



## Crystal growth, luminescence and scintillation properties of mixed Ce:Cs<sub>2</sub>LiLa<sub>x</sub>Y<sub>1-x</sub>Cl<sub>6</sub> (0 < x ≤ 0.4) scintillators

Shangke Pan<sup>a,c,\*</sup>, Peng Zhang<sup>a</sup>, Hebing Zhu<sup>a</sup>, Jianyu Zhang<sup>a</sup>, Jianguo Pan<sup>a,c</sup>, Hongbing Chen<sup>a,c</sup>, Guohao Ren<sup>b</sup>, Huanying Li<sup>b</sup>

<sup>a</sup> State Key Laboratory Base of Novel Function Materials and Preparation Science, School of Material Sciences and Chemical Engineering, Ningbo University, No. 818 Fenghua Road, Jiangbei District, Ningbo City, Zhejiang 315211, PR China

<sup>b</sup> Shanghai Institute of Ceramics, Chinese Academy of Sciences, No.585 Road, Jiading District, Shanghai 201899, PR China

<sup>c</sup> Key Laboratory of Photoelectric Materials and Devices of Zhejiang Province, No. 818 Fenghua Road, Jiangbei District, Ningbo City, Zhejiang 315211, PR China



### ARTICLE INFO

#### Keywords:

Elpasolite  
Vertical Bridgman method  
Crystal Growth  
Scintillator

### ABSTRACT

Ce:Cs<sub>2</sub>LiYCl<sub>6</sub> (CLYC) crystal is a marketable halide inorganic scintillator with very high light yield, excellent energy resolution and pulse-shape discrimination between gamma rays and thermal neutrons. Although the scintillation performance of Ce:Cs<sub>2</sub>LiLaCl<sub>6</sub> (CLLC) crystal is better than CLYC crystal, the promising application was restricted by the crystal growth difficulties. To utilize the advantage of La<sup>3+</sup> halide, research on the growth of Ce:Cs<sub>2</sub>LiLa<sub>x</sub>Y<sub>1-x</sub>Cl<sub>6</sub> (0 < x ≤ 0.4) crystals were undertaken. The Ce:Cs<sub>2</sub>LiLa<sub>x</sub>Y<sub>1-x</sub>Cl<sub>6</sub> with x = 0.05, 0.1, 0.2 and 0.4 were grown by the vertical Bridgman technique, and transparent Ce:Cs<sub>2</sub>LiLa<sub>0.1</sub>Y<sub>0.9</sub>Cl<sub>6</sub> samples were successfully obtained. The crystal structure and composition of the as-grown crystals were characterized by powder x-ray diffraction patterns. The luminescence and scintillation properties of the mixed elpasolites Ce:Cs<sub>2</sub>LiLa<sub>x</sub>Y<sub>1-x</sub>Cl<sub>6</sub> (0 < x ≤ 0.4) crystals were also investigated. Finally, it was found that Ce:Cs<sub>2</sub>LiLa<sub>0.1</sub>Y<sub>0.9</sub>Cl<sub>6</sub> is a very promising gamma-rays and thermal neutrons scintillator with relatively high optical quality grown from vertical Bridgman method, acceptable energy resolution and relatively fast decay time.

### 1. Introduction

Since Tl:NaI scintillator was discovered in 1948 [1], much research has been devoted to halide crystals, such as Tl:CsI [2], Ce:LaBr<sub>3</sub> [3] Eu:SrI<sub>2</sub> [4] and Ce:Cs<sub>2</sub>LiYCl<sub>6</sub> [5] for their very high light yield, good energy resolution and easily feasible growth techniques with relatively low melting points. Among these typical halide scintillators, Ce:Cs<sub>2</sub>LiYCl<sub>6</sub> (CLYC) crystal can simultaneously detect gamma rays and thermal neutrons for the reaction of Li-6 isotopes with thermal neutrons [6]. CLYC is one of the Li-based elpasolite family scintillators, which have super-high light yield, excellent energy resolution and fast response [5,7–11]. Generally, Elpasolite halides belong to cubic crystal structure with space group *Fm* $\bar{3}$ *m*, which are able to be achieved with high-quality single crystal easily because of their highly structural symmetry. Besides CLYC crystal, the other representative crystals are Ce<sup>3+</sup> ions doped Cs<sub>2</sub>LiLaCl<sub>6</sub> (CLLC), Cs<sub>2</sub>LiLaBr<sub>6</sub> (CLLB) and Cs<sub>2</sub>LiYBr<sub>6</sub> (CLYB) crystals. Among these four elpasolite scintillators, both CLLC and CLYC crystals exhibit core valence luminescence (CVL) with less than 2 ns decay time constant, which are not available in CLLB and

CLYB crystals. The CVL only appears under gamma ray excitation but is absent under thermal neutron irradiation, which can be used to discriminate between gamma rays and thermal neutrons by means of pulse shape discrimination (PSD). In the energy spectra of both CLLC and CLYC crystals, the full energy thermal neutron peaks typically are more than 3 MeV gamma equivalent energy (GEE). So it may also be implemented with these materials for effective pulse height discrimination (PHD). While CLYC crystal achieves light yield of 21000 ph/MeV and energy resolution of 3.9% under <sup>137</sup>Cs gamma ray irradiation [8], CLLC crystal can be as high as 35000 ph/MeV and 3.4%, respectively [12]. The light yield of CLLC crystal can reach 110,000 ph/n excited by neutron, which is much higher than that of CLYC crystal with the light output of 70000 ph/n [8,12]. These results indicate that the CLLC crystal has significantly better scintillation performances, especially for the light yield, than CLYC crystal.

Although CLLC crystal also has excellent scintillation properties for neutron detection compared to CLYC crystal, so far no high-quality transparent CLLC crystal has been reported in the literatures. And the luminescence and scintillation performance of CLLC crystal were

\* Corresponding author at: State Key Laboratory Base of Novel Function Materials and Preparation Science, School of Material Sciences and Chemical Engineering, Ningbo University, No. 818 Fenghua Road, Jiangbei District, Ningbo City, Zhejiang 315211, PR China.

E-mail address: [panshangke@nbu.edu.cn](mailto:panshangke@nbu.edu.cn) (S. Pan).

<https://doi.org/10.1016/j.jlumin.2018.04.062>

Received 28 February 2018; Accepted 27 April 2018

Available online 30 April 2018

0022-2313/ © 2018 Elsevier B.V. All rights reserved.

investigated based on polycrystal or opaque crystal with one inch diameter boule [12,13]. So it might be very difficult to obtain transparent CLLC single crystal during the crystallization process. On the contrary, the large size and high-quality CLYC single crystal can be grown by the vertical Bridgman technique very easily [5,8]. Comparing to  $Y^{3+}$  ions in CLYC crystal,  $La^{3+}$  ions have larger ions radius, which is more suitable to introduce the luminescence centre  $Ce^{3+}$  ions. Furthermore, the Lanthanum halides, such as  $Ce^{3+}$  ions doped  $LaCl_3$  [14],  $LaBr_3$  [3] and  $K_2LaCl_5$  [15] have been widely investigated for their ultra-high light yield and excellent energy resolution. So mixed crystal strategy is considered as a promising method to optimize the light yield and energy resolution of CLYC crystal by  $La^{3+}$  partial substitution. In this paper, we will report the growth of mixed  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  ( $0 < x \leq 0.4$ ) crystals and investigate their luminescence and scintillation properties.

## 2. Experimental section

### 2.1. Crystal growth

0.5% mol  $Ce^{3+}$  doped  $Cs_2LiLa_xY_{1-x}Cl_6$  ( $0 < x \leq 0.4$ ) crystals were grown using the vertical Bridgman technique. Polycrystalline materials of  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  with  $x$  of 0.05, 0.1, 0.2 and 0.4 were prepared by melting the raw materials in the quartz ampule. Stoichiometric amounts of raw materials of anhydrous  $CsCl$  (3 N),  $LiCl$  (3 N),  $LaCl_3$  (4 N),  $Cs_2LiY_{0.995}Ce_{0.005}Cl_6$  (3 N) and  $CeCl_3$  (4 N) from Beijing Grimm Advanced Materials Co. Ltd. were grounded and subsequently transferred into silica ampoules in a nitrogen purged glove box maintaining oxygen and moisture levels less than 10 ppm. The quartz ampoules with the capillary tubes cleaned with HF acid and deionized water were baked in an oven before they were used. In order to drive out the residual moisture, the mixed raw materials were baked in a vacuum at about  $200^\circ C$  for several hours and sealed under dynamic vacuum of  $\sim 10^{-1}$  Pa using oxy-acetylene torch. During the crystal growth process, the temperature of the furnace was controlled at  $740^\circ C$  monitored by Pt-Pt/Rh thermocouples and the translation speed was maintained at 0.4 mm/h. The crystals crystallized spontaneously from the bottom of the capillary tubes. After the growth, the ampoules were cooled down to room temperature at a cooling rate of  $10^\circ C/h$ . The cutting, grinding and polishing of the crystals were finished in a drying chamber with the dew-point below  $-40^\circ C$ .

### 2.2. Characterization

The phase identification of  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  ( $0 < x \leq 0.4$ ) mixed crystals were investigated by powder x-ray diffraction (PXRD, Bruker D8 Focus diffraction) equipped with  $CuK\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at room temperature. The PXRD analysis was conducted in the two-theta angle range from  $10^\circ$  to  $70^\circ$  with the step size of  $0.02^\circ$ , high voltage of 40 kV and current of 40 mA. The samples were grounded and then loaded into the sample holder covered with Kapton film in a nitrogen-purged glove box to prevent any degradation due to exposure to moisture during the measurement. The optical transmission spectra of  $Cs_2LiLa_{0.1}Y_{0.9}Cl_6$  crystal with a dimension of  $\phi 12 \times 2 \text{ mm}^3$  polished sample was measured by a TU-1901 spectrophotometer in the range of 200–800 nm at room temperature. Before the measurement, the crystal was covered with the silicone oil to prevent the reaction with moisture. The photoluminescence (PL) excitation and emission spectra were measured by a HITACHI F-4600 spectrophotometer using a xenon lamp as the excitation source at room temperature. The photoluminescence decay curves were measured by HORIBA FL3-111 fluorescence spectrometer at room temperature. The x-ray stimulated luminescence (XSL) spectra were measured at room temperature. The x-ray tube with tungsten target was used as the excitation source operating at high voltage of 50 kV and current of 0.5 mA. Before the PL and XSL measurement, the crystals were firstly cut into 2 mm thick cylinders, then

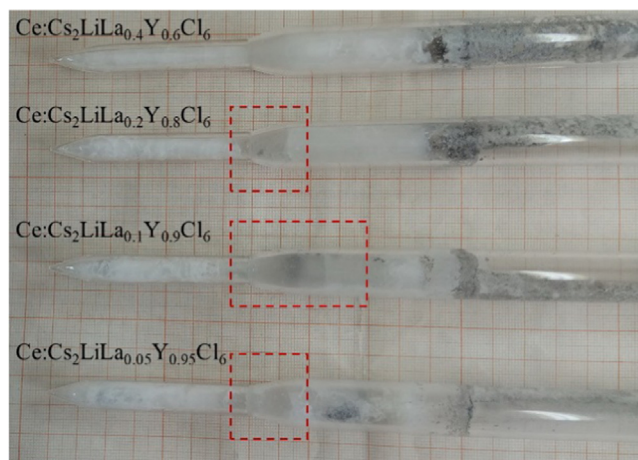


Fig. 1. Photos of  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  ( $0 < x \leq 0.4$ ) crystal ingots in the silica ampoules and the crystals in the red bricks are transparent or translucent.

polished and sealed in the quartz cuvettes in the nitrogen-purged glove box to minimize their exposure to moisture during the measurement. Pulse height spectrum under excitation of 662kV  $\gamma$ -rays from a  $^{137}Cs$  source was recorded using a Hamamatsu ET9813QSB PMT. The signal was fed into a shaping amplifier (ORTEC 572A), a multichannel analyzer (ORTEC Easy-MCA), and finally to a computer. The shaping time was set as 6  $\mu s$  and the high voltage of the PMT was set to  $-1700$  V. The scintillation decay profiles under  $^{137}Cs$  source irradiation were evaluated using a photomultiplier tube (PMT, ET9813QSB) connected to an oscilloscope Tektronix DPO5104. The scintillation performance measurements were conducted in the drying chamber and the crystals with the dimension of  $\phi 12 \times 5 \text{ mm}^3$  were covered by Teflon-tape to prevent the losses of the refracted light during the measurement.

## 3. Results and discussion

### 3.1. Crystal growth and structural analysis

Fig. 1 shows the as-grown  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  mixed crystals in the quartz ampoules. Except for the parts in the red bricks, most parts of the as-grown crystals in the ampoules were white, which meant that most of the as-crystals were polycrystal and opaque. But the crystals in the red bricks are transparent or translucent and  $Ce:Cs_2LiLa_{0.1}Y_{0.9}Cl_6$  crystal had the largest transparent part. The wafers with the dimension of  $\phi 12 \times 5 \text{ mm}^3$  were cut and polished with two sides, which are shown in Fig. 2.  $Ce:Cs_2LiLa_{0.1}Y_{0.9}Cl_6$  crystal has the best optical quality, in which the wafer was transparent except that little cracks could be found at the edge of the wafer. For  $Ce:Cs_2LiLa_{0.05}Y_{0.95}Cl_6$  and  $Ce:Cs_2LiLa_{0.2}Y_{0.8}Cl_6$  crystals, only part of the wafers were transparent. But the wafer was totally opaque when the  $x$  value reached at 0.4. So it's very difficult to obtain the single transparent crystal of the mixed scintillator with the composition of  $Ce:Cs_2LiLa_{0.4}Y_{0.6}Cl_6$ .

The powder x-ray diffraction patterns of  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  ( $0 < x \leq 0.4$ ) are shown in Fig. 3. The PXRD data obtained from  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  single crystals indicated that major peaks of these samples were consistent with the standard PDF card (No. 79 – 0771) of  $Cs_2LiYCl_6$  compound. The XRD results speculated that the mixed  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$  crystals belong to the cubic elpasolite family with the space group of  $Fm\bar{3}m$ . Meanwhile,  $Cs_3LaCl_6$  impurity phases were observed (as shown with \*) in  $Ce:Cs_2LiLa_{0.4}Y_{0.6}Cl_6$  crystal, which caused the crystal ingot totally opaque (seen in Fig. 2). This means that when  $x$  value increased to 0.4, the component segregation of the crystal happened seriously during the growth process. So from the results of as-grown crystal transparency and the PXRD analysis, to obtain highly transparent single crystal of  $Ce:Cs_2LiLa_xY_{1-x}Cl_6$ , the  $x$  value should be

Download English Version:

<https://daneshyari.com/en/article/7839943>

Download Persian Version:

<https://daneshyari.com/article/7839943>

[Daneshyari.com](https://daneshyari.com)