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Articles

Powders and Coatings of $LiYF_4$:Eu^{3+} Obtained via an Original Way Based on the Sol−Gel Process

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The sol−gel process has proven to be a convenient route to produce inorganic oxide materials with various shapes. We report here the use of this technique to prepare for the first time to our knowledge high-quality powders and spray-coated films of $LiYF_4$. Powdered samples were structurally as well as morphologically characterized by means of conventional solid-state techniques. Furthermore, the optical properties were investigated with europium ions as luminescent probe. X-ray diffraction measurements enabled identification of monophased $LiYF_4$ films coated onto Pyrex substrates. Eventually coatings microstructure was analyzed by scanning electron microscopy and atomic force microscopy.

Introduction

Fluorides are well-known as efficient host lattices of phosphors involved in numerous applications, for instance, as media for laser action,[1,2] optical frequency upconverters,[3] neutron scintillation detectors,[4] or lamp phosphors.[5,6] An optical transparency over a wide wavelengths range in addition to a low phonon energy and an outstanding chemical stability contribute to their great interests as host materials for luminescent centers. Nevertheless, in several practical applications, some problems arise from either the synthesis procedure or the shaping method. A conventional preparation technique to obtain these materials consists of mixing, heating above their melting points, and cooling the fluorides of each element incorporated in the synthesized fluoride under an inert gas atmosphere or vacuum.[7] Fluorination by HF or F_2 is also performed if necessary to purify the final compound.

Recently, however, different preparation techniques have been successfully applied to synthesize fluorides, notably a multistep process such as sol−gel synthesis and reactive atmosphere processing for preparation of fluoride glasses[8] or direct sol−gel method using metal acetates, metal alkoxides, and trifluoroacetic acid as starting materials.[9,10]

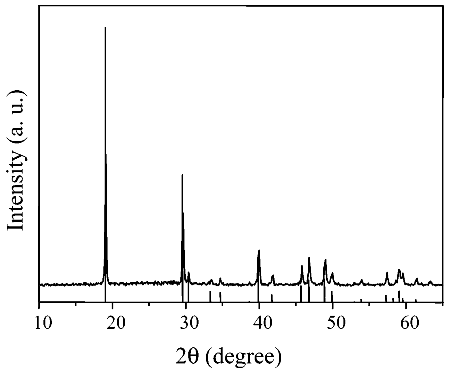

Figure 1. XRD pattern obtained from $LiYF_4$ powder sintered for 2 h at 600 °C in an inert atmosphere.

In this work, we have investigated the preparation of $LiYF_4$ through the sol−gel process, a versatile method giving rise to the ability to produce materials as a powder or thin film. The great interest in $LiYF_4$ arises from its efficient capability as laser material, lamp phosphor, and scintillator material when activated by rare-earth ions.[5,6,11] The sol−gel-derived powders were characterized structurally and optically by using the Eu^{3+} dopant as a local probe. Furthermore, spray-coated films were achieved and analyzed by X-ray diffraction and AFM.

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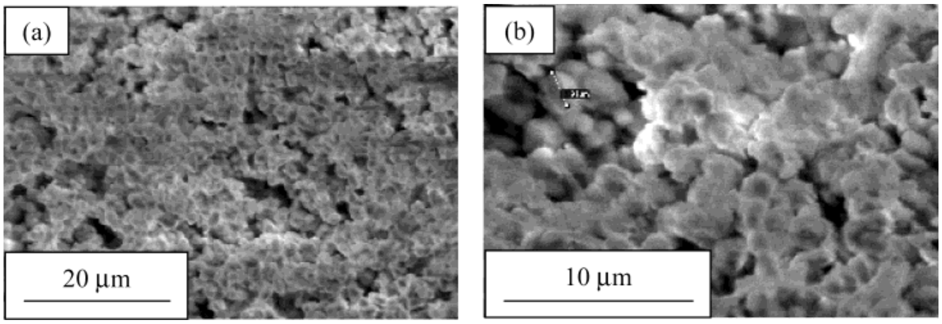

Figure 2. SEM micrographs recorded at (a) 2000× and (b) 5000× magnifications from LiYF$_4$ powder sintered for 2 h at 600 °C in an inert atmosphere.

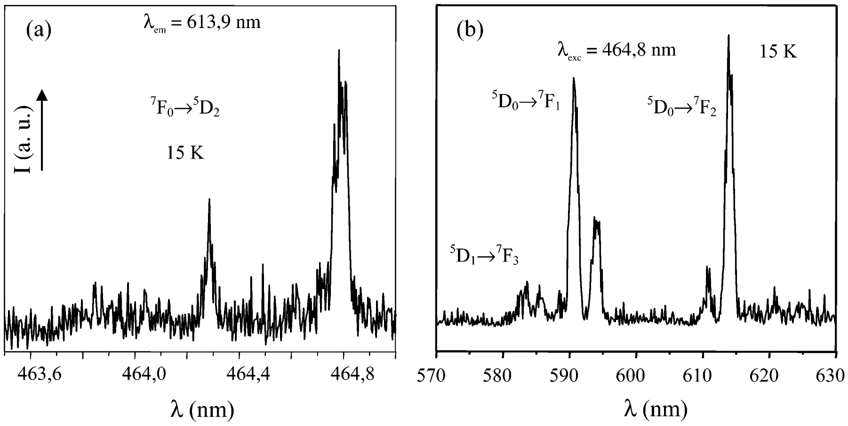

Figure 3. (a) Excitation spectrum of LiYF$_4$:Eu^{3+} 2% monitoring $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} (613.9 nm) and (b) emission spectrum of LiYF$_4$:Eu^{3+} 2% upon $^7F_0 \rightarrow {}^5D_2$ excitation on Eu^{3+} (464.8 nm), both at 15 K.

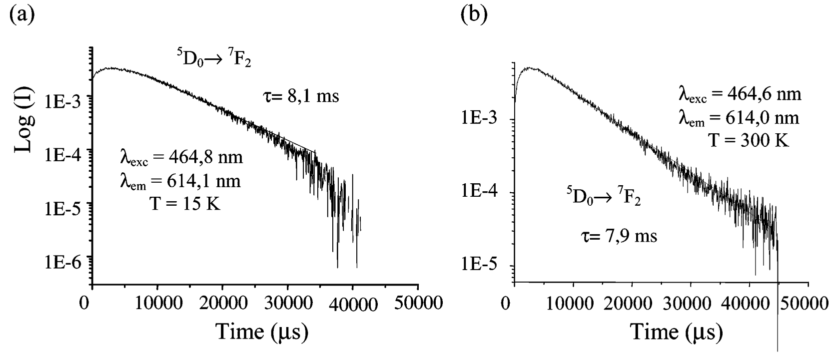

Figure 4. Decay curves of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ emission in LiYF$_4$:Eu^{3+} 2% upon $^5D_2$ excitation at (a) 15 K and (b) 300 K.

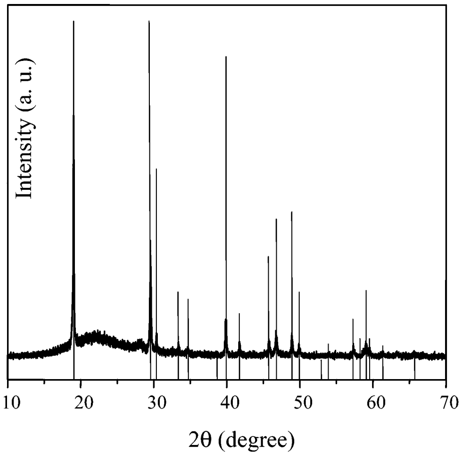

Figure 5. XRD pattern resulting from LiYF$_4$ spray-coated film annealed for 2 h at 300 °C.

Experimental Section

Materials Preparation. All experiments were carried out under a free-moisture atmosphere to prevent any alteration of starting materials and intermediate chemical reagents during the synthesis. The first step consists of preparing a mixed alkoxides solution by dissolving anhydrous yttrium (1 equiv, Aldrich) and lithium (1 equiv, Aldrich) chlorides in anhydrous isopropanol (^{i}PrOH), and a solution of potassium isopropoxide from metallic potassium (3 equiv, Aldrich) in ^{i}PrOH. Chunks of potassium need to be handled in a nonpolar and highly anhydrous solvent such as distilled cyclohexane and cleaned of any storage oil prior to the addition of ^{i}PrOH.

The latter solution is slowly added to the former one with vigorous stirring, the reaction is highly exothermic, and KCl is immediately formed. After a 1-h reflux of the mixed solutions at 85 °C, trifluoroacetic acid (1 equiv, Aldrich) was added directly to the solution. A homogeneous solution was obtained after further refluxing (85 °C) and stirring vigorously for 4 h. After cooling, KCl was separated by centrifugation and a clear sol was isolated. A xerogel was obtained after drying the sol at 80 °C (4 h) and thereafter LiYF$_4$ as a powder was provided by further heating at 600 °C for 2 h under a nitrogen atmosphere to prevent any oxidation. On the other hand, to realize LiYF$_4$ coatings, the sol was stabilized by adding a small

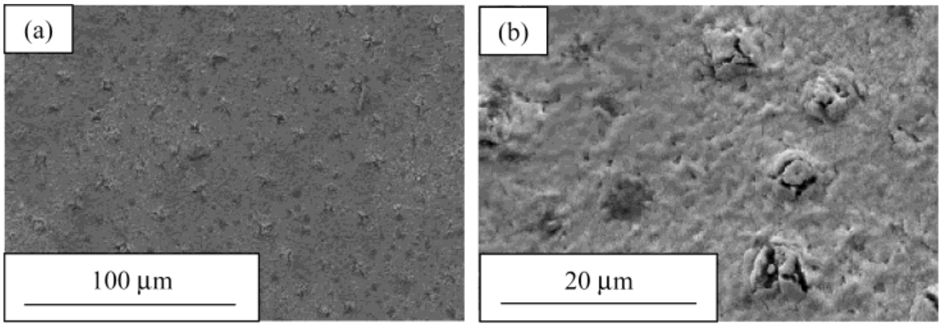

Figure 6. SEM micrographs recorded at (a) 500× and (b) 2500× magnifications from $LiYF_4$ spray-coated film annealed for 2 h at 300 °C.

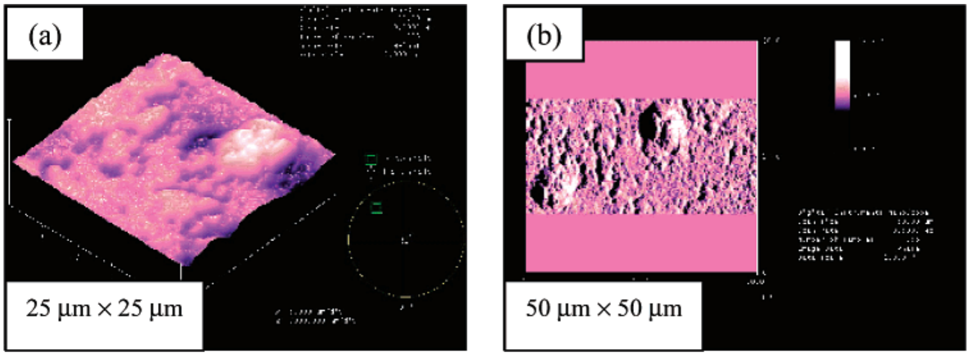

Figure 7. Images from (a) tapping mode and (b) contact mode AFM measurements on $LiYF_4$ spray-coated film annealed for 2 h at 300 °C. The size of the analyzed surfaces is 25 × 25 μm and 50 × 50 μm, respectively.

amount of acetylacetone to prevent any hydrolysis reaction. The deposition was performed into Pyrex substrates with a homemade spray-coating device. The spray solution was conveyed to an atomizing nozzle through a nitrogen flow at a 2 mL·min^{-1} rate. The substrate was disposed onto a heating hotplate at 280 °C and kept 15 cm from the nozzle. Finally, the sample was sintered at 300 °C for 2 h under an air atmosphere.

Characterization Techniques. XRD measurements were carried out at room temperature on a Siemens D5000 diffractometer operating with Cu Kα radiation. Micrographs were recorded using a Cambridge Scan 360 SEM operating at 20 kV. AFM was performed on a Nanoscope III digital instruments in both tapping and contact modes.

The luminescence spectra were recorded with a monochromator Jobin-Yvon HR 1000 spectrometer, using a dye laser (continuum ND62) pumped by a frequency doubled pulsed YAG: Nd^{3+} laser (continuum surelite I). The dye solution was prepared by mixing Rhodamines 590 and 610. To achieve a resonant pumping in the blue wavelength range, that is, in the $^5D_2$ manifold, the output of the dye laser was upshifted by 4155 cm^{-1} by stimulated Raman scattering in a high-pressure gaseous H_2 cell.

Fluorescence decays were measured with a LeCroy 400 MHz digital oscilloscope.

Results and Discussion

Powders Characterizations. Prior to the XRD analysis, the xerogel sample had undergone a thermal treatment for 2 h at 600 °C under a nitrogen atmosphere. Superimposition in Figure 1 of the X-ray diffraction patterns resulting from the crystallized powder and reference data[12] reveals undoubtedly a phase consistent with $LiYF_4$.

Samples microstructure was observed by SEM. Both micrographs displayed in Figure 2 were recorded from the specimen previously analyzed in XRD and calcined for 2 h at 600 °C. According to these pictures, the powder consists of a few micrometers uniform particles. The grain boundaries are typical of shrunk particles, indicating that the densification process has begun to occur. The micrograph obtained at higher magnification (Figure 2a) emphasizes the homogeneity of the $LiYF_4$ powder prepared by the sol–gel process.

The $^7F_0 \rightarrow {}^5D_2$ excitation spectrum of $LiYF_4$: Eu^{3+} 2% is presented in Figure 3a. That spectrum was recorded at 15 K, monitoring the $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} (613.9 nm). Since the strongest excitation band is located at 464.8 nm, we have selected that excitation wavelength to record the emission spectrum within a spectral region lying from 570 to 630 nm (Figure 3b). The different bands are assigned to the Eu^{3+} $^5D_1 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ transitions. The number of lines is in agreement with the local symmetry of lanthanide ions site in $LiYF_4$ structure,[13] that is, S_4.

Decay times of the $^5D_0 \rightarrow {}^7F_2$ emission were also investigated upon $^7F_0 \rightarrow {}^5D_2$ excitation. It is shown that whatever the measurement temperature, either 15 K (Figure 4a) or 300 K (Figure 4b), the time constant remains around 8 ms. As a comparison, G. Blasse and co-workers[14] have measured a lifetime of 7.3 ms at 4.2 K for Eu^{3+} (1 mol %) in the isostructural $LiGdF_4$ synthesized by solid-state reaction. That result signifies that the nonradiative de-excitation process is inefficient in this material so that it can be assumed that hydroxide ions are not present in our specimens as expected using the wet synthesis route.

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Coatings Analyses. Spray-coated film of $LiYF_4$ was first characterized by XRD analysis. Figure 5 shows a diffraction pattern recorded from a sample annealed for 2 h at 300 °C. The crystallization process has already occurred and a pure $LiYF_4$ phase is detected. The crystallization takes place at a much lower temperature as for $LiYF_4$ powders synthesized from the same mixed alkoxides solution.

SEM micrographs were recorded from the sample previously analyzed by X-ray diffraction. As can be seen in both pictures (Figure 6a,b), the surface microstructure exhibits a lot of defects similar to spherical aggregates of few micrometers in diameter. They likely result from the dried spray droplets.

Additionally, AFM analysis was performed to give further details about the surface morphology of $LiYF_4$ coatings. Both images in Figure 7 show the topography of a small area of the $LiYF_4$ coating heat-treated for 2 h at 300 °C. These pictures confirm the presence of the dried spray droplets on the surface, but they also reveal a low roughness despite these defects.

Conclusions

$LiYF_4$ fluoride was successfully produced through the sol−gel process. Thanks to the rheological properties of sols, powders synthesis and coatings depositions were achieved. XRD measurements allowed control of the materials purity as well as the crystallization temperature. We have noticed that the latter depends on the thickness and is much lower for $LiYF_4$ films. A luminescence study on europium-doped samples confirmed the S_4 local symmetry of lanthanide ions sites in the inverse scheelite structure, space group $I4_1/a$. Finally, SEM and AFM observations revealed the presence of dried spray droplets on the surface coatings. This work opens up the possibility to produce versatile shaped fluorides and consequently the ability to widen their application fields as well as their efficiency.

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