the electron microscopy showed the formation of a better crystallized product using IL2- [choline] H_2PO_4 . For that reason, we first will describe the spectroscopic studies for this material. Fig. 8 presents the absorption spectra of sample measured at room and liquid helium temperature. The absorption spectra of monazite Nd^{3+} -doped lanthanum orthophosphate in the visible and NIR regions involves parity forbidden $f-f$ transitions from the $^4I_{9/2}$ ground state to the various excited states. We clearly observe the line narrowing at low temperature what points to on ordered structure. The narrow and well separated peak that typically observed for high-symmetry systems such as Nd^{3+} -doped YAG. It is well known that for highly symmetric systems where the Nd^{3+} features site symmetry such as O_h and D_{4h} , the intensities of two transitions: the hypersensitive $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ and the $^4I_{9/2} \rightarrow ^4F_{7/2}$, $^4S_{3/2}$, $^4I_{9/2} \rightarrow ^4F_{5/2}$, $^2H_{9/2}$ ones in IR region are about one half of those of the $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ transition, while in low symmetry environments the ratio is significantly higher [28]. According to these rules it is possible to conclude that system under investigations exhibits quite low symmetry because the intensities of two transitions in the IR region are comparable and even higher than for the $^4I_{9/2} \rightarrow ^4G_{5/2}$,

$^2G_{7/2}$.one. Moreover, according to the Judd-Jørgensen [29] statement the $f-f$ transitions which obey the $\Delta J = 2$, $\Delta L = 2$ selection rules are the most sensitive to the lanthanide ion environment, and are commonly referred to as hypersensitive. The $Nd^{3+} \ ^4I_{9/2} \rightarrow \ ^4G_{5/2}$ absorption transition satisfies the above criteria, and therefore its intensity is often use as a probe for structural changes, similarly to the $^4I_{9/2} \rightarrow \ ^4F_{5/2}$ transition in the IR region, which also partially satisfies the selection rule for a hypersensitive transition. In practice the energy of the $^2G_{7/2}$ term is very close to that of the $^4G_{5/2}$, thus at room temperature the $^4I_{9/2} \rightarrow \ ^4G_{5/2g}$, $^2G_{7/2}$ transitions cannot be separated and must be analyzed together. The highest intensity is observed for the hypersensitive $^4I_{9/2} \rightarrow \ ^4G_{5/2}$, $^2G_{7/2}$ transitions, due to the structural distortion of the site occupied by Nd^{3+} . Because of the low point symmetry of the lanthanide sites and the absence of transition selection rules between the CF (crystal field) components, the maximum number of lines for each transition from the $^4I_{9/2}$ level is given by the J multiplicity of the excited level, *i.e.* $J + 1/2$. One can clearly observe more than $J + 1/2$ lines for the $^4I_{9/2} \rightarrow \ ^2H_{11/2}$ and $^4I_{9/2} \rightarrow \ ^4G_{7/2}$, $^4G_{5/2}$ transitions. In the absorption spectra presented in Fig. 8 six well resolved lines are observed.

Since at 4K only the lowest Stark component of this multiplet is populated, the number of components of the Kramer's doublet $^4I_{9/2} \rightarrow \ ^2P_{1/2}$ transition is consisted with the number of metal sites in the crystal structure. At room temperature more than one (even four) components of the $^4I_{9/2} \rightarrow \ ^2P_{1/2}$ transition are well observed: *i.e.* the lines line located at 428.5 nm ($23\ 337\ cm^{-1}$), 429.7 nm ($23\ 272\ cm^{-1}$), 432.4 nm ($23\ 127\ cm^{-1}$) and 434 ($23\ 041.5\ cm^{-1}$). Going to the 4K three lines located at 429.7 nm, 432.4 nm and 434 nm disappear what suggests that they represents the transitions from the higher energy Stark components of the $^4I_{9/2}$ ground state of one Nd^{3+} site (69, 210 and $296\ cm^{-1}$, respectively). One line at 4K for $^4I_{9/2} \rightarrow \ ^2P_{1/2}$ transition (428.5 nm) indicates one distribution of Nd^{3+} ion in investigated $LaPO_4$.

The second very important from the structural point of view transition is the $^4I_{9/2} \rightarrow \ ^4F_{3/2}$ one. In this transition for one symmetry site one should observe two peaks at 4K. The low-temperature absorption spectra of Nd^{3+} -doped $LaPO_4$ presented in Fig.8 reveals two well defined lines at 862.5 nm ($11\ 594\ cm^{-1}$) and 871 nm ($11\ 481\ cm^{-1}$) which correspond to $^4I_{9/2}(Z1,2) \rightarrow \ ^4F_{3/2}(R2)$ and $^4I_{9/2}(Z1,2) \rightarrow \ ^4F_{3/2}(R1)$ transitions, respectively. Both peaks are quite broad and not resolved. Based on these results one can suggest again the presence of one main distribution of the Nd^{3+} ion in this structure and so confirm the previous assignment.

Different results we observe in the case of compounds using BmPyrH₂PO₄ (1IL) (see Fig. 9). For the $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition at room temperature a very broad band with a maximum at 429 nm a much weaker transition at 432 nm have been observed. At 4K event 4 bands become apparent: 427.5 nm (23 392 cm⁻¹), 429 nm (23 310 cm⁻¹), 430 nm (23 256 cm⁻¹) and 432 nm (23 148 cm⁻¹). Based on this observation one can conclude the presence more than one Nd³⁺ site in the material with a huge disorder in the structure. The confirmation of multisite character in the sample we can find in the spectra from the 840-890 nm spectral region presenting the $^4I_{9/2} \rightarrow ^4F_{3/2}$ transition. Here at room temperature two broad lines with maxima at 86 and 870 nm are present which correspond to $^4I_{9/2}(Z1,2) \rightarrow ^4F_{3/2}(R2)$ and $^4I_{9/2}(Z1,2) \rightarrow ^4F_{3/2}(R1)$ transitions, respectively. At liquid helium temperature two additional bands at 864.5 and 881.5 nm occurred..

This disorder of the active ions in the structure in this sample manifests also very well for other transitions what is clearly seen on the overview absorption spectra recorded at room and low temperature in the 200-900 nm spectral range. The bands in the room-temperature absorption spectra are relatively broad. Going to liquid helium temperature due to the depopulation of the crystal field components of the $^4I_{9/2}$ ground state multiplet, all the bands occurring in the absorption spectra become slightly narrower. However, even at low temperature the splitting of the bands is not as good as it was observed for Nd³⁺-doped LaPO₄ obtained with using the IL2- [choline]H₂PO₄ precursor.

3.4. Luminescence spectra

Fig. 10 shows the room and low (77 K) temperature emission spectra recorded under excitation with an Ar⁺ laser (λ_{ex} = 514 nm) for LaPO₄ activated with 5 mol% Nd³⁺ prepared from both ILs. The emission spectra of diluted neodymium lanthanum orthophosphates can also be used to check the structure of the metal center in this matrix. The effective phonon energy of phosphates is around 1075 cm⁻¹, so the $^4F_{3/2}$ level of Nd³⁺ ion in this compound should relax by radiative transition. As in case of the absorption measurements the better results were obtained for the sample from IL2 precursor. The high resolution emission spectra exhibit the lines originating from the $^4F_{3/2} \rightarrow ^4F_{9/2}$ transition. It is well known from the group theory consideration that the $^4F_{3/2}$ multiplet splits into two Kramer's doublets and the number of components correlates with $J + 1/2$ levels for one site. In the band corresponding to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transition ($\lambda \sim 900$ nm) we can distinguish more than five lines (the number predicted by the complete lifting of the degeneracy of the $^4I_{9/2}$ level). For the IL2 precursors we observe well separated lines with the same number (7 components) both at room

temperature as well as at 77K. Then, the two lines at highest energy (shortest wavelength 863 and 868 nm) are corresponding to emission transition coming from the R2 levels which is still populated at 77K.

In the emission spectra presented in Fig. 10 we can see a significant difference in the shape of the spectrum and the amount of components for the nanomaterial from IL1 precursor, what confirm the inhomogeneity of the sample and multisite character. In contrary of the IL2 sample one can well distinguish 10 lines which are not attributed to the R2 population but to a second kind of site distribution. In addition the intensity of the emission from the sample from IL2 is about ten times stronger than from IL1 (in the spectrum presented in the Fig 10 the slits for the IL2 were much smaller than for IL1).

Fig. 11 shows the low temperature emission spectra for diluted samples obtained from both precursors under excitation in $^4G_{5/2}$, $^2G_{7/2}$ multiplet with using a non-selective excitation source: a LED at 590 nm. As under Ar^+ line excitation, the samples prepared from the IL2 show stronger emission from the $^4F_{3/2}$ level to the three: $^4I_{9/2}$ (850–955 nm), $^4I_{11/2}$ (1045–1080 nm) and $^4I_{13/2}$ (1300–1450 nm) terms of 4I_J multiplet. We clearly see the differences for both type of analyzed compounds: for instance, in the second range, the most intense lines are observed at shorter or longer wavelength than 1065 nm for IL1 and IL2 respectively.

In Fig. 12 we present also the emission spectra for the stoichiometric sample ($NdPO_4$) from IL2 precursor recorded at room temperature and 77K under 805 nm excitation. Analogous spectra than lower concentrated sample are obtained especially at low temperature with no drastic broadening effect proving a good homogeneity of this choline compound.

3.5. Luminescence decays

The luminescence decay profiles of fluorescence from the $^4F_{3/2}$ metastable state (monitored at 1060 nm) for both types of $LaPO_4:Nd^{3+}$ materials (IL1 and IL2) with different concentrations of Nd^{3+} ion recorded at room temperature and 77 K are presented in Figs 13a and b. The decay curves were measured under pulsed $\lambda_{ex} = 581$ nm of OPO laser excitation in the hypersensitive $^4I_{9/2} \rightarrow ^4G_{5/2}$, $^2G_{7/2}$ transitions.

For the samples obtained using IL1 the decay time τ are very similar whatever the concentration does not experience a significant lengthening as temperature is lowered to 77K with a fast decay time of about 150 ns, which should be due to energy transfer and the slowest radiative neodymium emission of few microseconds. Such a lack of thermal dependence due to the presence of the high-energy stretching vibrational modes of the H_2O molecule as clearly shown in the IR spectra displayed in Fig. 6. Most probably, the fast decay times of the

$^4F_{3/2}$ fluorescence measured in these materials originate from the coupling of the Nd^{3+} excited states to the vibrational modes of the water molecules located on the surface of powder. Similar values of decay times around 120 ns were observed in the concentrated $La_{1-x}Nd_xP_3O_9 \cdot 3H_2O$ cyclotriphosphates [30] which is about three orders of magnitude lower than those measured in concentrated anhydrous metaphosphates materials [20].

Longer luminescence lifetimes can be observe for the samples obtained from IL2, what confirm that the product obtain with choline ionic liquid is well crystalized and possess less water molecules on the surface of the powder, in accordance with the IR spectra (Fig.6). Here also decay curves are non-exponential with a lifetime at I_0/e of about 1.4 μs and integrated lifetime of 2.8 μs for 10 mol% of Nd^{3+} and about 1 μs and 2.0 μs respectively for the concentration 15%. In low temperature decay times slightly elongate for 10% of Nd^{3+} (1.5 μs at RT and 1.4 μs at 77K) and for 15% of Nd^{3+} (1.0 μs at RT and 1.1 μs at 77K). Fluorescence quenching is pointing out for the highest concentration (50 mol% of Nd^{3+} ions $\tau = 0.6 \mu s$) due to energy transfer by self-trapping process between the optically active Nd^{3+} ions and also by usual up/down conversion and cross-relaxation mechanisms due to the great numbers of resonances between Nd^{3+} levels. For the sample contained of 50 mol% of Nd^{3+} decay curve follows a single exponential decay, even in the presence of energy transfer processes. This exponential decay of the Nd^{3+} (donor ions, in this case) fluorescence in presence of energy transfer is characteristic of migration assisted energy transfer processes [31,32].

For the Nd^{3+} stoichiometric crystal ($NdPO_4$) the average distance between adjacent Nd^{3+} ions is relatively small (of the order of 4 Å), leading to an efficient donor–donor interaction and decay times of Nd^{3+} fluorescence from the $^4F_{3/2}$ metastable state (monitored at 880 nm) are equal to 1.7 at RT and 2.6 μs at 15 K [33]. These results obtained for the stoichiometric single crystal do not differ dramatically from our values obtained for the $Nd:LaPO_4$ nanoparticles prepared with using choline IL. The first reason of quenching process is probably OH group after energy transfer Nd-OH. In addition these OH groups create defects within the lattice and then some inhomogeneities.

At this point, it is worth noting that the relatively short value of the Nd^{3+} $^4F_{3/2}$ fluorescence decay time in $LaPO_4:Nd^{3+}$ (IL2) should lead to a very weak fluorescence intensity, a fact which is not reflected in our experiments.

The obtained results stay in a good agreement with others results obtained for both series of compounds and confirm that grain size, quality and homogeneity of samples play very

important role on the decays and luminescence quenching processes occurring in the series of samples under investigation.

Very important from the point of view the fluorescence quenching problem in the Nd^{3+} -doped nanophosphates is research performed by Samsonova for $\text{Nd}^{3+}:\text{YPO}_4$ nanoparticles where she applied the energy transfer probing based on the analysis of kinetics of impurity quenching to determine the presence and spatial position of $-\text{OH}$ fluorescence quenching acceptors in the impurity-containing nanoparticles present. The authors claim that the impurity quenching kinetics of the 0.1 at% Nd^{3+} doped YPO_4 nanoparticles is a two stage (ordered and disordered) static kinetics, determined by a direct energy transfer to the $-\text{OH}$ acceptors. Analyzing the ordered stage, they assumed that the origin of the $-\text{OH}$ groups is the protonation of the phosphate groups, while analyzing the disordered stage, they assumed the presence of water molecules in the mesopores. As the main result they have established that the majority of $-\text{OH}$ acceptors is located not on the surface of the $\text{Nd}^{3+}:\text{YPO}_4$ nanoparticles, as many researchers assumed, but in their volume, and can be either associated with crystal structure defects or located in the mesopores [22].

As it was reported earlier using the $[\text{choline}]\text{H}_2\text{PO}_4$ ionic liquid as a reactant and in-situ stabilizer led to obtained $\text{LnPO}_4:\text{Eu}^{3+}$ nanoparticles with very well luminescent performance and relatively long decay times without any need for post reaction heat treatment [6].

Conclusions

Two series of nano-crystalline Nd^{3+} -doped LaPO_4 and stoichiometric NdPO_4 were obtained by microwave treatment of simple lanthanide precursors such as $\text{Ln}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$, $\text{OAc} = \text{acetate}$) with the task-specific dihydrogen phosphate ILs of $\text{BmPyrH}_2\text{PO}_4$ (IL1) and $[\text{choline}]\text{H}_2\text{PO}_4$ (IL2). Fine analysis performed by using X-ray powder diffraction confirmed formation of the pure monoclinic high-temperature monazite phase with space group $P2_1/n$. For all as-prepared raw materials the powder diffraction patterns show very broad reflections which are characteristic for nanomaterials. The microwave assisted conversion of simple lanthanide precursors in task-specific ionic leads to formation of this high-temperature variety of phosphates in the form of nano-crystallites directly from the process even at low temperatures ($T = 140^\circ\text{C}/10 \text{ min}$) without the need for a post reaction heat treatment. However, the synthesis using $\text{BmPyrH}_2\text{PO}_4$ (IL1) leads to creation more amorphous materials than from $[\text{choline}]\text{H}_2\text{PO}_4$ (IL2). Also the morphology analysis performed by using SEM and TEM microscopes shows more homogeneous nanoparticles from $[\text{choline}]\text{H}_2\text{PO}_4$ (IL2). Analysis of the spectra of the neodymium orthophosphates synthesized with using two ILs

points to strong differences both in the structure of these two types of phosphates, as well as the symmetries of the neodymium centers in those structures.

The absorption spectra recorded at room temperature and at 4K show that the samples obtained by using [choline]H₂PO₄ (IL2) are indicative of a big arrangement in the network and most probably one symmetry site of Nd³⁺, however with quite low point symmetry. The samples obtained from BmPyrH₂PO₄ (IL1) show a very large degree of structural disorder with inhomogeneity and multisite character of the lanthanide ion. The ⁴I_{9/2} → ²P_{1/2} transition shows an unexpected high number of components (four instead of one, expected for this symmetry). The symmetry of the compounds from the synthesis with IL1 seems to be slightly higher than for IL2.

The emission spectra present a huge difference in the shape of the spectrum and the amount of components for the nanomaterial obtained from IL1 precursor and IL2, what confirm the huge inhomogeneity of the sample from IL1 and multisite character. The lanthanum orthophosphates obtained by using IL2 have shown a stronger emission. Those compounds present also longer luminescence lifetime, decay curves are non-exponential with of about 1.5 μs while for IL1 the time constant at I₀/e are order of about 150 ns. Our research has demonstrated that the [choline]H₂PO₄ (IL2) is good media for fast low temperature synthesis of nanoparticuled Nd³⁺-doped LaPO₄ than the BmPyrH₂PO₄ (IL1). The particles obtained by this way have a good performance as phosphors and even they are not H₂O/OH completely free the nanoparticules of Nd:LaPO₄ obtained from IL2 present the excellent optical properties with efficient emission in infrared spectral range. Well resolved absorption and emission spectra allow for good definition of the structure. These results stay in good agreement with the previous investigations performed for the Eu³⁺:LaPO₄ which have proved that [choline]H₂PO₄ is a very good media to obtain the well crystalized good quality nanoparticles in the low temperature fast way. In case of IL1 the predominant role in the fluorescence quenching played by the water molecules in the Nd³⁺ luminescence in LaPO₄ was established. The quenching may be caused by vibrations of the –OH groups located in the volume of NPs and Nd–Nd energy migration with subsequent quenching caused by vibrations of the –OH groups.

Summarizing the photoluminescence investigations one can conclude that using very fast and low temperature (T = 140°C/10 min) synthesis route described in this paper we are able to produce good quality luminophor operating in NIR range however only [choline]H₂PO₄ (IL2) precursor should be used. Other ionic liquid of - BmPyrH₂PO₄ (1IL) with keeping exactly the same conditions of synthesis leads to an inhomogeneous material.

Deeper investigations in the properties of this fluorescent emission will be of interest of our future research.

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Figures

IL1- BmPyrH₂PO₄

IL2-[choline]H₂PO₄

IL1 - 1-Butyl-1-methylpyrrolidinium dihydrogenphosphate

IL2 - 2-hydroxyethyl-N,N,N-trimethylammonium dihydrogenphosphate

Fig. 1 ILs (IL1- BmPyrH₂PO₄ and IL2-[choline]H₂PO₄) used to synthesis of nano-particuled LaPO₄:Nd³⁺.

Fig. 2 View of polyhedral connection of LaO_9 and PO_4 tetrahedra in the structure of monoclinic LaPO_4 (top) and polyhedral connection of LaO_8 and PO_4 tetrahedra in the structure of hexagonal LaPO_4 (bottom).

Fig.3 X-ray powder diffraction of Nd³⁺-doped LaPO₄ (IL2) and simulated XRD patterns of monoclinic LaPO₄ (ICSD#01-071-6745). The insert contains the simulated from the Database of Inorganic Crystal Structure XRD pattern of monoclinic and hexagonal forms.

Fig.4 X-ray powder diffraction of Nd³⁺-doped LaPO₄ and simulated XRD patterns of monoclinic LaPO₄ (ICSD#01-071-6745) and XRD patterns for the samples doped with different concentration of Nd³⁺ obtained by using IL1 and IL2 as reaction media.

IL1- BmPyrH₂PO₄

IL2-[choline]H₂PO₄]

TEM

SEM

Fig.5 Representative TEM (up) and SEM (down) micrographs of LaPO₄:Nd³⁺ nanoparticles obtained by using two ILs (IL1 (left) and IL2 (right)).

Fig.6 IR spectrum of $\text{LaPO}_4:\text{Nd}^{3+}$ 50% obtained with IL1 and IL2.

Fig. 8 Absorption spectra of $\text{LaPO}_4:\text{Nd}^{3+}(\text{choline})\text{H}_2\text{PO}_4$ recorded at room and liquid helium temperature.

Fig. 9 Absorption spectra of $\text{LaPO}_4:\text{Nd}^{3+}$ ($\text{BmPyrH}_2\text{PO}_4$) recorded at room and liquid helium temperature

Fig. 10 Emission spectra of $\text{LaPO}_4:\text{Nd}^{3+}$ 5% recorded at room and 77 K under Ar^+ laser excitation, $\lambda_{\text{ex}}=514$ nm.

Fig. 11 Emission spectra of Nd^{3+} - doped LaPO_4 containing 10 and 15 mol% of activator recorded at 77 K, $\lambda_{\text{ex}} = 590$ nm of LED.

Fig. 12 Room and low temperature emission spectra of $\text{NdPO}_4(\text{choline})\text{H}_2\text{PO}_4$ under excitation with OPO laser, $\lambda_{\text{ex}} = 805$ nm of LED.

Fig. 13 Luminescence decays at room temperature and at 77K of Nd³⁺ ⁴F_{3/2} meta-stable level (at $\lambda_{em} = 1060$ nm) for LaPO₄ (IL1–Fig. a) and (IL2–Fig.b) doped with different concentration of Nd³⁺ ions, $\lambda_{ex} = 581$ nm of OPO laser.

Graphical abstract