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Synthesis and luminescence properties of the lithium-containing lanthanum-oxycarbonate-like borates

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ABSTRACT

The lithium-containing lanthanum-oxycarbonate-like borate, $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$, has been synthesized by solid-state reactions and was found to be isostructural with the type II lanthanum-oxycarbonate $La_2O_2(CO_3)$. The new compound, lithium-containing lanthanum-oxycarbonate-like borate $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$ has been synthesized and its structure characterized by the Rietveld method using powder X-ray diffraction data. It crystallizes in space group $P6_3/mmc$ with lattice parameters of $a=b=4.03396(3)$ Å, $c=16.5863(2)$ Å, $V=233.746(4)$ Å^3. The mechanism of the lithium incorporation in the borate is that four Li^+ cations replace one $(B_2O)^{4+}$ group, i.e. $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$ can be described as $Li_{2x}La_2O_{1.5+2.5x}(BO_3)_{1-x}$, $x=0.3$ and the lithium incorporation stabilized the type II borate. The luminescent properties of $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$ doped with Eu^{3+} were studied, indicating a potential application in white light emitting diodes (WLEDs).

1. Introduction

Lanthanide oxycarbonates $Ln_2O_2CO_3$ have three different crystal structures: type I, type Ia and type II [1,2]. The type II is the most thermal and chemical stable polymorph, which adopts a hexagonal structure consisting of alternative La_2O_2 and CO_3 layers along the *c*-axis (Fig. 1a) [1,3–5]. The relation of type II of lanthanide oxycarbonates to the A-type La_2O_3 ($P\overline{3}ml$) trigonal structure (Fig. 1b) is that the replacement of the O layers in the A-type La_2O_3 by the CO_3 groups leads to lanthanide oxycarbonate type II structure with expanded *c*-axis compared with that for the A-type La_2O_3 [6]. The structures of the type II lanthanide oxycarbonates and the A-type La_2O_3 are illustrated in Fig. 1. The lithium-intercalated lanthanide oxycarbonate $[Li_{2x}La_2O_{2+2x}(CO_3)_{1-x}]$ in Fig. 1c is isostructural with the type-II lanthanide oxycarbonates. From a structural analysis of neutron diffraction data, Attfield et al. [7] proposed an incorporation mechanism of lithium into type II lanthanum oxycarbonates as that partial CO groups in the CO_3 blocks are replaced by lithium atoms according to the equation $(CO)^{2+} \leftrightarrow 2Li^+$ [7–11].

Recently, lanthanide hexagonal type-II oxycarbonates attract attention because of their amazing luminescence properties [12–17]. The green-emitting phosphors $Gd_2O_2CO_3{:}Tb^{3+}$ and $(Gd_{0.95}Y_{0.05})_2O_2CO_3{:}Tb^{3+}$ exhibited high relative emission intensity, which was 111% and 131% of that of a commercial $LaPO_4{:}Ce^{3+},Tb^{3+}$ phosphor, respectively [2,17]. Type II $La_2O_2CO_3{:}Eu^{3+}$, $Gd_2O_2CO_3{:}Eu^{3+}$, and $Y_2O_2CO_3{:}Eu^{3+}$ have been synthesized and studied as red phosphors [18]. Among these phosphors, the most efficiency emission was obtained at the composition of $R_2O_2CO_3$: 7% Eu^{3+} ($R=$La, Gd, and Y), and the corresponding emission intensities to that of the commercial $Y_2O_3{:}Eu^{3+}$ phosphor were 23%, 27% and 22% for La, Gd and Y, respectively. It has been found that the charge transfer bands between Eu^{3+} (4*f*) and O^{2-} (2*p*) are dominant in some Eu^{3+} doped type II $R_2O_2CO_3$ ($R=$Y, La and Gd) compounds [18]. In the layer structure, energy transfer from a luminescent center to another one across the CO_3^{2-} layer is probably forbidden because of the long R^{3+}–R^{3+} distance. Accordingly, phosphors based on type II lanthanide oxycarbonates are expected to be resistant to concentration quenching [2]. In this study, we report the isolation, structural characterization of lithium-containing type II lanthanum-oxycarbonate-like borate $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$ and luminescence properties of the Eu^{3+}-doped materials.

2. Experimental

2.1. Synthesis

Polycrystalline samples were synthesized by solid-state reactions at high temperature. The starting materials are analytical reagent (A. R.) grade H_3BO_3, Li_2CO_3, Ln_2O_3 (99.99%, $Ln=$La, Eu).

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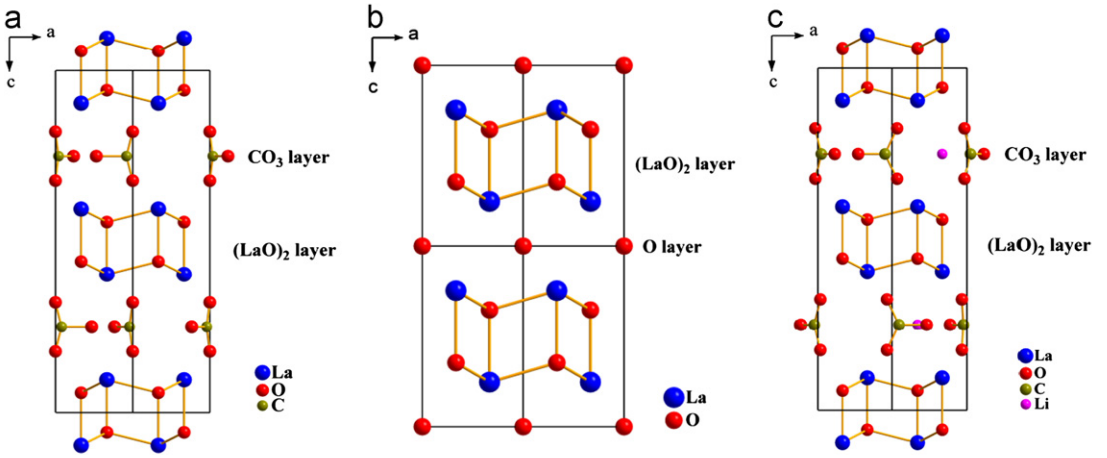

Fig. 1. Projections along the *b*-axes of crystal structures for (a) type-II $La_2O_2CO_3$, (b) A-type La_2O_3, and (c) $Li_{0.52}La_2O_{2.52}(CO_3)_{0.74}$. In (a) and (c) the planar CO_3 groups exhibit orientational disorder over three sets of positions and each CO_3 group is shown along only one orientation for clarity.

Stoichiometric starting materials were weighed according to the formula of $Li_{3y}La_2O_{1.5+3y}(BO_3)_{1-y}$ ($y=0.18$–0.29) (where $3Li^+$ replace B^{3+}) and 5% excesses of H_3BO_3 and Li_2CO_3 were used to compensate the lithium and boron loss due to their volatilization during the reaction. Only $y=0.28$ to be used in the Eu^{3+} doped samples ($Li_{3y}La_{2-2z}Eu_{2z}O_{1.5+3y}(BO_3)_{1-y}$ ($y=0.28$, $z=0.05$, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35)) synthesized.

The mixtures were ground thoroughly in an agate mortar and heated at 1040 °C (for undoped samples) or 1070 °C (for Eu^{3+}-doped samples) for 8 h and cooled down to room temperature (RT) by switching off the muffle furnace. The products were ground into fine powders. The undoped samples are white and the Eu^{3+}-doped samples are light pink.

2.2. Characterization

2.2.1. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

The undoped sample was washed with deionized water and its cationic ratio was analyzed using an IRIS Advantage Floor Model Radial Plasma Spectrometer.

2.2.2. Powder X-ray diffraction (XRD)

The phase purity was characterized by powder X-ray diffraction (PXRD) using a Rigaku D/max-2200 VL/PC X-ray diffractometer (Cu*K*α radiation). XRD data of the un-doped sample for Rietveld refinement was collected over a 2θ range of 8°–100° at 0.02° interval on a Bruker D8 Advance X-ray diffractometer (Cu*K*α radiation). Structural refinement on the XRD data was performed using the TOPAS-Academic program [6,19].

2.2.3. Photoluminescence Properties

The UV-excitation and emission spectra of the phosphors were recorded on an Edinburgh FSP 920 combined with fluorescence lifetime and steady-state spectrometer. An Xe900 xenon lamp was used as the excitation source and a μF920H microsecond flash lamp with a pulse width of 2 μs and a pulse period of 10 ms was hired to measure the luminescence decay curves, FSP 920 is equipped with a time-correlated single photon counting (TCSPC) card.

2.2.4. Electroluminescence Properties

The electroluminescence properties of the phosphors were recorded on an EverFine PMS-80 UV–vis–IR Spectrophotometer under a direct current of 20 mA at RT.

3. Results and discussion

3.1. Structure analysis

The $La_2O_{1.5}BO_3$ sample ($Li_{3y}La_2O_{1.5+3y}(BO_3)_{1-y}$, $y=0$) would form a mixture of La_2O_3 and $LaBO_3$. The same single phase material was obtained on $Li_{3y}La_2O_{1.5+3y}(BO_3)_{1-y}$ ($y=0.18$–0.29). The XRD patterns of the borate samples are similar to that of the type II oxycarbonate, suggesting that the borate and carbonate are isostructural compounds. The XRD reflections of the $y=0.28$ borate sample can be indexed using a hexagonal cell: $a=b=4.03396(3)$ Å, $c=16.5863(2)$ Å with space group $P6_3/mmc$. The composition $y>0.29$ in $Li_{3y}La_2O_{1.5+3y}(BO_3)_{1-y}$ led to a mixture containing the type II oxycarbonate-like borate phase and $Li_4B_2O_5$.

The ICP elementary analysis result for $Li_{3y}La_2O_{1.5+3y}(BO_3)_{1-y}$ ($y=0.28$) gave a Li:La:B cationic ratio of 0.63:2:0.71, leading to a chemical formula of $Li_{0.63}La_2B_{0.71}O_{4.38}$ for the sample. This discrepancy between the cationic ratios in the final product and the starting mixture is ascribed to the volatilization of lithium and boron in the synthesis processing. The formula $Li_{0.63}La_2B_{0.71}O_{4.38}$ can be rewritten as ($Li_{0.63}La_2O_{2.25}(BO_3)_{0.71}$) and this indicates the incorporation of four Lithium cations replace one $(B_2O)^{4+}$ group in the borate instead of the initially presumed substitution of $3Li^+ \leftrightarrow B^{3+}$. Therefore, the composition for the borate can be described as $Li_{2x}La_2O_{1.5+2.5x}(BO_3)_{1-x}$, ($x=0.3$) and the composition for the sample $Li_{3y}La_2O_{1.5+3y}(BO_3)_{1-y}$ ($y=0.28$) now is referred as to $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$.

The comparison of unit cell parameters of $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$, $Li_{0.52}La_2O_{2.52}(CO_3)_{0.74}$, type II $La_2O_2CO_3$, and A-type La_2O_3 are given in Table 1. The lithium incorporation into the type II oxycarbonate increases the cell volume and has anisotropic impacts on the *a*-axis and *c*-axis, i.e. the *a*-axis is shortened but the *c*-axis is lengthened, which increase the c/a ratio from 3.91 in type II $La_2O_2CO_3$ to 4.00 in $Li_{0.52}La_2O_{2.52}(CO_3)_{0.74}$. Compared with $Li_{0.52}La_2O_{2.52}(CO_3)_{0.74}$, the lithium-containing borate $Li_{0.63}La_2O_{2.25}(BO_3)_{0.71}$ exhibits even larger cell volume and bigger c/a ratio (4.11).

Rietveld analysis of $Li_{0.6}La_2O_{2.25}(BO_3)_{0.7}$ structure on XRD data was carried out using the structure model of the $La_2O_{2.52}(CO_3)_{0.74}Li_{0.52}$, which contains 1 La site (4*f*), 4 distinct oxygen sites O_1(4*f*), O_2(12*k*), O_3(6*h*) and O_4(12*k*), 1C site (6*h*) and 1 Li site (2*d*). In $Li_{0.52}La_2O_{2.52}(CO_3)_{0.74}$, each planar of CO_3 group exhibits orientational disorder over three sets of positions, derived from the C, O_2 and O_3 sites with occupancies $\leq 1/3$. The incorporation of Li^+ cations replaces partial C–O_3 units from the CO_3 groups