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Short communication

Lanthanum trifluoride nanoparticles prepared using ionic liquids

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ABSTRACT

Lanthanum fluorides are important materials for their optical properties especially in the form of thin film or nanoparticles. In this paper we describe preparation of LaF_3 nanoparticles by simple one-step synthesis. Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) was used both as fluorination agent and solvent in the first preparation method and KPF_6 (fluorination agent) dissolved in ionic liquid 1-butyl-3-methylimidazolium chloride (bmimCl) in the second synthesis procedure. In both cases liquid $La(NO_3)_3$ was used as the source of lanthanum. Reaction was performed at 200 °C for 90 min. Obtained white powders were washed by distilled water and methanol, dried on air and analyzed by Nanophox (particle size distribution), X-ray diffraction and by SEM and HRTEM. Nanoparticles of pure LaF_3 were prepared and their size was estimated from X-ray pattern to be 11.0 and 11.6 nm in the first and second case, respectively. Sizes of nanocrystals were conformed by HRTEM. It was observed by SEM that nanoparticles tend to form irregular aggregates and their average size was estimated by Nanophox. Although nanocrystals prepared by both ways are of very similar size, the sizes of their aggregates differ significantly (730 nm from $bmimPF_6$ vs. 3600 nm from KPF_6 in bmimCl).

1. Introduction

Rare earth elements are commonly used industrially in lasers, glasses, magnets and in many other applications. Lanthanum itself is widely used in special glasses, scintillators, hydrogen sponge alloys, nickel-metal hydride batteries and other applications. Lanthanum is relatively abundant element on Earth so there is a large industrial potential for its use.

Lanthanum based fluorides are important materials for their optical properties. In the form of thin films [1–3] or as nanoparticles [4–6], rare earth doped lanthanum fluorides show interesting up-conversion effect from near IR to visible light. Also X-ray luminescence has been observed on doped lanthanum fluorides [7]. Luminescent properties of these materials can be used in many applications such as in biological applications [8–11] or for light emitting applications such as their use in diodes [12,13].

Lanthanum fluoride nanoparticles have been prepared by several ways. Often used ways to prepare these materials are hydrothermal syntheses [14–16]. Co-precipitation method [6,17], micellar emulsion method [11] or using ionic liquid based synthesis [18] have been also used.

Ionic liquids are low melting salts composed of organic cations and mostly inorganic anions. Their low melting temperatures (often near to room temperature) are due to the delocalization of a charge on voluminous ions. The first ionic liquid was prepared almost a hundred years ago [19], however they have experienced boom in last two decades. Their utilization in solvent extraction, organic synthesis and catalysis has been extensively studied, but their utilization in inorganic synthesis has just begun. Their advantages in comparison to common organic solvents are their non-flammability, negligible vapor pressure, thermal stability, liquid-state at wide range of temperature, tunable solubility for both organic and inorganic molecules, synthetic flexibility and easy purification by crystallization. Moreover they can act as templates and precursors to inorganic materials, as well as solvents [20,21].

1-Butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and 1-butyl-3-methylimidazolium chloride (bmimCl) are two of the most widely used commercially available ionic liquids. $BmimPF_6$ is a colorless, viscous, hygroscopic, and hydrophobic liquid exhibiting low aqueous solubility caused mainly by hydrophobicity of hexafluorophosphate anion [22]. BmimCl is solid at room temperature, colorless, and hygroscopic, however much less hydrophobic and more soluble in water than $bmimPF_6$. Ionic liquids are commonly described as environmentally friendly “green solvents” due to their negligible vapor pressure but they can suffer from environmentally unfriendly degradations. Especially, hexafluorophosphate anion is known to very slowly decompose in the presence of water forming hydrofluoric acid. This process is fastened by higher temperature. Generally PF_6^- hydrolyze to form POF_4^-, $PO_2F_2^-$ and

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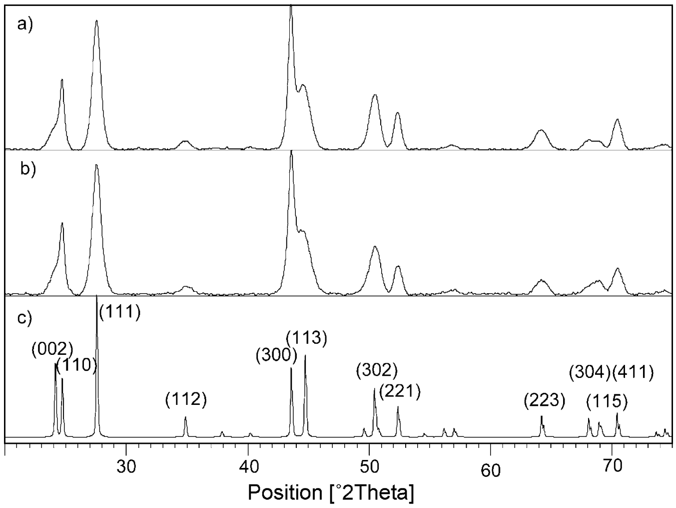

Fig. 1. XRD patterns of LaF_3 nanocrystals prepared by reaction of $La(NO_3)_3$ with KPF_6 in bmimCl (a) and with $bmimPF_6$ (b). Difference is visible by eye at 44°. All peaks belong to LaF_3. In (c) is LaF_3 standard simulated from JCPDS card NO. 32-0483.

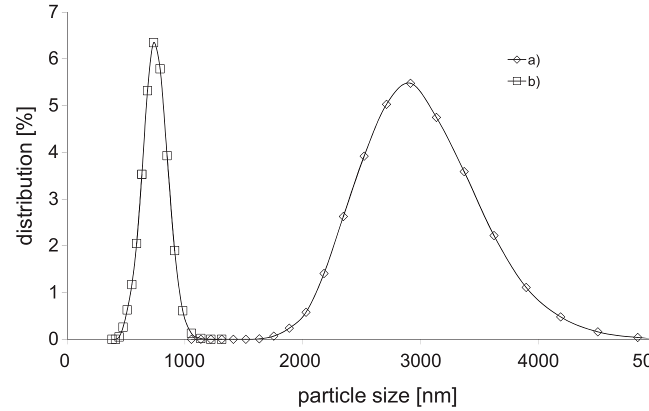

Fig. 2. Particle size distribution of aggregates measured by Nanophox. (a) samples prepared by reaction with KPF_6 in bmimCl, (b) samples prepared by reaction with $bmimPF_6$.

PO_3^- products while HF is formed. It has been described also formation of minor products such as PO_3F^{2-} and PO_4^{3-}. It was observed that imidazolium cation remains unchanged during anion hydrolysis [23,24]. Due to decomposition of anion, $bmimPF_6$ can be used both as solvent and source of fluoride ions [18,25].

2. Results and discussion

Lanthanum trifluoride was prepared by reaction of liquid lanthanum nitride with ionic liquid $bmimPF_6$ or KPF_6 in bmimCl. From experiments brightly white powder was obtained. All prepared samples were analyzed by XRD for estimating of sizes of crystals and clarifying of samples composition. All peaks on XRD pattern were identified as belonging to LaF_3 and no any other phase was found in XRD patterns of the samples prepared by procedure described in Section 3. Peak broadening clearly indicates that LaF_3 is in form of nanocrystals (Fig. 1). Using Scherrer formula, the average diameter of crystals in samples prepared by reaction with $bmimPF_6$ was calculated to be 11.0 nm. From XRD pattern of samples prepared by reaction with KPF_6 in bmimCl slightly larger diameter of about 11.6 nm was evaluated. This difference is clearly visible by eye in Fig. 1 on broadening of peak around $2\theta \sim 44°$. Peaks in patterns of the samples prepared by reaction with $bmimPF_6$ are broader and therefore crystals are in average larger. Although difference in crystal size seems to be negligible, it should be noted that this difference systematically appears in repeated measurements.

It is usual that tiny nanocrystals in such concentrations tend to form agglomerates. It is interesting that particle size distribution from Nanophox (Fig. 2) and SEM images (Fig. 3) show significantly different average size of agglomerates. Smaller agglomerates of average size 730 nm have been formed by reaction in pure $bmimPF_6$. Samples prepared by reaction with KPF_6 in bmimCl have nearly five-times larger agglomerates with average diameter of about 3600 nm. From SEM (Fig. 3) results irregular shapes of agglomerates therefore spherical approximation used for evaluation by Nanophox could be taken as valid in orders of hundreds of nm. It should be noted that Nanophox measures hydrodynamic radius, it means the effective size of the particle as detected by its diffusion (Brownian motion).

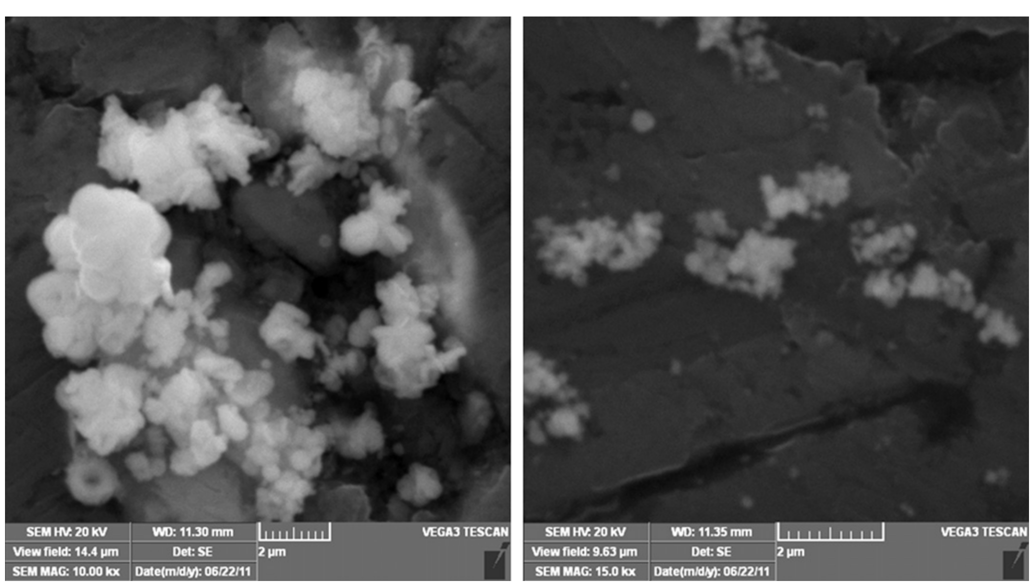

Fig. 3. SEM image of LaF_3 agglomerates. On the left, is picture of agglomerates prepared by reaction of KPF_6 in bmimCl. On the right side is picture of much smaller agglomerates prepared by reaction with $bmimPF_6$. Agglomerates are structured irregular aggregates of LaF_3 nanocrystals.

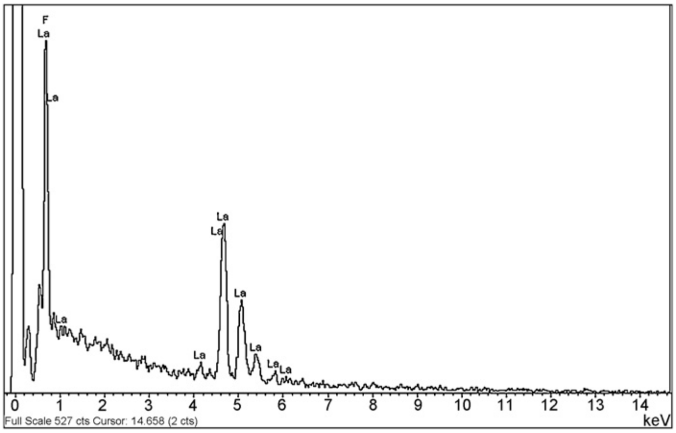

Fig. 4. EDS specter of sample prepared by reaction with $bmimPF_6$.

Reaction mechanism of both reactions could be similar like in [25]. LaF_3 is formed by reaction of La^{3+} ions present in solution with HF from hydrolyzed hexafluorophosphate anion and forms nanoparticles of size between 11 and 12 nm.

Small difference between crystals sizes and different sizes of agglomerates is probably caused by different physical and chemical properties of reaction mixtures. KPF_6 is only partially dissolved in bmimCl and thus solid KPF_6 presented in solution of melted $La(NO_3)_3$ and bmimCl could act as template for formatting of larger agglomerates of LaF_3. After dissolving of KPF_6 in distilled water large agglomerates preserve. From SEM observations and mentioned mechanism of formation we suppose agglomerates are breakable easily enough for example by ultrasound.

The advantage of this method lies in possibility of regeneration of ionic liquids by crystallization because they are used mostly as solvents and reaction environment, mainly in case of bmimCl that is used only as solvent and is not used as source of fluorine. We believe this approach that was successfully used for preparation of LaF_3 is usable for simple one step preparation of more rare earths elements fluorides for some conditions.

Elemental composition was confirmed by EDS analyses. EDS specter of sample prepared by reaction with $bmimPF_6$ is in Fig. 4. Sample is sufficiently pure.

To confirm of sizes and for illustrating shapes of nanocrystals HRTEM measurements were performed. In Fig. 5, nanocrystals about approximately the same sizes as was calculated from Scherrer formula are visible. Nanocrystals have mostly elliptical shapes. Sample prepared by reaction with $bmimPF_6$. The second sample is very similar (not shown here).

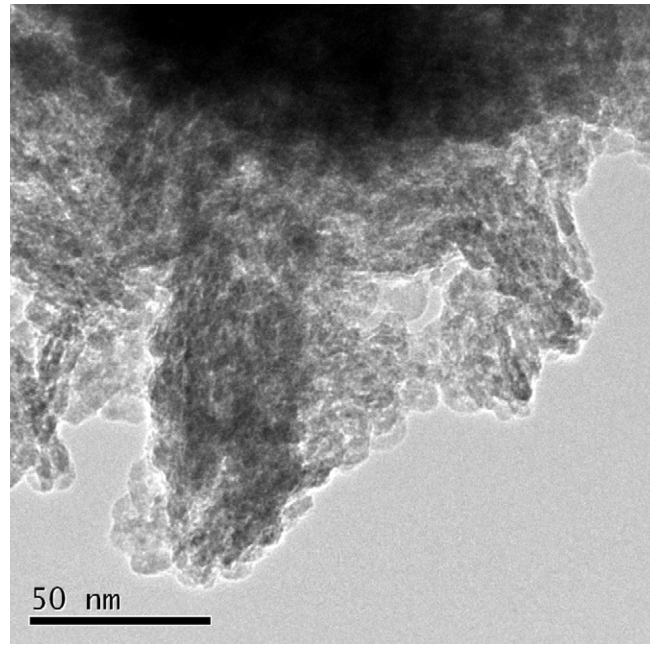

Fig. 5. HRTEM image of LaF_3 nanocrystals of sample prepared by reaction with $bmimPF_6$.

3. Experimental

Ionic liquids 1-butyl-3-methylimidazolium chloride (bmimCl), 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and KPF_6 were purchased from Sigma-Aldrich Co. $La(NO_3)_3$ was prepared by reaction of equimolar amounts of La_2O_3 (p.a.) with concentrated nitric acid. Obtained two phase system comprised of saturated water solution of $La(NO_3)_3$ in the top phase and melted $La(NO_3)_3$ on the bottom. For experiments second phase was used. Experiments were performed in the sealed Teflon tubes, 4 mm internal diameter and about 5 cm long. Tubes were penetrated and placed to the mixture of silica gel and $CaCO_3$. About 0.2 ml of $La(NO_3)_3$ and 0.5 ml of ionic liquid was used in one experiment. Used KPF_6 was redundant to $La(NO_3)_3$. BmimCl was melted before use. All samples were placed to the furnace and treated at 200 °C for 90 min. Subsequently samples were cooled, taken of Teflon tubes and washed by methanol and distilled water. After multiple washing, powder was dried on air and analyzed.

Nanophox (Sympatec GmbH) uses dynamic light scattering to measure particle size distribution of emulsions and suspensions in range 1 nm–10,000 nm. Data are evaluated from Brownian motion using 3D Cross Correlation technique. Scattering angle is 90°, light source is HeNe laser, wavelength 632.8 nm, couvette size 10×10 mm, measured at room temperature.

SEM pictures and EDS specter were made using electron microscope Tescan Vega 3 with EDS analyzer Oxford Instruments INCA 350.

X-ray powder diffraction data were collected at room temperature with X'Pert PRO θ–θ powder diffractometer with parafocusing Bragg-Brentano geometry using CuK_α radiation (λ = 1.5418 Å, U = 40 kV, I = 30 mA). Samples were characterized by XRD measurements and nanoparticles sizes were identified from the width in half high of peak 27.6° 2θ. This peak was used due to its relative single position in XRD pattern of LaF_3 and due to its high intensity. X'Pert HihgScore Plus program was used for processing data from XRD and calculating of nanoparticles sizes were made using Scherrer formula.

HRTEM pictures were made by HRTEM JEOL JEM 3010.

4. Conclusion

Fine nanocrystals of LaF_3 were prepared by reaction in ionic liquids. As a precursor it was used liquid $La(NO_3)_3$ and as a source of fluorine $bmimPF_6$ in the first and KPF_6 in the second synthesis procedure, respectively. Prepared nanocrystals have diameter of 11.0 and 11.6 nm, respectively. Sizes of nanocrystals were conformed by HRTEM. These sizes could seem to be very similar, however nanocrystals prepared from $bmimPF_6$ form agglomerates with average diameter 730 nm and nanocrystals from KPF_6 in bmimCl form agglomerates of average size about 3600 nm. This difference was measured by Nanophox and confirmed by SEM measurements. Difference in size of agglomerates could be explained by different physical properties of reaction mixtures mainly by presence of solid KPF_6 in the second case. The importance of this preparation route is in its simplicity and easy use for the preparation of doped lanthanum fluoride and as we believe in general for more fluorides of rare earths elements.

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