

***In situ* growth of blue-emitting thin films of cerium-doped barium chloride hydrate at low temperatures**

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Blue emission was observed from thin films of barium chloride hydrate doped with cerium. The films were deposited by spray pyrolysis of aqueous solutions with substrate temperatures between 250 and 450 °C. The cathodoluminescence (CL) spectrum consists of two peaks at 443 and 485 nm due to $4f-5d$ transitions of cerium ion. The dependence of the emission band on deposition temperature and Ce/Ba ratio is discussed. The CL luminance and luminous efficiency at 5 kV were 120 cd/m² and 0.48 lm/W, respectively, for the films deposited at temperatures as low as 250 °C. The results indicate barium chloride hydrate doped with cerium is a blue phosphor that exhibits relatively efficient luminescence after processing at low temperatures. © 2003 American Institute of Physics. [DOI: 10.1063/1.1558891]

Cerium-activated materials have been studied extensively in the last several decades. These studies were directed to a variety of applications, such as optoelectronics, flat-panel displays, and x-ray imaging systems. Recently, Ce-doped thin films, such as Y₂SiO₅ and SrGa₂S₄, have been shown to produce blue emission.¹⁻³ However, because as-grown films are usually amorphous or have poor crystallinity, annealing them at relatively high temperatures was required for both crystallization of compounds and diffusion of Ce ions before sufficient brightness was obtained. Unfortunately, high temperature processes are not suitable for some applications involving displays that require glass substrates. Considerable research is being focused on *in situ* growth of Ce-doped thin films. Recently, Tanaka *et al.*⁴ observed cathodoluminescence (CL) from thin films of SrGa₂S₄:Ce deposited *in situ* using a molecular beam epitaxy. They considered the growth temperature of the films (472.5 °C) to be the lowest value ever achieved. While improving the deposition process for the thin films of existing Ce-activated hosts is important, it is known that quantum efficiencies of variety of cerium-doped hosts can differ substantially.⁵ Thus, it is desirable to investigate other host materials for Ce ion.

For alkaline earth halide lattices, BaF₂:Ce has attracted much attention as a scintillator material.⁶ Besides that, only photoluminescence in bulk of Ce-doped alkaline earth (Ca, Sr, Ba) chlorides had been observed in the UV region (330–400 nm).⁷ There is little work on the CL study of alkaline earth chlorides. In this letter, the blue CL characteristics at room temperature are reported for thin films of barium chloride hydrate doped with cerium. Spray pyrolysis was used to deposit the films. The films were grown *in situ* from 250 to 450 °C, and no postannealing was employed.

Thin films of BaCl₂·2H₂O:Ce were deposited on Corning 7059 glass substrates by a spray pyrolysis technique. The starting materials were 0.1 M BaCl₂ (anhydrous and 99.998% from Alfa) and CeCl₃ (anhydrous and 99.5% from Alfa). The stock precursor solutions were mixed in an appropriate ratio to provide solutions in the range of 5–15 at. % Ce dopant relative to Ba. The spray system was described in detail elsewhere.⁸ Briefly, the spray, which was developed by an ultrasonic nebulizer, was directed towards the substrate. The spray chamber was mounted on an *x*–*y* translation table to raster the aerosol to cover an area of 25×50 mm². Humid air was used as a carrier gas at a flow of 1.2 L/min rate.

The crystal structure determination and phase identification of the films were carried out using a Rigaku Geigerflex II x-ray diffractometer (XRD) with Co *K*α radiation. The chemical composition of thin films was analyzed by using induced coupled plasma (ICP) atomic absorption spectroscopy and energy dispersive x-ray spectroscopy (EDS). The morphology of the films was observed by a field emission scanning electron microscopy (FE-SEM) (Hitachi S-4500). The CL spectra were obtained using a CL luminoscope (Relion Industries ELM-2B). Luminescence spectra were measured using an Ocean Optics S2000 charge coupled device spectrometer (350–900 nm). The spectrometer provides a resolution of 1.5 nm of the full width at half maximum. A Minolta T-1M illuminance meter was used to determine the luminance of the films.

Figure 1(a) shows the XRD spectrum of an as-grown thin film deposited at 250 °C. For comparison, a standard BaCl₂·2H₂O powder pattern from the JADE-PDF card No. 25-1135 is presented in Fig. 1(b). Figure 1(a) illustrates that the as-grown film deposited at 250 °C formed a polycrystalline structure. All diffraction peaks of XRD agreed well with BaCl₂·2H₂O having monoclinic structure ($a=6.72$, $b=10.91$, $c=7.14$). We excluded some possible compounds,

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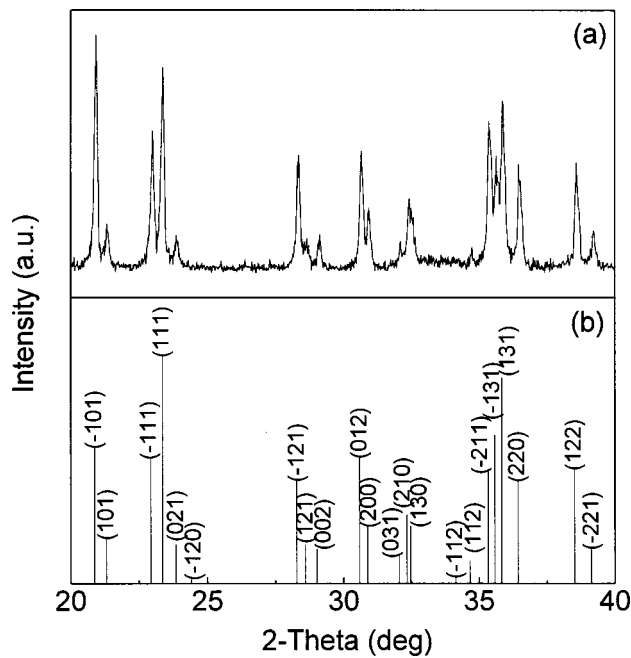


FIG. 1. XRD patterns for BaCl₂·2H₂O:Ce thin films grown on glass substrates: (a) as-grown at 250 °C, (b) standard BaCl₂·2H₂O powder pattern from the JADE-PDF card No. 25-1135.

such as BaCl₂, BaO, and Ba₄Cl₆O by comparing their standard power patterns with Fig. 1(a). These results indicate that sprayed thin films of BaCl₂·2H₂O crystallized at an exceptionally low temperature in comparison with other thin film materials grown by this technique.⁹⁻¹¹ In those cases the as-grown thin films showed no or broad peaks of x-ray pattern, indicating poor crystallization.

Figure 2 shows the FE-SEM image of thin films deposited at 250 °C. The films exhibited much less dense morphology. The highly porous structure was formed over the whole film.

Figure 3 shows the CL spectra of the as-grown films for different Ce concentration relative to Ba in the spray solutions. All films deposited at 250 °C were about 1.5 μm thick. ICP analysis revealed that the ratio of Ce and Ba measured in the films was about one-third of that in the spray solution, due to different sticking probability for each element. A 5 kV excitation voltage was used for CL measurement at room temperature. The current density on the sample surface was

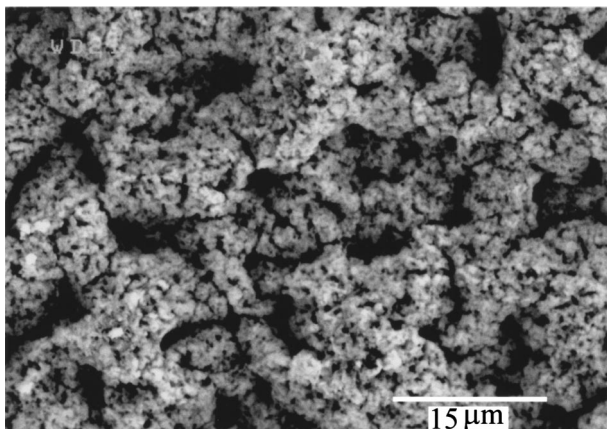


FIG. 2. FE-SEM image of BaCl₂·2H₂O:Ce thin films deposited at 250 °C.

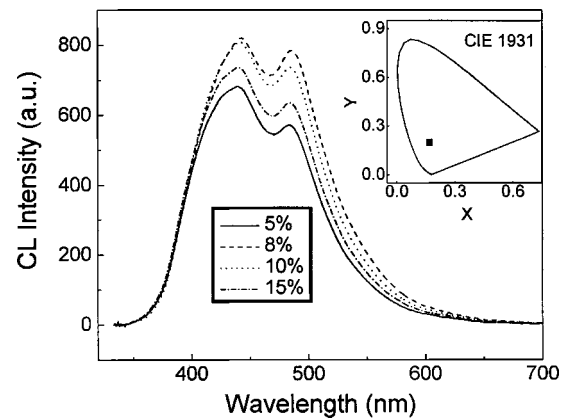


FIG. 3. CL for BaCl₂·2H₂O:Ce thin films doped with different Ce concentration relative to Ba in the spray solutions. A CIE chromaticity diagram showing the chromaticity point is presented in inset.

estimated to be 62 μA/cm² for a beam current of 0.5 mA. The CL spectra of the as-grown films deposited at 250 °C exhibited broad multibands covering the blue region, which consisted of two peaks at 443 and 485 nm. For comparison, the emission spectrum of cerium-doped anhydrous barium chloride had a maximum at 352 nm and a shoulder at 380 nm.⁷ The emission maximum shifted from 352 to 360 nm with increasing activator concentration from 0.05% to 5%. Our characteristic emission bands are similar to those exhibited in other Ce-activated hosts, like Y₂SiO₄ and SrGa₂S₄.¹⁻⁴ The overlapping bands in Fig. 3 correspond to two allowed 4*f*-5*d* transitions of Ce³⁺.¹² Furthermore, the line position did not change as the Ce concentration changed, showing that the nature of the cerium activation did not change with concentration. However, the CL intensities changed with Ce concentration. Consequently, the film from 8% Ce-dopant solution had the maximum intensity, indicating self-quenching at the higher concentrations. The location of the color coordinates of BaCl₂·2H₂O:Ce thin films on the CIE chromaticity diagram is presented in the inset of Fig. 3. The chromaticity coordinates were *x*=0.169 and *y*=0.199 with a dominant wavelength of 480 nm and 68% color purity.

For films grown at various substrate temperatures, Fig. 4

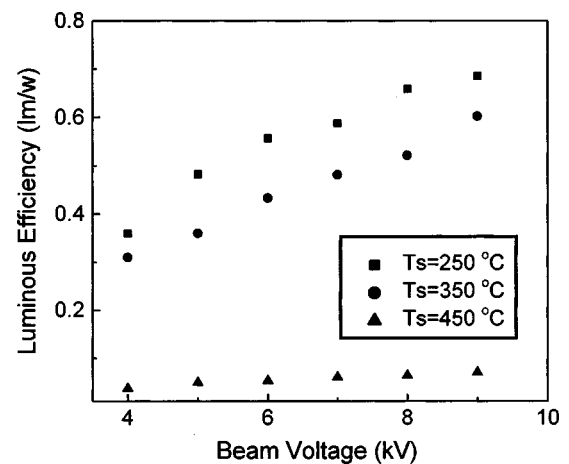


FIG. 4. Variation of CL luminous efficiency of BaCl₂·2H₂O:Ce thin films deposited at various substrate temperatures as a function of electron beam voltage. The current density on the films was 62 μA/cm².

shows the dependence of the CL efficiency as a function of electron beam voltage. The CL efficiency increased continually as the acceleration voltage increased from 4 to 9 kV at a constant current density of $62 \mu\text{A}/\text{cm}^2$, and saturation was not evident. In our measurements, the luminescence was measured on the side irradiated by the electron beam, and the lower efficiency at low voltage indicates that the transfer of the recombination energy of the electron-hole pair to a luminescent ion occurred with lower probability near the surface than deeper in the film. In addition, the CL increase could be attributed to an increase in electron penetration depth as applied voltage is increased, resulting in an increase in the number of Ce^{3+} ions that can luminescence. In general, the dependence of CL brightness L_{CL} on the electron beam current and voltage for many phosphors is governed by $L_{\text{CL}} = f(I_b)(V - V_0)^m$, where V_0 is a "dead voltage" and $1 \leq m \leq 2$ for most phosphors.¹³ Typically, the CL luminance and luminous efficiency at 5 kV were $120 \text{ cd}/\text{m}^2$ and $0.48 \text{ lm}/\text{W}$, respectively, for the film deposited at 250°C .

On the other hand, the luminous efficiency decreased significantly for all excitation voltages when the growth temperature increased. This observation could be due to a decrease of amount of Cl remaining in thin films with increasing growth temperature. This was in evidence from the EDS analysis of thin films. As the growth temperature was increased, most Cl was replaced by the oxygen element. This result is consistent with the observation of other films prepared from chloride solutions.¹⁴ Furthermore, the XRD of the films grown at 450°C exhibited very weak peaks, perhaps associated with BaO, indicating that the films had poor crystallinity.

From a practical point of view, the stability and morphology play important roles in the performance of the final phosphor.¹⁵ Preliminary studies showed that there is no obvious change for the CL of the films in ambient atmosphere for two months, showing that is relatively stable material. However, about 20% of the decrease from initial values of CL was observed during the first 1 min of electron beam operation for all samples measured both before and after two months. This phenomenon could be related to either halide

instability or the relaxation behavior of CL observed in other phosphors.¹⁶ The porosity of the films shown in Fig. 2 could cause the reduction of resolution and efficiency in some phosphor screen applications. If the precursor solutions with lower concentration are used to deposit the films, the films would become denser and it will result in the improvement of the performance.

In summary, as-grown thin films of cerium-doped barium chloride hydrate exhibit blue CL emission, and CL intensity decreased significantly with increasing the growth temperature between 250 and 450°C . Our results indicate that the material studied as thin film phosphor is rather unique since it contains water. It seems that the $4f$ - $5d$ transition in Ce is so energetic that the O-H phonons cannot disturb it.

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