

# SYNTHESIS, CRYSTAL STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF A NEW RARE-EARTH CARBONATE $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$

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## ABSTRACT

A new sodium europium carbonate hydrate,  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ , has been prepared using the hydrothermal method, and its structure was determined by single crystal X-Ray diffraction analysis for the first time. It crystallizes in the polar hexagonal space group  $P6_3$  with  $a = 11.382(9) \text{ \AA}$ ,  $c = 5.989(5) \text{ \AA}$ ,  $V = 672.06(9) \text{ \AA}^3$ ,  $Z = 2$ ,  $M_r = 509.06$ ,  $D_c = 2.516 \text{ g/cm}^3$ ,  $F(000) = 492$ ,  $\mu(\text{MoK}\alpha) = 4.84 \text{ mm}^{-1}$ ,  $R_1 = 0.015$  and  $wR = 0.038$ . The structure features a three-dimensional (3D) framework composed of planar  $(\text{CO}_3)^{2-}$  triangles,  $\text{Eu}^{3+}$  ions and  $\text{Na}^+$  ions, which delimits 1D infinite chains with a hexangular star appearance along the  $c$ -axis. The IR spectrum and the self-activated photoluminescence properties were studied. Under the excitation of near UV light (395nm), it shows strong red emission at 618 nm with a lifetime of 348.7  $\mu\text{s}$ . Present research indicates that  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  is a promising red phosphor for white light-emitting diodes.

**Keywords:** hydrothermal; carbonate; X-ray diffraction; photoluminescence

## 1. INTRODUCTION

In the last few decades, an extensive research has been carried out for new rare earth luminescent materials, owing to their potential applications in optical information transmission, display imaging, solar photovoltaic conversion, fluorescent powder, electrical conduction, new light source and X-ray intensifying screen.<sup>1-3</sup>  $\text{Eu}^{3+}$  ion doped material is an effective red phosphor due to its intense near UV absorption and excellent pure red emissions corresponding to the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j = 1, 2, 3, 4$ ) transitions of  $\text{Eu}^{3+}$ .<sup>4-8</sup> In recent years, a large amount of rare earth carbonates system has been prepared, such as  $\text{Na}_3\text{Eu}(\text{CO}_3)_3$ ,<sup>9</sup>  $\text{NaLiRe}(\text{CO}_3)_3$  (Re = Eu-Er, Yb, Lu, Y),<sup>10</sup>  $\text{Na}_3\text{Eu}(\text{CO}_3)\text{F}$ ,<sup>11</sup>  $\text{BaEu}(\text{CO}_3)_2$ ,<sup>12</sup>  $\text{Ba}_3\text{Eu}(\text{CO}_3)_2\text{F}_3$ ,<sup>13</sup>  $\text{Na}_3\text{La}(\text{CO}_3)_4\text{F}$ :  $\text{Eu}^{3+12}$  and  $\text{KGd}(\text{CO}_3)_2\text{F}_2$ :  $\text{Eu}^{3+}$ .<sup>14</sup> However, there were few reports on their luminescence properties.<sup>15</sup> In order to explore a new europium carbonate that might afford red luminescent emission, we started a research using the hydrothermal method and a new alkali sodium europium carbonate hydrate  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  was successfully prepared. The crystal structure, IR spectrum and photoluminescence properties at room temperature were studied for it.

## 2. EXPERIMENTAL

### 2.1 Materials and Methods

All of the chemicals,  $\text{NaCO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were purchased from Shanghai Reagent Factory and were analytically pure without further purification. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000–400  $\text{cm}^{-1}$ . Photoluminescence (PL) properties were performed on EDINBURGHFLS980 fluorescence spectrophotometer.

### 2.2 Synthesis

Single crystal was prepared by the follow procedure: a mixture of  $\text{Na}_2\text{CO}_3$  (0.44 g, 4  $\mu\text{mol}$ ),  $\text{NaHCO}_3$  (0.2 g, 2  $\mu\text{mol}$ ) and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.035 g, 0.1  $\mu\text{mol}$ ) was dissolved in 2 ml deionized water, which was then placed in a 20 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and heated at 170 °C under autogenously pressure for 72 h. After being slowly cooled to room temperature at a rate of 5 °C/h, colorless needle like crystals were collected by filtration, and washed by distilled water.

### 2.3 X-ray crystal structure determination

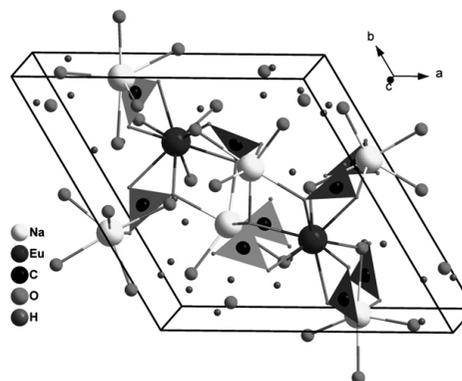
Single crystal X-Ray diffraction analysis (SC-XRD) for  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  was performed on a Bruker Smart Apex2 CCD diffractometer equipped with a graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). An appropriate single crystal (0.20mm×0.05mm×0.05mm) was selected and mounted on a fiberglass. The data was collected by the narrow frame means at 296(2)K with a scan width of 0.5°. After that, the data was scaled for absorption using *Apex2* package.<sup>16</sup> The crystal structure was solved by a software *Shelx-2013* and refined by full matrix least squares on  $F^2$  with XYZ-centeroids of reflections above  $2.0\sigma(I)$ .<sup>17</sup> In the structure, all non-hydrogen atoms were refined by harmonic anisotropic atomic displacement parameters (ADP), whereas all hydrogen atoms were located at the geometrically calculated positions, and the thermal parameter was confined to be 0.20. The final refined solutions obtained were checked with the program *PLATON*,<sup>18</sup> and no higher symmetry was

found. Crystallographic data and structural refinement, the atomic coordinates and thermal parameters are given as supporting information (Tab. S1, S2 and S3). Further details of the crystal structure investigations can be obtained from the Fachin formation szentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number of CSD 431473.

## 3 RESULTS AND DISCUSSION

### 3.1 Crystal structure

Single-crystal X-Ray diffraction analysis revealed that compound  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  crystallizes in the hexagonal polar space group  $P6_3$ , which is different from the other reported sodium europium carbonate<sup>19</sup> and isotype with yttrium analogy compound  $\text{Na}_3\text{Y}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ .<sup>20</sup> The structure features a three-dimensional (3D) framework constructed by planar  $(\text{CO}_3)^{2-}$  triangles,  $\text{Eu}^{3+}$  ions and  $\text{Na}^+$  ions, as shown in Fig. 1. There is one sodium (I) atom, one europium (III) atom, one  $(\text{CO}_3)^{2-}$  group and two coordinated water molecules in the asymmetric unit of  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Carbon atoms are all surrounded by three atoms, forming near planar triangle  $(\text{CO}_3)^{2-}$  groups. The C–O bond distances range from 1.271 Å to 1.324 Å and O–C–O bond angles range from 117.4° to 123.2° (Tab. 1), which are common values comparing with other reported carbonates.<sup>21</sup> The  $(\text{CO}_3)^{2-}$  groups are isolated from each other and are further connected by  $\text{Eu}^{3+}$  ions and  $\text{Na}^+$  ions to form a 3D structure. Europium atoms reside among  $(\text{CO}_3)^{2-}$  groups and are coordinated by six oxygen atoms of three  $(\text{CO}_3)^{2-}$  groups and three water molecules, forming distorted  $\text{EuO}_9$  polyhedra (Fig. 2a). The Eu–O bond distances ranges from 2.421 Å to 2.524 Å, which is comparable with other reported europium oxides.<sup>22</sup> Sodium atoms are 6-coordinated by six O atoms from four  $(\text{CO}_3)^{2-}$  groups and two water molecules, forming distorted  $\text{NaO}_6$  octahedra (Fig. 2b). The Na–O bond distances range from 2.363 to 2.591 Å, with an average value of 2.44 Å, which is comparable with other reported sodium oxides.<sup>23</sup>

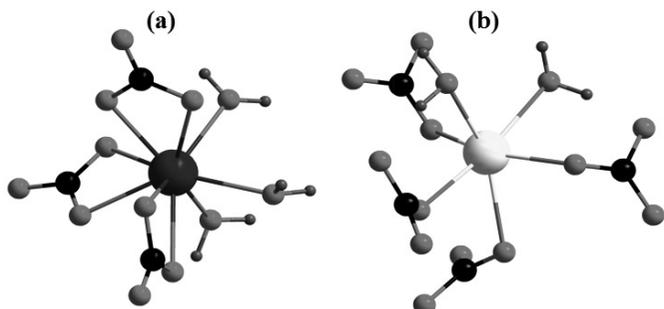


**Figure 1.** View of the crystal structure of  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  to show the  $(\text{CO}_3)^{2-}$  groups,  $\text{Na}^+$  ions and  $\text{Eu}^{3+}$  ions.

**Table 1. Selected Bond Lengths (Å) and Angles (°) for Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O**

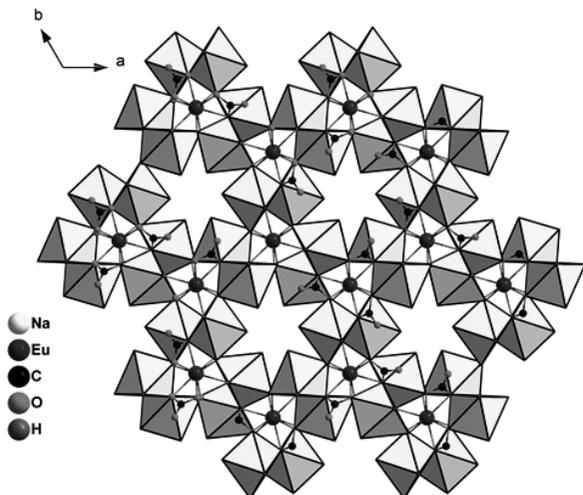
Na1—O1 <sup>i</sup>	2.359 (4)	Eu1—O4	2.439 (4)
Na1—O2	2.368 (3)	Eu1—O4 <sup>iv</sup>	2.439 (4)
Na1—O5	2.410 (5)	Eu1—O4 <sup>v</sup>	2.439 (4)
Na1—O3 <sup>ii</sup>	2.437 (4)	Eu1—O2 <sup>v</sup>	2.524 (3)
Na1—O2 <sup>iii</sup>	2.501 (4)	Eu1—O2 <sup>iv</sup>	2.524 (3)
Na1—O4 <sup>iv</sup>	2.593 (4)	Eu1—O2	2.524 (3)
Eu1—O3 <sup>v</sup>	2.417 (4)	C1—O1	1.273 (5)
Eu1—O3 <sup>iv</sup>	2.417 (4)	C1—O2	1.284 (5)
Eu1—O3	2.417 (4)	C1—O3	1.315 (6)
O1—C1—O2	123.2 (4)	O2—C1—O3	117.2 (4)
O1—C1—O3	119.6 (4)		

Symmetry codes: (i)  $x, y, z-1$ ; (ii)  $x-y+1, x, z-1/2$ ; (iii)  $-x+1, -y+1, z-1/2$ ; (iv)  $-x+y, -x+1, z$ ; (v)  $-y+1, x-y+1, z$ ; (vi)  $x, y, z+1$ ; (vii)  $-x+1, -y+1, z+1/2$ ; (viii)  $y, -x+y+1, z+1/2$ .

**Figure 2.** Coordination environments of Eu (a) and Na (b) atoms.

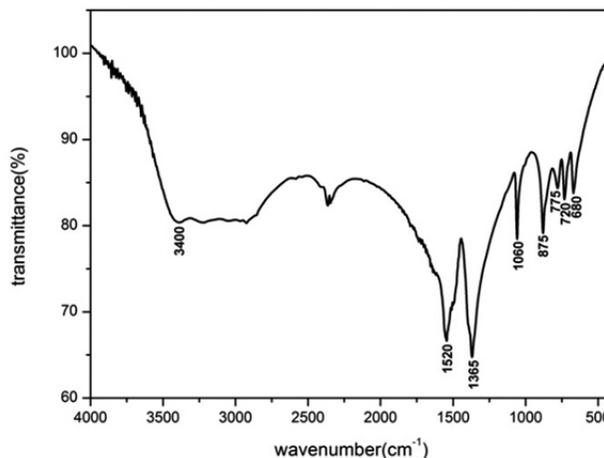
The EuO<sub>6</sub> groups are isolated from each other and are in linear array along the *c*-axis. In an alternatively view, the 3D structure of Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O can be described as Eu(III) atoms residing among cavities which are delimited by (CO<sub>3</sub>)<sup>2-</sup> groups and NaO<sub>6</sub> octahedra. On the other hand, 1D infinite chains with a hexangular star appearance are delimited in the structure, as shown in Fig. 3.

Bond valence calculation indicates that all atoms are in reasonable oxidation states: +1 for Na, +3 for Eu and +4 for C. The calculated total bond valences for Na(1), Eu(1) and C(1) are 0.976(4), 3.201(11) and 3.93(3), respectively.

**Figure 3.** View of the 1D infinite chains with a hexangular star appearance along the *c*-axis.

### 3.2 Infrared spectrum

Fig. 4 shows the section of the IR spectrum of Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O from 400 to 4000 cm<sup>-1</sup>. The IR spectrum exhibits absorptions which are assigned referring to literatures.<sup>24</sup> The wide and scattered peaks from 3500 to 3000 cm<sup>-1</sup> can be attributed to O—H stretching vibrations (O—H) of coordinated water molecules which are intensely affected by hydrogen bonding.<sup>25</sup> The lattice vibration observed around 415 cm<sup>-1</sup> can be assigned to the Eu—O stretching vibration,<sup>26</sup> whereas the vibration of Eu—O is very weak and cannot be observed. The main IR absorption region between about 1350 and 1500 cm<sup>-1</sup> reveals two absorption bands (1365 and 1520 cm<sup>-1</sup>) owing to C—O stretching vibrations of (CO<sub>3</sub>)<sup>2-</sup> groups. There is a medium-weak band at 680–775 cm<sup>-1</sup>, which corresponds to the bending vibration of δ-(OCO) of (CO<sub>3</sub>)<sup>2-</sup> groups.<sup>27</sup>

**Figure 4.** IR spectrum of Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O.

### 3.3 Photoluminescence properties

As shown in Fig. 5a, the photoluminescence (PL) excitation spectrum was recorded from 320–420 nm by monitoring the most intensity emission at about 618 nm. The excitation spectrum is made up of several sharp peaks that can be assigned to the intrinsic *f*→*f* transition of Eu<sup>3+</sup> ions, 361 nm for <sup>7</sup>F<sub>0</sub>→<sup>5</sup>D<sub>4</sub>, 380 nm for <sup>7</sup>F<sub>0</sub>→<sup>3</sup>L<sub>6</sub>, 384 nm for <sup>7</sup>F<sub>0</sub>→<sup>3</sup>L<sub>7</sub>, 395 nm for <sup>7</sup>F<sub>0</sub>→<sup>3</sup>L<sub>6</sub>, and 417 nm for <sup>7</sup>F<sub>0</sub>→<sup>3</sup>D<sub>5</sub>. The highest excitation peak at 395nm corresponding to the <sup>7</sup>F<sub>0</sub>→<sup>5</sup>L<sub>6</sub> transition of Eu<sup>3+</sup> matches well with the emission from the near-UV LED chip, implying that the red phosphor Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O has potential application in white-LED as the red component of tricolor luminescent materials.<sup>28</sup>

As shown in Fig. 5b, the emission spectrum is composed of several distinct groups of sharp lines in the range of 500–750 nm with the most intensive line at 618 nm, which can be assigned to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>*j*</sub> (*j*=0, 1, 2, 3, 4) transitions of Eu<sup>3+</sup> ions. The spectral features of Eu<sup>2+</sup> were not observed, revealing that the europium ions are in the trivalent oxidation state which is in accordance with the crystal structure analysis of Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The peaks centered at 591 nm (orange-red) is caused by the magnetic dipole <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition, whereas the most intensive sharp lines centered at 618 nm (red) are caused by the electric dipole <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition from Eu<sup>3+</sup> ions. Other weak emission peaks centered at 536 nm, 652 nm and 696 nm can be attributed the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>3</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>4</sub> transitions of Eu<sup>3+</sup>, respectively. It is well known that the transition intensity is intensely influenced by the external environment of Eu<sup>3+</sup> ions.<sup>29</sup> If Eu<sup>3+</sup> ions located in a site with inversion symmetry, the magnetic dipole transition <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> is frequently the strongest one, while in a site without inversion symmetry the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> electronic transition usually becomes dominant. For Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, the significantly higher intensity of the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition compared to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition typically indicates that the Eu<sup>3+</sup> sites are not inversion centers and the electric dipole transition <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> is dominant in the host lattice. The result is in accordance with the crystal lattice of Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O which crystallizes in the polar space group *P*6<sub>3</sub> and all atom sites including Eu<sup>3+</sup> ions locate in non-centrosymmetric sites.

The decay curve of Na<sub>3</sub>Eu(CO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with λ<sub>em</sub> = 618 nm and λ<sub>ex</sub> = 395 nm was measured, as shown in Fig. 6. The decay curve can be well fitted with a single-exponential function:

$$I_{(t)} = I_0 + A_1 \exp(-t/\tau)$$

Where  $I_{(t)}$  and  $I_0$  are the luminescence intensities at time 0 and  $t$ ,  $A_1$  is

the pre-exponential factor obtained from the curve fitting and  $\tau$  represents the lifetime of the excited state. The value of  $\tau$  is calculated to be 348.7  $\mu$ s. It should be noted that there is only one decay phenomenon revealed by the experiment, meaning that the divalent europium is located in only one crystallographic site which is well fitted with the crystal structure analysis.

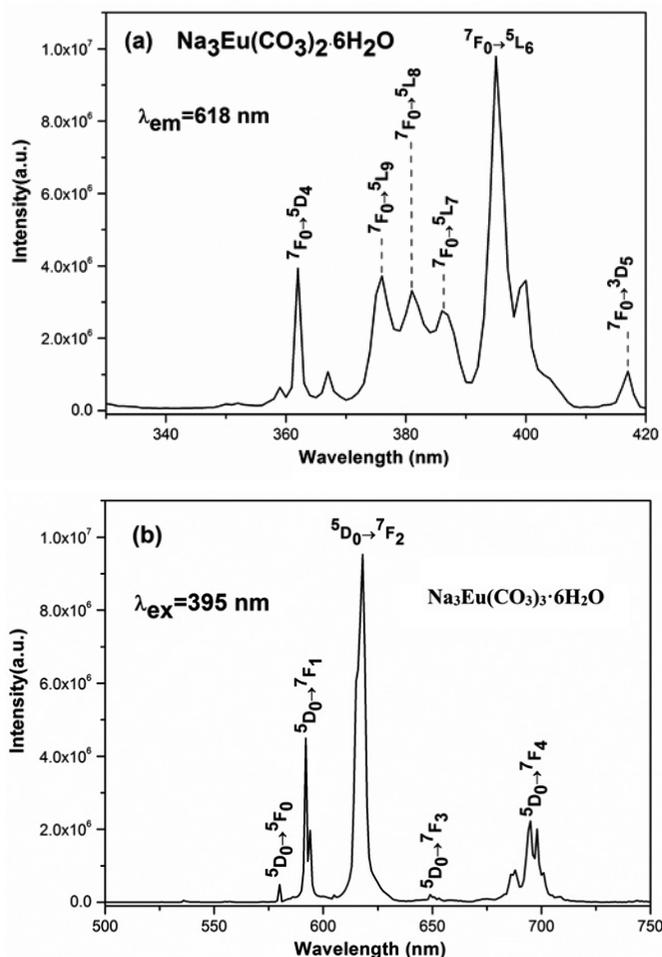


Figure 5. Excitation (a) and emission (b) spectra of  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

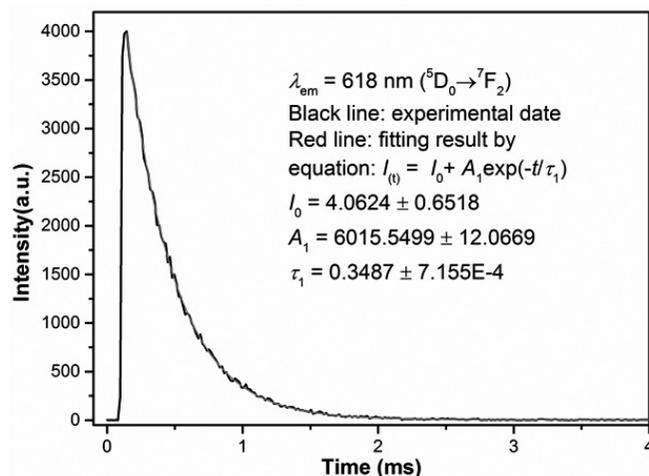


Figure 6. Decay curve of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$  transition under the excitation of 395 nm for  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

It is well-known that three main colors recognized by the human vision system are red, green and blue. These three colors are usually referred to as the 1931 color coordinates, which is the current standard for lighting specifications on the market.<sup>30,31</sup> In general, the color of any light source in this color space can be represented as an (x, y) coordinate. The location of the color coordinates of  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  red phosphor on the CIE chromaticity diagram was presented in Fig. 7. Under the excitation at 395 nm, the calculated CIE chromaticity coordinate is (0.660, 0.340), which is very close to the standard red chromaticity coordinates (0.670, 0.330) for National Television Standard Committee system (NTSC). We may expect that compound  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  can be used as a good red phosphor for the three colors white LEDs.

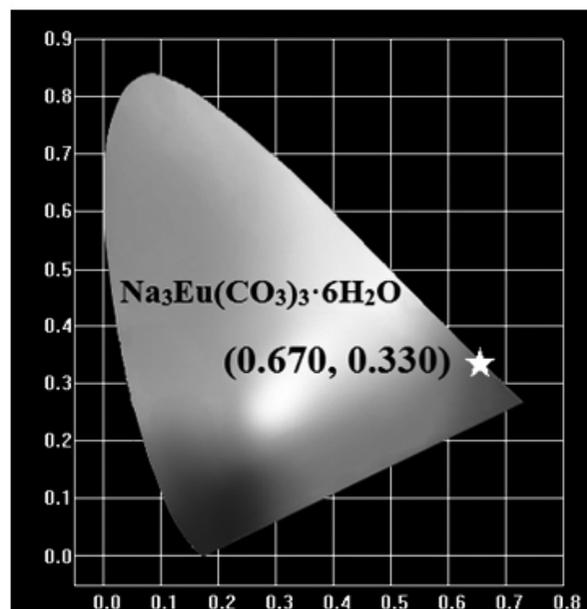


Figure 7. CIE chromaticity diagram showing the chromatic coordinates of red phosphor  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ .

#### 4. CONCLUSION

In the present work, we reported the synthesis, crystal structure, and PL properties of a new sodium europium carbonate hydrate,  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Its structure features a 3D framework constructed by planar  $(\text{CO}_3)^{2-}$  triangles,  $\text{Eu}^{2+}$  ions and  $\text{Na}^+$  ions, which delimits 1D infinite chains with a hexangular star appearance along the *c*-axis. Under the excitation of near UV light (395nm), a strong red emission peak centered at 618 nm can be observed with a lifetime of 348.7  $\mu$ s. Meanwhile, the CIE chromaticity coordinates is calculated to be (0.660, 0.340). The excitation spectrum covers a wide range from 361 to 417 nm, and matches well with the emissions of near-UV InGaN-based LED chips, making  $\text{Na}_3\text{Eu}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$  promising as a red phosphor for efficient excitation by radiation of commercial InGaN based LEDs.

#### ACKNOWLEDGMENTS

This work was financially supported by National Science Foundation of China (Grant No.21201056, 21307028).

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