Crystal growth of La³⁺-substituted BaCl₂ by the micro-pulling-down technique and their luminescence properties

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Abstract

Due to the phase transition near 920 °C and hygroscopicity, the growth of BaCl₂ single crystals is difficult. However, owing to the suppression of the cubic–orthorhombic phase transition by La substitution and careful handling to prevent contact with the starting powders and moisture in the air, crack-free BaCl₂ single crystals were grown by the micro-pulling-down technique under ambient pressure. In addition, photo- and radio-luminescence in non-activated and Eu²⁺-activated compounds were reported for scintillator applications.

1. Introduction

Melt growth of hygroscopic halide crystals including BaCl_2 is difficult as special efforts must be made to avoid direct contact of the starting materials and grown crystals with the surrounding atmosphere containing moisture. Therefore, the Bridgman–Stockbarger technique is widely used for the crystal growth of halide compounds because the starting powders and grown crystals are isolated from the atmosphere in vacuum containers during and after growth. BaCl_2 crystals have been grown by this technique [1-5] and lately by the Czochralski (Cz) technique [6]. Due to a cubic–orthorhombic phase transition near 920 °C in pure BaCl_2 [7] during the cool-down process from the melting point [8], the crystal growth of BaCl_2 from the melt is difficult. Therefore, the crystal rods grown by the Bridgman–Stockbarger and Cz techniques have cracks. Some crack-free small pieces were harvested from the grown rods and used for characterization [1, 6]. Recently, the La-stabilized “cubic” BaCl_2 (not single crystals) was fabricated by substituting nominal 10–12.5 at% La at Ba sites, heating up the starting materials to above the melting point [9-12], and a special cooling program to room temperature [9-12]. Through these processes, the cubic phase (high temperature phase) was maintained at room temperature [9-12]. However, the actual La concentration required to maintain the cubic structure was not measured using energy-dispersive X-ray spectroscopy (EDX) and/or wavelength-dispersive X-ray spectroscopy [9]. According to the database [13], BaCl_2 forms an orthorhombic structure at room temperature, and La 10 at% doping might prevent the phase transition from occurring (the cubic phase disappears at high temperature). However, accurate La concentration is not revealed in the database [13]. Therefore, the effects of La doping on crystal structure and the phase transition should be investigated. Recently, halide compounds such as Ce:LaBr_3 , CeCl_3 , and Tl:CsI were grown by the micro-pulling-down technique [14-15]. Therefore, the crystal growth of BaCl_2 by this technique may be favorable with appropriate La doping.

Scintillators have been widely used for non-destructive inspections, nuclear medicine diagnosis, high energy physics and astrophysics, exploration for underground mineral resources, and environmental radiation measurements. Desirable properties for X- and γ -ray scintillators are high density, high effective atomic number (Z_{eff}), fast decay, matching between emission wavelengths and quantum efficiency of photon detectors, non-hygroscopicity, and a low cost of production. BaCl_2 is attractive because it is inexpensive. In addition, its melting point, i.e., approximately 960 °C, is lower than that of garnet-related compounds, which have melting points ranging from 1850 °C to 1970 °C, such as $\text{Ce:Y}_3\text{Al}_5\text{O}_{12}$, $\text{Pr:Lu}_3\text{Al}_5\text{O}_{12}$, and $\text{Ce:Gd}_3(\text{Al}_2\text{Ga}_3)\text{O}_{12}$ [16], single crystals of which are well known as traditional phosphors and bright scintillators. Therefore, the fabrication cost (i.e., consumption of electric power) of BaCl_2 crystals is more economical than that of garnet-related compounds. Scintillators emit through

the photoelectric effect after X- and/or γ -ray irradiation. The reaction cross-section for the photoelectric effect is proportional to the product of the density and Z_{eff} . Therefore, high density and high Z_{eff} are desirable for X- and γ -ray scintillators. The density of BaCl_2 is 3.86 g/cm^3 [17], which is not high, but Z_{eff} is relatively high (50.5), close to the values for Tl:NaI (45.8) and Tl:CsI (54) that are well-known γ -ray halide scintillators. Thus, this compound is an attractive candidate for use in X- and γ -ray scintillators.

In general, emission mechanisms of scintillators are classified into two categories. First is intrinsic emission, including self-trapped exciton emission and core–valence luminescence [18]. On the other hand, emissions originating from trapped excitons and activators including Eu^{2+} , Ce^{3+} , and Tl^+ are considered as extrinsic. In this study, emission bands from non-activated (intrinsic) or Eu^{2+} -activated (extrinsic) and non-substituted or La^{3+} -substituted BaCl_2 crystals were investigated under photo and X-ray excitation.

This paper describes the growth of non-substituted or La^{3+} -substituted BaCl_2 single crystals, with or without Eu^{2+} activators, by the micro-pulling-down technique. Specifically, the effects of La substitution on crystal growth are discussed based on powder X-ray diffraction (XRD) patterns and chemical composition analysis. Moreover, their luminescence properties derived from intrinsic and extrinsic emissions under photo and X-ray excitation are reported and compared.

2. Experimental methods

Non-activated or Eu^{2+} -activated and non-substituted or La^{3+} -substituted BaCl_2 single crystals ($\phi = 4\text{--}5 \text{ mm}$) were grown by the micro-pulling-down technique. EuCl_2 (4N), LaCl_3 (4N), and BaCl_2 (5N) were used as starting materials. These compounds were well mixed in an agate mortar and pestle before crystal growth in a glove box with less than 0.1 ppm of H_2O and 0.1 ppm of O_2 . Growth was performed using a Pt crucible, a Pt after-heater, and Al_2O_3 heat insulators. The size of the Pt crucible was $\phi = 16 \text{ mm}$ and height 30 mm with a 5 mm^2 square die. The edge of the die of the crucible was almost spherical. Our micro-pulling-down facility is not equipped with a removable chamber to prevent the starting powders from absorbing moisture from the air [14, 15]. Therefore, the starting ingredients were exposed to the air once when setting the growth chamber. However, exposing the powders to the air for few minutes is not a large problem because BaCl_2 has low hygroscopicity. All crystal growths were performed after heating for one night (i.e., more than 24 h) to evaporate any moisture attached on the raw powders, the chamber, the crucible, the after-heater, and the heat insulators. All growths were performed under ambient pressure. Slow and long cool-down processes were performed over 48 h. The pulling down rate was 0.05–0.1 mm/min. High purity Ar (5N) was used as the growth atmosphere. BaCl_2 ceramics and crystals were used as seeds. All grown specimens were stored

in the glove box to prevent them from absorbing moisture from the air.

A scanning electron microscope (Hitachi S-4300SE/N)–energy-dispersive X-ray spectrometer (NORAN System SIX X-ray Microanalysis System, Thermo Electron Corporation) (SEM–EDX) was used to investigate the exact chemical composition of the compounds. Secondary electrons accelerated by 15 kV were used to observe the surface and analyze chemical compositions. The characteristic X-rays for each element were detected for 120 s in order to reduce measurement inaccuracy. Measurements were performed using the points and line scan mode. Polished pellets cut from grown rods and some residual solid in the crucible after growth were used for EDX measurements.

Powder XRD patterns were obtained under excitation by X-rays from a Nonius FR591 water-cooled rotating copper-anode X-ray generator (50 kV, 60 mA). Samples were sealed with two plastic tapes, attached to a nylon washer, and set in a special rotating chamber. The X-ray passed through the samples and was absorbed by a Mar detector (Mar USA, Inc., Evanston, IL). Fit 2D software was used to transform the two-dimensional diffraction pattern (Debye–Scherrer ring) to a one-dimensional pattern [19].

Photo-luminescence (PL) spectra under Xenon lamp excitation and radio-luminescence spectra under X-ray excitation (50 kV, 60 mA) were observed by a SpectraPro-2150i (Acton Research Corp., Acton, MA), connected to a PIXIS:100B charged-coupled device (CCD) (Princeton Instruments, Inc., Trenton, NJ), cooled to $-70\text{ }^{\circ}\text{C}$. The measurements were performed using three different spectrometers equipped with three gratings (i.e., red, green, and blue). Finally, emission spectra were measured by combining the three spectra into a single spectrum on a PC. The emission spectra were corrected by considering the background, grating efficiency, and CCD quantum efficiency [19]. The discontinuity around 360 nm in the luminescence spectra is caused by a grating change in the SpectraPro-2150i monochromator.

3. Results and Discussion

3.1. Crystal growth, composition analysis, and phase identification

Single crystals grown by the micro-pulling-down technique are presented in Fig. 1. This shows (a) BaCl_2 crystal with cracks, (b) La^{3+} (11 at%)-substituted BaCl_2 single crystal, (c) Eu^{2+} (0.5 at%)-activated BaCl_2 crystal with cracks, and (d) Eu^{2+} (0.5 at%)-activated and La^{3+} (7.7 at%)-substituted BaCl_2 single crystal. (a)–(d) are used as simplified signatures in this study. Due to the cubic–orthorhombic phase transition at approximately $920\text{ }^{\circ}\text{C}$ [13], crack-free pure BaCl_2 crystals could not be grown from the melt, as shown in Fig. 1 (a). Similarly, Eu^{2+} -activated BaCl_2 crystals without cracks could not be synthesized, as shown in Fig. 1 (c). The cracks in both crystals were not caused by the cooling process because this was performed over 48 h. On the other hand, La substitution at the Ba sites enables us to grow BaCl_2 single crystals without

cracks, as displayed in Figs. 1 (b) and (d). As mentioned, growth rates ranging from 0.05 to 0.1 mm/min were selected for all growth. Cracks in the La-substituted rods did not occur. Therefore, we conclude that the occurrence of cracks was due to the phase transition (not the growth rate). Since BaCl_2 has high wettability, the melt always crept on the walls of the crucible after dropping from the hole at the bottom of the crucible. Therefore, the meniscus condition and growth rate were carefully controlled to prevent the melt from overflowing and creeping during growth. The edge of the die of the crucible was almost spherical. Therefore, the control of the crystal shape was difficult, as displayed in Fig. 1. The volatilization of the starting powders and grown rods was inevitable at approximately 960 °C. When setting up the hot zone, the uniformity of temperature distribution close to the crucible was an important factor to provide the stability of the growth environment. Nominal La concentrations were tested from 3% to 20%. In this range, (b) and (d) were synthesized as single crystals without cracks. These growths were the first of crack-free La^{3+} -substituted BaCl_2 single crystals by the micro-pulling-down technique. Nominal Eu^{2+} and La^{3+} concentrations and the crystal appearance are summarized in Table I.

Residual solids were always seen in the crucible after each growth. Therefore, nominal La^{3+} and Eu^{2+} concentrations were definitely different from the actual concentrations. Actual La^{3+} concentrations (at%) at the Ba site were estimated using Ba weight% and La weight%. Estimated concentrations at all points were averaged and are shown in Table II. Eu^{2+} concentrations were not estimated because the Eu^{2+} signal was buried in the noise due to low signal intensity and/or lower than the detection limit of the EDX. Therefore, La^{3+} concentration at the Ba sites was calculated without the Eu^{2+} concentration. Considerable discrepancies between nominal and actual La concentrations indicate that not more than La^{3+} 3 at% is substituted in the Ba sites in the BaCl_2 host during melt growth. This might be related to a difference of effective ionic radii [20], as explained in the next paragraph, and charge compensation between Ba^{2+} and La^{3+} . In terms of charge balance, replacing 2+ cation sites with 3+ cations is difficult. The La^{3+} concentration in the residual solid in the crucible after (d) growth was estimated to be approximately 17 at%. The residual La concentration in the crucible proves that doping by more than 3 at% is impossible. According to a previous report [8] and the database [13], orthorhombic BaCl_2 crystals might be grown with La 10 at% substitution without the phase transition. However, the exact La concentration required to avoid the phase transition is unclear in the BaCl_2 – LaCl_3 phase diagram [8, 13] because the phase transition line is inaccurate (despite database [13] referring to ref. [8], both show different lines). Considering the inadequacy of the phase diagram and EDX results, it is possible that approximately 3 at% La substitution in BaCl_2 led to the avoidance of the phase transition. Distributions of each scanned element were uniform in the measurement area. However, scans were conducted in a small area.

Therefore, any non-uniform distribution of La in the crystals might not be observed. For the melt growth techniques, including the micro-pulling-down and Cz techniques, inhomogeneous distribution of the dopant (segregation) is a unique phenomenon. Therefore, segregation in samples in this study must occur. For convenience, nominal chemical compositions were used in the sample notations.

Fig. 2 shows the XRD patterns for phase identification. Most of the peaks of all samples were identified as orthorhombic BaCl_2 phase (PDF 24-0094). Although heating for one night was performed before every growth in order to dry the starting powders, all four samples contained a small amount of $\text{BaCl}_2(\text{H}_2\text{O})$ and/or $\text{BaCl}_2(\text{H}_2\text{O})_2$. Actual ratios of BaCl_2 hydrates in BaCl_2 are not clarified from XRD patterns because peak intensity depends on arrangement and the type of atom. There might be possibilities that BaCl_2 absorb moisture from the air when measuring XRD peaks. Cubic phase peaks were not identified from these patterns, as reported [9-12]. In addition, hexagonal BaCl_2 peaks were not seen at room temperature. All peak positions for La-substituted samples ((b) and (d)) were slightly shifted to the low angle side compared to non-substituted samples. Thus, La doping had some effects on the crystal structure.

The coordination number of Ba ion in BaCl_2 is 9 [21]. As per Shannon's study, the effective ionic radii for Ba^{2+} and La^{3+} with coordination number 9 are 1.47 and 1.216 Å [20], respectively. Based on the effective ionic radii and actual La concentrations in Table II, the average cation radii of (b) and (d) were estimated to be approximately 1.463 Å for both compounds. These values were estimated without considering the Eu^{2+} ionic radii due to the abovementioned reason. These values decreased by 99.5% with reference to the Ba ion radius in pure BaCl_2 . The average cation radius in $\text{La}(12.5 \text{ at}\%):\text{BaCl}_2$, with the cubic structure previously reported [9, 10], was calculated to be 1.438 Å, a decline of 97.8% from that in the pure compound. This might be one of the reasons we could not grow "cubic" La-stabilized BaCl_2 single crystals.

3.2. Luminescence properties

Fig. 3 shows PL mapping spectra of (I) sample (c) and (II) sample (d). A wide excitation band and Eu^{2+} emission band at 400 nm for both (c) and (d) were observed in (III), as reported in a previous study [1]. The emission band at approximately 400 nm was assigned to Eu^{2+} ($4f^6$)($5d^1 \text{ } ^2D_{5/2, 7/2}$) $\rightarrow$ ($4f^7 \text{ } ^8S_{7/2}$) transitions that are typical Eu^{2+} broad peaks [9, 12]. However, unidentified weak peaks appeared at approximately 450 nm. Unfortunately, PL spectra for (a) and (b) were not observed.

Radio-luminescence spectra were obtained under X-ray irradiation in Fig. 4. As reported previously [2, 5, 7, 22], two luminescence bands at 300 and 390 nm were observed for (a) and (b). The luminescence band at 300 nm is considered to be intrinsic. A luminescence band at 475

nm was not seen in (a) and (b), as reported [2, 7]. On the other hand, Eu^{2+} -activated BaCl_2 shows a typical Eu^{2+} 5d–4f spin forbidden transition and a parity allowed transition around 400 nm. This band was also assigned to two transitions $(5d^1\ ^2D_{5/2, 7/2})(t_{2g} \text{ and } e_g) \rightarrow (4f^7\ ^8S_{7/2})$ [9, 12] and is considered extrinsic. Moreover, an unidentified weak peak was observed at approximately 450 nm, as observed in the PL spectra in Fig. 3. This peak might be assigned to the F [2, 23, 24, 25] or H centers [9]. Further study is necessary to clarify this.

4. Conclusions

BaCl_2 growth from the melt is difficult due to the need to isolate the starting materials and the crystals from moisture in the air. Another difficulty is that the crystal growth is related to the phase transition that is observed when the material is cooled down to room temperature. These problems were solved by careful handling during the growth process and partial substitution of La to impede the phase transition. La^{3+} -substituted BaCl_2 single crystals with and without Eu^{2+} activator were initially grown by the micro-pulling-down technique. The crack-free single crystals were grown after approximately La 3 at% substitution in the BaCl_2 host. Thus, clear progress in fabricating single crystalline BaCl_2 was demonstrated. The single crystals formed orthorhombic structures at room temperature. Greater than 3% La substitution in BaCl_2 , to form a cubic structure at room temperature, was impossible in crystals grown by the micro-pulling-down technique. Emission bands at approximately 300 (intrinsic) and 390 nm were observed in the radio-luminescence spectra of compounds without an Eu^{2+} activator. An emission band at 390–400 nm (extrinsic) was observed in the photo- and radio-luminescence spectra of compounds containing an Eu^{2+} activator.

Acknowledgments

This work was supported by the U.S. Department of Energy/NNSA/NA22 and carried out at Lawrence Berkeley National Laboratory under Contract NO. AC02-05CH11231. The author is grateful to Edith D. Bourret-Courchesne, Gregory Bizarri, Martín Gascón, Christopher Ramsey, Stephan Hanrahan, Ivan Khodyuk, Kathleen Brennan, and Woon-Seng Choong for their help.

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Figure captions

Fig. 1. Photographs of (a) BaCl_2 , (b) $\text{La}^{3+}(11 \text{ at\%})\text{:BaCl}_2$, (c) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:BaCl}_2$, and (d) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:La}^{3+}(7.7 \text{ at\%})\text{:BaCl}_2$ single crystals grown by the micro-pulling-down technique. (a)-(d) are used as simplified signatures in this paper.

Fig. 2. Powder X-ray diffraction patterns of (a) BaCl_2 , (b) $\text{La}^{3+}(11 \text{ at\%})\text{:BaCl}_2$, (c) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:BaCl}_2$, and (d) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:La}^{3+}(7.7 \text{ at\%})\text{:BaCl}_2$. Hump from 10 to 25 degree shows plastic tape to seal the powder. BaCl_2 peaks were identified as PDF 24-0094.

Fig. 3. Photo-luminescence mapping spectra of (I) (c) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:BaCl}_2$ and (II) (d) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:La}^{3+}(7.7 \text{ at\%})\text{:BaCl}_2$. (III) Excitation and emission spectra of (c) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:BaCl}_2$ and (d) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:La}^{3+}(7.7 \text{ at\%})\text{:BaCl}_2$. Measurements were performed at room temperature.

Fig. 4. Radio-luminescence spectra of (a) BaCl_2 , (b) $\text{La}^{3+}(11 \text{ at\%})\text{:BaCl}_2$, (c) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:BaCl}_2$, and (d) $\text{Eu}^{2+}(0.5 \text{ at\%})\text{:La}^{3+}(7.7 \text{ at\%})\text{:BaCl}_2$ under X-ray excitation. Measurements were performed at room temperature.

Table captions

Table I. Summary of nominal Eu^{2+} and La^{3+} concentrations and crystal appearances.

Table II. Actual La concentration (at%) at the Ba site measured by energy dispersive X-ray spectroscopy (EDX) together with nominal La concentration. La concentrations (at%) were calculated without Eu^{2+} concentration because signal from Eu^{2+} was less than detection limit of EDX and/or buried into noise. Nominal chemical compositions were used as sample notations in this study.

Chemical formula	Nominal Eu^{2+} concentration (at%)	Nominal La^{3+} concentration (at%)	Appearance of crystals
(a) BaCl_2	none	none	Cracks
(b) $\text{La}(11 \text{ at\%}): \text{BaCl}_2$	none	11	No cracks
(c) $\text{Eu}(0.5 \text{ at\%}): \text{BaCl}_2$	0.5	none	Cracks
(d) $\text{Eu}(0.5 \text{ at\%}): \text{La}(7.7 \text{ at\%}): \text{BaCl}_2$	0.5	7.7	No cracks

Nominal chemical compositions	Nominal La concentration at the Ba site (at%)	Actual La concentration at the Ba site (at%)
(b) $\text{La}(11 \text{ at\%}): \text{BaCl}_2$	11	2.7
(d) $\text{Eu}(0.5 \text{ at\%}): \text{La}(7.7 \text{ at\%}): \text{BaCl}_2$	7.7	2.9
Residual solid in the crucible after (d) $\text{Eu}(0.5 \text{ at\%}): \text{La}(7.7 \text{ at\%}): \text{BaCl}_2$ growth	NA	17

Figure(s)

(a)

(b)

(c)

(d)

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.