

Bridgman growth of $\text{LaCl}_3:\text{Ce}^{3+}$ crystal in non-vacuum atmosphere

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Abstract

Growth of $\text{LaCl}_3:\text{Ce}^{3+}$ crystal by the vertical Bridgman process in non-vacuum atmosphere has been studied. Based on the dehydration procedure of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ investigated by DTA/TG, anhydrous LaCl_3 and CeCl_3 were prepared by heating $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ at 200–230 °C for 6–7 h in dried HCl atmosphere. Using the feed materials prepared from the anhydrous lanthanon chlorides, a 4 mol% Ce^{3+} doped LaCl_3 crystal with a size of $\varnothing 28 \text{ mm} \times 70 \text{ mm}$ was successfully grown. The crystal was grown under the optimum conditions such as a growth rate of 0.5–0.8 mm/h and a temperature gradient of around 30 °C/cm across solid–liquid interface at a furnace temperature of 940–960 °C. The Bridgman process is confirmed to be promising for growing large size $\text{LaCl}_3:\text{Ce}^{3+}$ crystals with high quality.

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1. Introduction

$\text{LaCl}_3:\text{Ce}^{3+}$ crystal is a novel cerium activated halide scintillator discovered in recent years [1,2]. The crystal has attractive scintillation properties such as high light output and fast decay time constant. The unique properties make the crystal a very promising scintillator for medical imaging [3–6]. However, it is difficult to grow large crystals with high quality owing to its hygroscopic nature. Shah et al. reported a small $\text{LaCl}_3:\text{Ce}^{3+}$ crystal with dimension of 2.5 cm³ grown by Bridgman method under vacuum atmosphere [6]. The main difficulties for the crystal growth are: (1) the preparation of high purity raw material without crystallized water and absorbed moisture and (2) the oxidation and volatilization of melt during the growth. Recently, a modified vertical Bridgman method was applied to grow $\text{LaCl}_3:\text{Ce}^{3+}$ crystals successfully under non-vacuum atmosphere in our laboratory. In our process, the oxidation and volatilization of melt was avoided by sealing the feed material in the platinum crucibles. The process is confirmed to be a favorable technique to overcome the difficulties in the crystal growth. The recent results about the Bridgman growth of $\text{LaCl}_3:\text{Ce}^{3+}$ crystal are reported in this paper.

2. Experimental

Fig. 1 shows the apparatus used in the dehydration process. The 400–500 g $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ or $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was charged in a vessel-shaped crucible, which was put into a silica glass tube in a resistance furnace. With the dried HCl piped into the system continuously, the hydrous chlorides were sintered at 200–230 °C for 6–7 h simultaneously. In the dehydration process, the crystallized water was removed with the flowing HCl gas and the tail gas was absorbed by NaOH solution. As the dehydration process was finished, the HCl flow was ceased and the furnace was cooled. After the residual HCl was driven away by nitrogen gas, the anhydrous LaCl_3 and CeCl_3 were taken from the crucible.

The feed material for crystal growth was prepared with the anhydrous LaCl_3 and CeCl_3 . The mixture containing LaCl_3 (96 mol%) and CeCl_3 (4 mol%) was ground in a nylon ball mill for 1 h. In order to eliminate the moisture absorbed in the process thoroughly, the feed material was sintered again at 200–230 °C for 2–3 h in HCl atmosphere. The platinum crucible used in crystal growth was 28 mm in diameter and 200–240 mm in length with a seed well of 10 mm in diameter at the conical bottom. After the dehydration treatment had finished, the feed material was filled in the crucible. To avoid the oxidation and volatilization of the melt, the assembled crucible was sealed immediately. A small amount of active carbon powder with 100 ppm or so was added to the crucible so as to exhaust the air sealed in the crucible in the crystal growth. A little carbon residual would not pollute the grown crystal but deposit on its top due to its low density.

Fig. 2 shows the resistively heated vertical Bridgman furnace used in the crystal growth. The furnace temperature was adjusted by a WJK-100A fine temperature controller with an accuracy of ± 0.5 °C during the experiments. According to the axial temperature distribution, the furnace chamber consists of three zones, i.e. the high-temperature zone, the gradient zone and the

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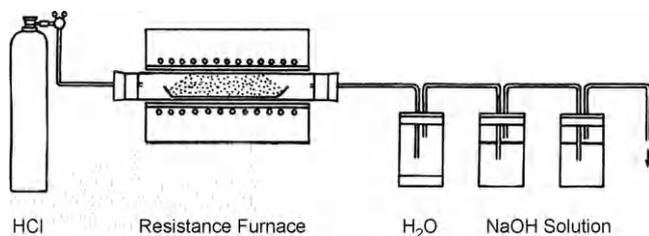


Fig. 1. Scheme of dehydration process.

low-temperature zone. During the crystal growth, the melt was homogenized in the crucibles in the high-temperature zone, while the grown crystal could be annealed in the low-temperature zone. The solid–liquid interface was located in the gradient zone. The high-temperature zone was controlled at 940–960 °C, which was about 80–100 °C higher than the melting point of crystal. The horizontal temperature distribution was kept as uniform as possible.

In order to obtain the seed crystal, the initial tries of the growth were done by spontaneous nucleation from the seed wells. Transparent single crystals with size of \varnothing (9–10) mm \times (35–45) mm were chosen as the seeds. The crucible was installed in a refractory tube filled with Al_2O_3 powder to isolate it from external temperature fluctuations. In order to detect the axial temperature along the crucible, it was fitted with two Pt–Pt/Rh 10% thermocouples, an upper one and a lower one. The lower thermocouple was located at the same height as the top of crystal. The refractory tube together with the crucible was put into the furnace chamber.

After the furnace had been heated to the controlled temperature, the seeding process was performed by adjusting the crucible to such a position that only the top of the seed was melted. The feed material and the top of the seed were kept at the melting state for 7–8 h so that the melt could be homogenized well and a stable solid–liquid interface could be established. The temperature gradient across solid–liquid interface was around 30 °C/cm. Growth process was driven by lowering the crucible at a rate of 0.5–0.8 mm/h. The furnace was cooled to room temperature at the rate of 20–50 °C/h after the growth had finished. The crucible was stripped after taking out from the refractory tube and as-grown crystal was obtained.

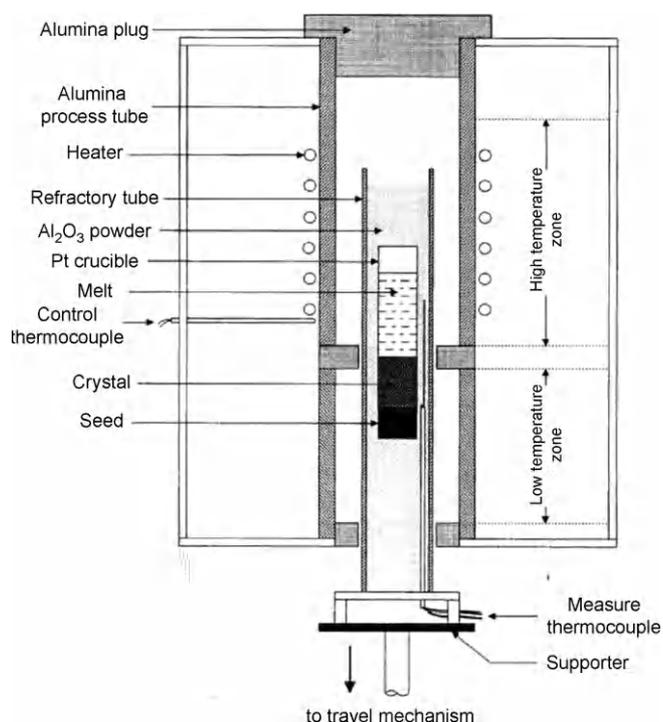
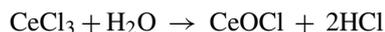
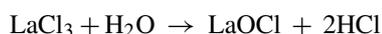


Fig. 2. Scheme of vertical Bridgman furnace.

3. Results and discussions

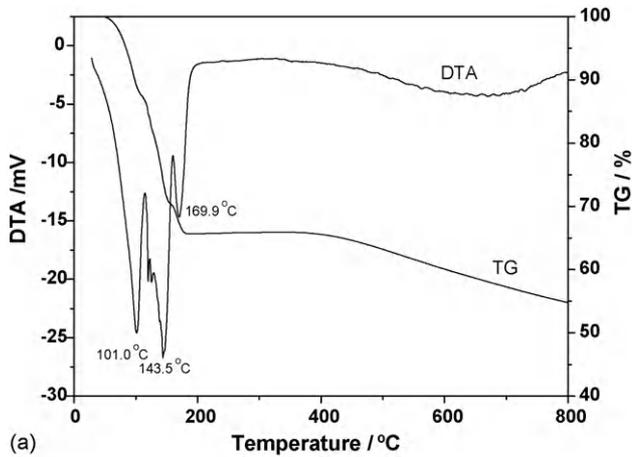
The anhydrous LaCl_3 and CeCl_3 with high purity are very important for growing $\text{LaCl}_3:\text{Ce}^{3+}$ crystal. The existence of crystalline or absorbed hydrates in the lanthanum and cerium chlorides is very harmful for the crystal growth. If the feed materials containing the hydrates were used in the crystal growth, the grown crystal would be somewhat opaque due to the formation of chlorioxides or oxides brought about with the hydrolysis reactions. However, the anhydrous rare earth chlorides with high purity are very difficult to be obtained commercially since the reagents are prone to crystallize as the hydrous chlorides and absorb the moisture in air. In this work, using $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (4N) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (4N) as the starting materials, the anhydrous LaCl_3 and CeCl_3 were prepared successfully by the dehydration process in HCl atmosphere.

In order to prepare the anhydrous LaCl_3 and CeCl_3 with high purity by the above process, the most important technical requirement is to prevent the hydrolysis reaction, which would bring about LaOCl and CeOCl . To explore an effective way to avoid the hydrolysis reaction, the dehydration procedures of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were investigated by DTA/TG analysis. $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were analyzed with a Seiko EXSTAR 6300 thermal analyzer calibrated by Al_2O_3 . Samples (7–8 mg) were tested at the heating and cooling rates of 10 °C/min. Fig. 3(a and b) present the DTA/TG curves of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, respectively. The results confirm that LaCl_3 and CeCl_3 can be obtained by three or four-step dehydration below 200 °C. The anhydrous LaCl_3 and CeCl_3 are verified to be stable relatively within the intermediate temperature ranges. However, the hydrolysis reactions began to take place as the temperature reaches 365 and 335 °C for $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, respectively. The hydrolysis reactions can be presented as follows:

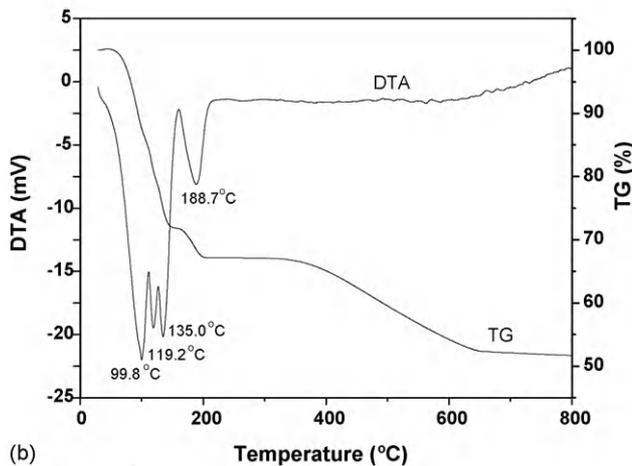


In the above dehydration procedures, two measurements were taken to avoid the hydrolysis reactions in this work. First, the heating temperature was controlled below 230 °C, at which evident hydrolysis reactions would not occur. Secondly, the dried HCl atmosphere was provided to suppress the possible hydrolysis reactions further in the dehydration process. By the above optimum conditions, the anhydrous LaCl_3 and CeCl_3 with high purity had been prepared successfully. As LaOCl and CeOCl are sparingly soluble in diluted HCl solution, the dissolubility test can be used as a simple method to check the purity of the chlorides. The anhydrous LaCl_3 and CeCl_3 obtained were verified to not containing LaOCl and CeOCl by the fact that the chlorides could dissolve in diluted HCl solution completely without any precipitate.

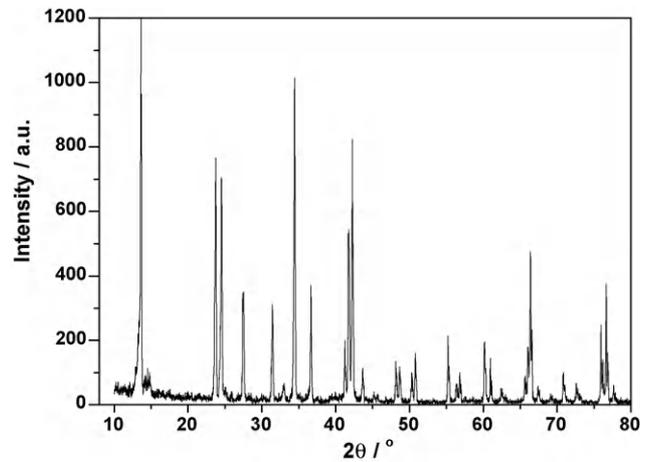
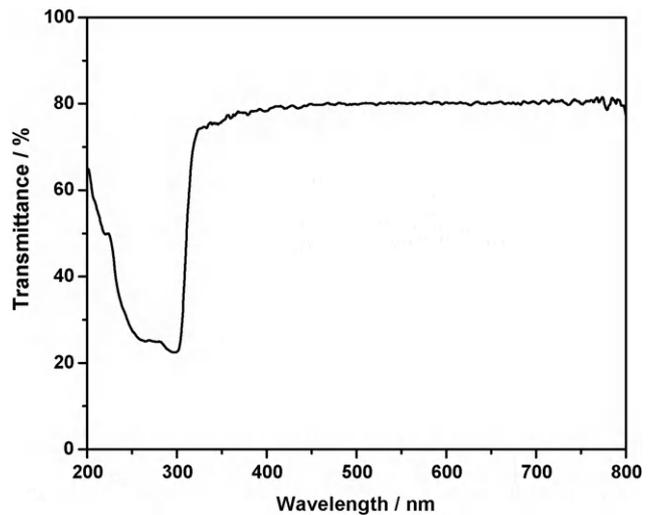
By means of the growth process described above, 4 mol% Ce^{3+} doped LaCl_3 single crystal has been grown successfully. A colorless and transparent crystal as large as \varnothing 28 mm \times 70 mm, as shown in Fig. 4, has been obtained. Examining the crystal



(a)



(b)

Fig. 3. DTA/TG curves: (a) $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$. (b) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$.Fig. 5. X-ray diffraction pattern of $\text{LaCl}_3:\text{Ce}^{3+}$ crystal.Fig. 6. Transmission spectrum of $\text{LaCl}_3:\text{Ce}^{3+}$ crystal.

by a He–Ne laser, the lower part of the crystal was free from scattering centers, while the optical quality of the upper part was deteriorating toward the growth direction. X-ray diffraction analysis of grown crystal was performed with a Rigaku D/max 2550 V diffractometer, using monochromatic $\text{Cu K}\alpha$ radiation with a working voltage of 40 kV and current of 100 mA. Fig. 5 presents the X-ray diffraction pattern of the crystal, which is in line with the data in JCPDS 12-0605. A sample with 2 mm in thickness was fabricated from the lower part of the crystal. The transmission spectrum of the sample was measured with a UV-2501PC spectrometer in the range of 300–800 nm at room temperature. The transmission spectrum in Fig. 6 shows that the

Fig. 4. $\text{LaCl}_3:\text{Ce}^{3+}$ crystal grown by vertical Bridgman method.

transmittance above 320 nm reaches as high as 80% without any absorption band.

4. Conclusions

$\text{LaCl}_3:\text{Ce}^{3+}$ crystal is a very promising scintillator with attractive properties. Trying to facilitate the practical application, researchers have been making their much effort to master the growth technique. Compared to other groups' work in recent years, this work provides a useful method to prepare the anhydrous rare earth chlorides and a modified process to grow the crystal in a non-vacuum atmosphere. The vertical Bridgman process in this work is confirmed to be a promising technique to grow the crystal. Now we are continuing to improve the process further to grow even larger size crystals with high quality. The scintillation properties of the crystal are under investigation.

Acknowledgements

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