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Growth and luminescence characteristics of undoped $LaCl_3$ crystal by Modified Bridgman Method

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Abstract

In this paper, we presented the crystal growth method and parameters suitable for $LaCl_3$ crystal. A $LaCl_3$ crystal with a dimension of ϕ 25 × 50 mm was grown by Modified Bridgman Method. The crystal was characterized by X-ray diffraction, optical transmittance, photoluminescence (PL) and X-ray stimulated luminescence (XSL). It was found that the crystal had very good optical transmittance within wavelength concerned. Transmittance at 405 nm was 80%. PL and XSL of the $LaCl_3$ crystal peaked at the same emission, which is 405 nm.

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Keywords: A1. Transmittance; A2. Bridgman Method; A2. Crystal growth; B1. $LaCl_3$; B2. Photoluminescence; B2. X-ray stimulated luminescence

1. Introduction

$LaCl_3$ has UCl_3 type structure, space group $P6_3/m$ [1]. In the last few years, pure $LaCl_3$ and Ce^{3+} activated $LaCl_3$ crystal have attracted much attention for its high light output as well as good energy resolution [2–7]. These unique properties made $LaCl_3$ crystal a promising material as scintillator in the field of high-energy physics experiments and medical imaging, as well. It is, however, difficult to produce a high-quality, crack-free large-size $LaCl_3$ crystal because of its hygroscopic nature. In the year 2003, Shah et al. [5] reported a small $LaCl_3$ sample with a dimension of 2.5 cm^3 produced by Bridgman Method. This is the largest volume reported so far. Another reason for the difficulty to produce high-quality $LaCl_3$ crystal is the oxygen contamination during crystal growth process.

In this paper, we present a simple, however, effective method for producing large-size crack-free $LaCl_3$ crystal by Modified Bridgman Method

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using $LaCl_3$ powder as the raw material. Crystal growth process, optical transmittance, photoluminescence (PL) and X-ray stimulated luminescence (XSL) spectra are presented. The crystal growth technique presented in this paper is effective for producing high-quality $LaCl_3$ crystal, and can be easily applied for growth of Ce^{3+}-doped $LaCl_3$ crystal by adding $CeCl_3$ to the raw material. Further researches on the growth and scintillating properties of Ce^{3+}-doped $LaCl_3$ are now under way, and the results will be reported in another paper.

2. Sample and experiments

The crystal was grown in Shanghai Institute of Ceramics (SIC) by Modified Bridgman Method. $LaCl_3$ crystal is rather hygroscopic, so that it usually contains crystallized water and absorbed water. Pretreatment is needed for raw material used. First, the raw material was heated at 235 °C for 10 h in flowing N_2 atmosphere to remove the moisture and crystallized water, and then weighted and loaded into the capillary platinum crucible. The dry powder was compressed as dense as possible and the crucible was sealed tightly to avoid oxygen contamination. The crucible was then loaded into an aluminum holder. A schematic view of the furnace used can be found in Ref. [8]. The furnace was controlled by a computer and the temperature fluctuation was less than 0.5 °C. Temperature gradient at the solid–melt interface was set to be 20 °C/cm, and lowering rate was 0.6 mm/h. Fig. 1 shows an as-grown $LaCl_3$ crystal with a dimension of ϕ 25 × 50 mm. A 4 mm thickness slice was cut from an as-grown ingot and polished to evaluate its optical and luminescence properties.

Fig. 1. As-grown $LaCl_3$ crystal by Modified Bridgman Method.

3. Experiments and results

3.1. X-ray diffraction

For phase analysis, a small block cut from an as-grown crystal was ground into powder. X-ray diffraction (XRD) pattern was taken by D/Max-2250 diffractometer with a Cu target running at 40 kV, 400 mA. Because of hygroscopy of the $LaCl_3$ crystal, the XRD was carried at 205 °C in N_2 atmosphere. XRD pattern of as-grown $LaCl_3$ crystal is shown in Fig. 2. As can be seen, the X-ray pattern of the crystal matches well with the standard JCPDS file of $LaCl_3$. No other phase was found [9].

3.2. Transmittance

Transmittance spectra were recorded by Shimadzu UV-2501 spectrophotometer. Fig. 3 shows

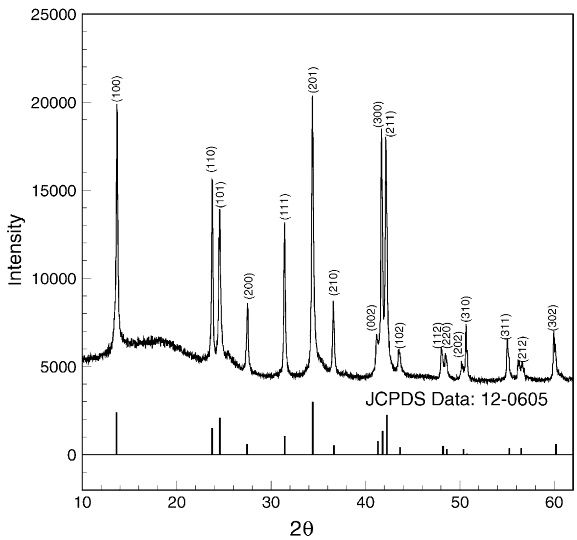

Fig. 2. XRD pattern of as-grown $LaCl_3$ crystal.

the optical transmittance of a 4 mm thickness sample. As is seen, transmittance between 300 and 650 nm is very good without any obvious absorption band. Transmittance at 405 nm, which is the peak of the scintillation spectrum according to Section 3.3, is as high as 80%. A high optical transmittance is crucial to the scintillating material, as in most applications a scintillator should transmit its own light. The good transmittance of the sample thus indicates that Modified Bridgman Method and parameters applied are suitable for $LaCl_3$ crystal.

3.3. Photoluminescence and X-ray stimulated luminescence

PL was performed by *Perkin-Elemer* LS50B fluorescence spectrophotometer at room temperature (20 °C). In the PL experiment, incident photons shot at the surface of the sample and luminescence directly from the surface (a few atoms depth) of the crystal was recorded and contributed the most to the emission spectrum. It is worthy to note that PL spectra from the surface (hereafter, 'surface emission') and inner part (hereafter, 'body emission') of the crystal are different with the body emission shifting to red [8,11,12] when self-absorption exists. A schematic of the measurement setup can be found in reference [10]. Fig. 4 shows emission and excitation spectra as a function of wavelength for $LaCl_3$ crystal. As can be seen, the emission peaked at 405 nm and excitation peaked at 251 nm.

XSL was performed by a self-made X-ray stimulated fluorescence spectrophotometer equipped with a Cu target running at 80 KV, 2 mA. The instrument was controlled by a computer and the XSL was recorded at room temperature. In the case of XSL, the whole body of the scintillator was exposed to incident X-ray, and the luminescence from both the surface and the inner part of the lattice was recorded. That is, the XSL was a combination of 'surface emission' and 'body emission'. Because of the large fraction of inner atoms compared with surface atoms and the high penetrability of X-ray, the XSL consisted of, mostly, the 'body emission'. Fig. 5 shows the XSL spectrum as a function of wavelength for $LaCl_3$ crystal. As is seen, the XSL peaked at 405 nm, which is the same as that of the PL spectrum.

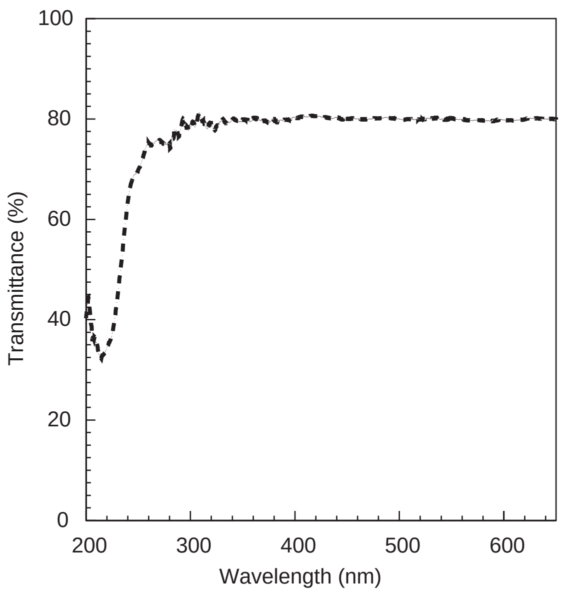

Fig. 3. Optical transmittance as a function of wavelength for $LaCl_3$ crystal (4 mm in thickness).

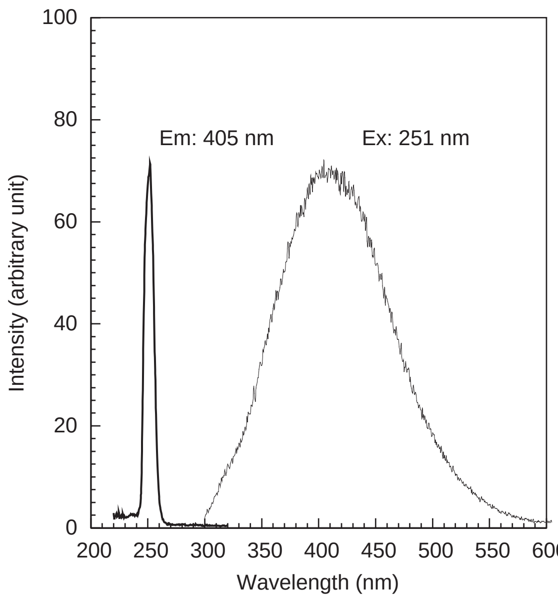

Fig. 4. Emission and excitation spectra as a function of wavelength for $LaCl_3$ crystal.

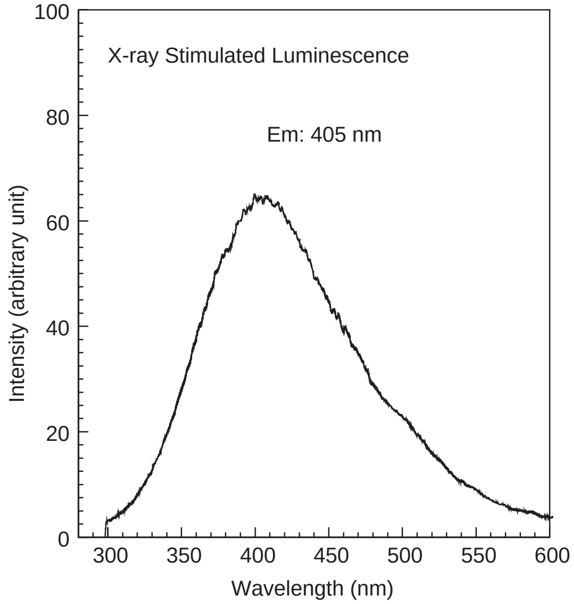

Fig. 5. X-ray stimulated luminescence spectrum as a function of wavelength for $LaCl_3$ crystal.

The PL spectrum, we recorded in this work, is so called, 'surface emission', while XSL spectrum is a combination of surface and body emission of the scintillator. A 'red shift' in body emission to surface emission can be found when optical transmittance of the scintillator is not good enough, especially the absorption band locates at the peak of scintillation spectrum. This red shift is known as the self-absorption effect of the scintillation materials [8,10–12]. In this work, however, the crystal we produced had very good optical transmittance and no absorption band located between 300 and 650 nm was found. PL and XSL, therefore, peaked at the same wavelength. The broad band located between 300 and 600 nm can be seen in the XSL spectrum, which had been proved to be a self-trapped-exciton (STE) luminescence [3,7]. A plenty of free holes and free electrons are created after the lattice being irradiated, and the STEs can be formed directly from electron–hole pairs or by trapping electrons in the V_k centers. During the diffusion of the STEs, they can be radiative recombinations leading to luminescence as seen in Fig. 5.

4. Conclusions

Crack-free LaCl3 crystal with a dimension of ϕ 25×50 mm was produced by the Modified Bridgman Method. The crystal had very good optical transmittance between 300 and 650 nm, and transmittance at 405 nm was 80%. Photoluminescence as well as X-ray stimulated luminescence peaked at the same wavelength, which was 405 nm. The study showed that the crystal growth method and the parameters applied are suitable for $LaCl_3$ crystal.

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