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Enhancement of structure stability and luminescence intensity of $LiYF_4:Ln^{3+}$ nanocrystals

XU Zhan (徐 展)*, GU Wenbin (顾文斌), FENG He (冯 鹤), ZHANG Zhijun (张志军), ZHAO Jingtai (赵景泰)*

(Department of Electronic Information Materials, School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China)

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Abstract: $LiYF_4$ nanocrystals with tetragonal structure were adopted as the host materials for the phosphors and scintillators owing to the low phonon energy and high optical transparency. $LiYF_4:Ln^{3+}(Ce^{3+},Eu^{3+})$ nanocrystals were fabricated by solvothermal method. Under UV excitation, they could emit visible light. In order to improve the luminescence intensity, the method of co-doping $LiYF_4$ nanocrystals with Sc was adopted. Sc^{3+} ions could reduce the lattice expansion caused by the doping of Ce^{3+} or Eu^{3+} whose ionic radius was larger than Y^{3+}. Crystal structure of $Li(Y,Sc)F_4:Ln^{3+}$ kept much more stable and the luminescence intensity could be significantly enhanced when the concentration of Sc was a moderate value. Thermoluminescence was employed to analyze the electron traps in $Li(Y,Sc)F_4:Ce^{3+}$. Results suggested that the suppression of the generation of electron traps with the co-doping of Sc contributed to the enhancement of luminescence intensity of $LiYF_4:Ce^{3+}$.

Keywords: $LiYF_4$; luminescence intensity; doping; rare-earth elements; thermoluminescence; rare earths

Lanthanide-doped fluorides have been regarded as ideal fluorescence materials. They attract increasing attentions since they have important potential applications in the fields of laser crystals, phosphors and bio-imaging[1–3]. They have characteristic optical properties due to their unique intra 4f transitions, which are less influenced by the outer crystal fields. They can absorb high-energy photons and convert them into low-energy emissions, which is well known as down-conversion (DC). Fluorides own much lower phonon energies which lead to the reduction of non-radiative transitions of rare-earth excited states and high visible light transparency due to their large band-gap[4–6]. These advantages enable them to have much higher luminescence emissions efficiency than oxide or sulfide based luminescent materials.

$LiYF_4$ is a tetragonal crystal of scheelite ($CaWO_4$) structure having the $I4_1/a$ space group. According to the structure image shown in Fig. 1, lithium is located at a $\overline{4}$ site with four equidistant fluoride ions. Yttrium is surrounded by eight fluorides ions forming a tetragonal dodecahedron yielding S_4 point group symmetry. Y^{3+} in $LiYF_4$ crystals can partly substitute for lanthanide ions as the application for luminescent materials. Also, the energy level parameters of Ln^{3+} in $LiYF_4$ were analyzed in detail[7], which will benefit the improvement of luminescent properties of $LiYF_4:Ln^{3+}$. Commonly adopted means to prepare $LiYF_4:Ln^{3+}$ nanocrystals by solvothermal method in which oleic acid is used as the solvent and surfactant[8,9]. The as-prepared nanocrystals can be easily dispersed in non-polar solvent which will help to the following applications in bio-imaging or composite materials. But Ohishi et al. have found that oleic acid groups absorbed at the surface of $LiYF_4:Ln^{3+}$ nanocrystals were harmful to the fluorescence emissions. Several groups have made their efforts to enhance $LiYF_4:Ln^{3+}$ emission intensities by increasing doping concentrations of Ln^{3+} or introducing sensitizer ions[10]. It was reported that when the doping concentrations of Eu^{3+} increased up to 35% (in molar fraction), the $LiYF_4$ crystal structure became unstable and decomposed to LiF and YF_3 phases[11]. We compared the ionic radii of two commonly used lanthanide ions Eu^{3+} and Ce^{3+} with that of Y^{3+}. It was found that the effective ionic radii of Eu^{3+} ($R_{\mathrm{Eu}^{3+}}$=0.121 nm) and Ce^{3+} ($R_{\mathrm{Ce}^{3+}}$=0.128 nm) under eight-coordinated conditions are larger than the value of Y^{3+} ($R_{\mathrm{Y}^{3+}}$=0.1155 nm), based on the information supplied by Shannon et al.[12], which may be one of the facts which caused $LiYF_4:Ln^{3+}$ crystals to decompose.

In this work, Sc with smaller effective ionic radius ($R_{\mathrm{Sc}^{3+}}$=0.101 nm) than Y^{3+}, was introduced to dope into $LiYF_4:Ln^{3+}$ crystals with the expectation to improve the crystal stability and emission intensities. We compared the structures and luminescent intensities of the $LiYF_4:Ln^{3+}$ nanocrystals with different doping concentrate of Sc. Thermoluminescene spectra were introduced to investigate the defects which are strongly correlated

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* **Corresponding authors:** XU Zhan, ZHAO Jingtai (**E-mail:** xuzhan@shu.edu.cn, jtzhao@shu.edu.cn; **Tel.:** +86-21-66138062, +86-21-66138033)

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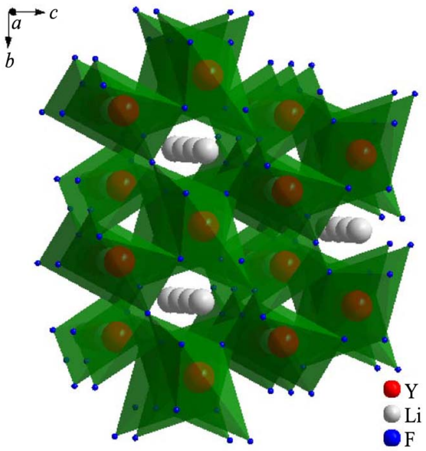

Fig. 1 Crystal structure of LiYF$_4$

with the emission intensities of LiYF$_4$:Ln^{3+} nanocrystals.

1 Experimental

1.1 Synthesis

All the chemical reagents used were of analytical grade and used without further purification. The synthesis of LiYF$_4$:Ln^{3+} nanocrystals was carried out by a rational solvothermal method using oleic acid as the solvent and stabilization agent. Typically, 35 mL oleic acid and 15 mL ethanol were mixed together to form a homogenous solution. Then 5 mL aqueous solution including 2 mmol RE(NO$_3$)$_3$ (RE=Y, Sc, Ce, Eu) was added under vigorously stirring and kept stirring for 30 min. After that 5 mL aqueous solution containing 30 mmol LiOH was dropped into the above solution and stirred for 30 min until a transparent complex was formed. Then 5 mL aqueous solution containing 8 mmol NH$_4$F was added and kept stirring for 1 h. The resulting solution was transferred into a 100 mL stainless Teflon-lined autoclave and heated at 180 ºC for 12 h. After complete reaction and naturally cooled to room temperature, the mixture was separated by centrifugation, washed several times with ethanol and deionized water to remove oleic acid and other by-products. The collected precipitates were dispersed in cyclohexane for further characterization.

1.2 Characterization

The structures of as-prepared Li(Y,Sc)F$_4$:Ln^{3+} nanocrystals were examined using Rigaku D/max-2550 with Cu Kα radiation (λ=0.154056 nm) at 18 kW with a graphite monochromator and scans at 8 (º)/min. Crystal morphologies were investigated using a JEOL JSM-7500F scanning electron microscope (SEM). The as-prepared samples were washed with 1 mol/L nitric acid solution to remove LiF phase before SEM observation. Luminescent properties were analyzed by an FLS920 (Edinburgh Instruments) fluorescence spectrometer with Xenon lamp as the source at room temperature. The test conditions like slit, lamp power and so on were kept constant during the test procedures of all samples. The thermal stimulated luminescence (TSL) curves were determined by an FJ-427A1 thermal spectrometer with a linear heating rate of 1 K/s. Prior to the TSL measurement, all of the Li(Y,Sc)F$_4$:Ce^{3+} were exposed under X-ray (Ray tube: 65 kV, 3 mA) irradiation for 30 s.

2 Results and discussion

Structures of the Li(Y,Sc)F$_4$:3%Ce^{3+} nanocrystals with different Sc doping concentrations were investigated by XRD. The patterns shown in Fig. 2 indicated that the main phase was LiYF$_4$ in the as-prepared sample without Sc doping. Besides, YF$_3$ and LiF phases were also observed. YF$_3$ was believed to be formed owing to the decomposition of LiYF$_4$ while LiF was generated owing to both the decomposition of LiYF$_4$ and excess addition of lithium during fabrication. So, the amount of YF$_3$ can be employed to evaluate the decomposition of LiYF$_4$:3%Ce^{3+} crystals. The relative amount of LiYF$_4$ phase increased significantly with respect to the YF$_3$ phase with the increase of the Sc substitution. It can be inferred that the doping of Sc can effectively reduce the decomposition of LiYF$_4$:3%Ce^{3+} crystals and stabilize LiYF$_4$ crystal lattice.

The lattice parameters and unit cell volumes of Li(Y,Sc)F$_4$:3%Ce^{3+} were also calculated as illustrated in Fig. 3. The unit cell volumes and lattice parameters of both *a* and *c* axes become smaller along with the increase of Sc doping concentration. It can be clearly deduced that Sc was successfully doped into LiYF$_4$ crystal lattice and led to the shrinkage of lattice. When the doping concentration of Sc was 30%, the amount of LiYF$_4$ reached a maximum value and no obvious YF$_3$ was found, which can be ascribed to the fact that a balance was established

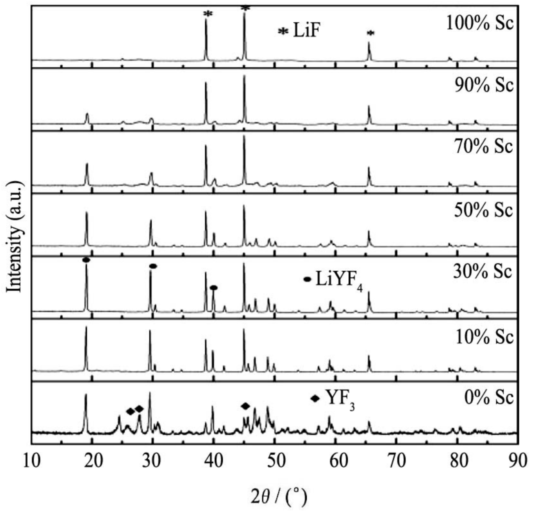

Fig. 2 XRD patterns of Li(Y,Sc)F$_4$:3%Ce^{3+} nanocrystals doped with different concentrations of Sc