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Luminescent properties of $LaKNaTaO_5$ and rare-earth-doped $LaKNaTaO_5$ synthesized by an improved hydroxide melt method

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ABSTRACT

Single crystals of $LaKNaTaO_5$ is facilely obtained in corundum crucible at 600 °C by adding a certain amount of water to the hydroxide flux of KOH/NaOH additionally, which is a green method to avoid the heavy metal silver pollution compared with the silver tuber. The addition of water plays a critical role in the reaction process by changing the auto-dissociation of OH^- in hydroxide melts. In addition, we have synthesized samples doped with Eu^{3+} and Tb^{3+} by the same route respectively and have investigated the effects of concentration and temperature on the photoluminescence (PL) properties. The results demonstrate that rare-earth-doped $LaKNaTaO_5$ is an ideal material for white light emitting diodes (WLEDs).

1. Introduction

Nowadays, the need of new luminescent materials increases dramatically. It has been proved that materials with paste or layered structure are both suitable to fabricate optoelectronic devices, such as electroluminescence panels which consist of a stack of functional layers and sheets [1–4]. A variety of materials with layered structure have been explored, such as layered perovskite $KLaNb_2O_7$ [3], hydrated tantalate $A_2SrTa_2O_7 \cdot nH_2O$ (A=H, K, Rb) [5], perovskite-like structure $KCa_2Nb_3O_{10}$ doped with Eu^{3+} and La^{3+} [6], pyrochlore $La_2Zr_2O_7$:Bi [7] and $Y_2Sn_2O_7$:Bi [8]. Among the above compounds, niobates and tantalates, as crucial luminescent materials [1–3,6,9–12], are famous representatives and can be utilized as the photoactive host materials when doped with optically active elements, such as Eu^{3+} and Nd^{3+} [3,6]. Moreover, their instinctive PL properties avoid the disadvantages of the doped luminescent materials like the fluorescence quenching. As a result, more and more attention has been paid to these materials and great progress has been achieved in pursuing novel metal compounds, including $EuKNaTaO_5$ [1], Sr_3NaNbO_6, Sr_3NaTaO_6 [9], $LnKNaNbO_5$ (Ln=La, Pr, Nd, Sm, Eu, Gd and Tb) [12], La_2KNbO_6 [13], Nd_2KNbO_6 [13], and $NaRbLnMO_5$ (Ln=La, Nd, Sm, Eu, Gd; M=Nb, Ta) [14]. These materials show strong PL properties, accompanying with the promising applications in the fields of dielectric [13], photocatalytic [13] and ion-exchange [15,16].

Niobates and tantalates can be synthesized in the hydroxide melts, which is considered to be one of the best solvent systems for metal oxides preparation [17–20]. H.-C. zur Loye's group reported that $EuKNaTaO_5$ single crystal could be obtained in either open or sealed silver reaction vessels while a series of layered tantalates $LnKNaTaO_5$ (Ln=La, Pr, Nd, Sm and Gd) single crystal only had been synthesized in the sealed silver tube [1,21]. Compared with the silver tube, corundum crucible is low-cost and pollution-less to express the idea of green chemistry. However, to the best of our knowledge, single crystals of such luminescent layered materials synthesized in the corundum crucible have not been reported because it is difficult to control the evaporation of water in the relatively open system and the corundum crucible is easily eroded by hydroxide melts at high temperature. Thus, it is worthwhile to explore the synthesis of lanthanum tantalates $LnKNaTaO_5$ in the corundum crucible to meet the idea of green chemistry.

In the present work, for the first time, single crystal of $LaKNaTaO_5$ and samples doped with Eu^{3+} and Tb^{3+} are successfully synthesized via an improved molten hydroxide route in the corundum crucible by adding additional water into the reaction system. The role of added water was discussed and the PL properties were characterized. Our results reveal that the samples are prospective for practical applications of WLEDs.

2. Experimental procedure

The $LaKNaTaO_5$ single crystal was obtained from the molten hydroxides KOH/NaOH. The raw materials La_2O_3, Eu_2O_3, Tb_4O_7,

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KOH, NaOH and the tantalum sheet were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further purification. La_2O_3 (0.5 mmol) and tantalum sheet (1 mmol) were mixed in the corundum crucible and then KOH (4 g), NaOH (1 g) and 0.75 ml deionized water were added into the reaction system. The corundum crucible was put in a furnace, heated (rate=5 °C/min) to 600 °C dwelling for 3 h and then cooled from 600 to 500 °C for 15 h. Finally, it was held at 500 °C for 1 h. After turning off the furnace, the mixture was cooled down to room temperature. The colorless paste single crystal $LaKNaTaO_5$ was obtained by washing the product with deionized water until it become neutral. As for $LaKNaTaO_5$ doped with Eu^{3+} and Tb^{3+}, except that a certain of La^{3+} was substituted by Eu^{3+} and Tb^{3+} (the reactant was Eu_2O_3 and Tb_4O_7), the other procedures were the same as above. In addition, to make contrast, we also synthesized single crystals in the silver tube according to the literature reported [21].

Powder X-ray diffraction (XRD) data was collected on a Rigaku D/Max 2550 diffractometer with a graphite monochromator using CuKα radiation (λ=1.5418 Å) operating at 50 kV and 200 mA at room temperature by step scanning in the angle range of $4^\circ \le 2\theta \le 90^\circ$ with increments of 0.02°. The morphology of the sample and EDS spectra were observed with a field emission scanning electron microscopy (FE-SEM) on a JSM-6700F electron microscope (JEOL, Japan) operating at an accelerating voltage of 5 kV equipped with EDS detector. X-ray photoelectron spectroscopy was performed in Thermo ESCALAB 250 spectrometer. The absolute quantum efficiency measurements were recorded with an integration sphere coupled with a photonic multichannel analyzer C10027 (HAMAMATSU). The emission and excitation spectra of the samples were recorded on an Edinburgh Instruments FLS 920 spectro-fluorimeter equipped with continuous (450 W) xenon lamp, which was equipped with a CTI-Cryogenics temperature controlling system. Lifetime measurements were performed with the same spectrophotometer and detectors using a 100 W pulsed xenon lamp μF920H (200–900 nm, 10–100 Hz), Edinburgh.

3. Results and discussion

The $LaKNaTaO_5$ single crystal has been successfully obtained in the experiments. In the process of synthesis, without the addition of water, we could only get some powder instead of single crystals in the corundum crucible. The single crystal is obtained only in the condition with water added. From this point of view, this improved method has an advantage over the traditional one. The difference between reacting in the sealed silver tube and the open corundum crucible lies in the water quantity in the reaction process. That is to say, the former one is a closed system while the latter one is open which could not avoid the evaporation of water. As the system is not sealed in the experiment, some water can evaporate unavoidably during the process of reaction. In hydroxide melts, the following auto-dissociation process takes place and the solubility of the metal oxide will change in acidic or basic conditions [19].

$$2OH^- \rightleftharpoons H_2O(\text{acid}) + O^{2-}(\text{base})$$

According to the Lux-Flood concept of oxo-acidity, an excess of water will increase the acidity and the solubility of the metal oxide [18]. Thus, to compensate the evaporation of water and increase the solubility of the metal oxide, we added 0.75 ml deionized water in the reaction system additionally, which is the first step for incorporating metal cations into a crystal [19] and make the synthesis of the single crystal feasible in the corundum crucible. Thus, the additional water is crucial to the growth of single crystal.

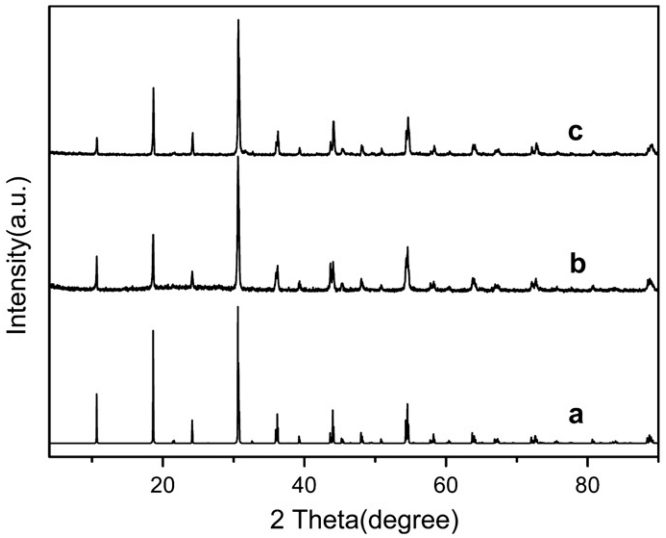

Fig. 1. XRD patterns of (a) $LaKNaTaO_5$ single crystal, (b) $La_{0.95}Eu_{0.05}KNaTaO_5$ single crystal, (c) $La_{0.95}Tb_{0.05}KNaTaO_5$ single crystal.

The XRD patterns of pure and doped single crystal of $LaKNaTaO_5$ are shown in Fig. 1. They are well indexed in a tetragonal unit cell of space group *P4/nmm* and agree with the data simulated from the single crystal structure (data not shown), indicating that the three samples crystallize well. The structure of $LaKNaTaO_5$ consists of LaO_8 distorted cubes, further edge-shared to the basal edges of TaO_5 and NaO_5 square pyramids. And K^+ is located at the space between the layers [1,21].

The XPS spectroscopy of the sample over a wide range of binding energies and detailed spectrum of Al 2p are shown in Fig. 2(a) and (b). As the corundum crucible is eroded by the molten alkali hydroxides in a relatively small fraction at high temperature, inevitably, alumina impurity is observed in the bulk sample, which is shown in the XPS spectrum of the Al 2p in Fig. 2(b). There are mainly Ta, Na, K, La, C, O elements and a trace of aluminum in the patterns. However, it does not affect the quality of $LaKNaTaO_5$ single crystal, since the signal of aluminum is not observed from the EDS results of the $LaKNaTaO_5$ single crystal. The EDS results of the single crystals clearly confirm the elemental composition of $LaKNaTaO_5$ in the formula of $La_{0.90}K_{0.90}Na_{0.96}TaO_{4.78}$, which is almost in accordance with the formula $LaKNaTaO_5$, without any impurity in the single crystal. In other words, the trace of Al impurity distributes among the single crystals. This fact can also be confirmed from the SEM image shown in Fig. 3. Although some unfairness might be discerned in the surface, overall, the samples have tetragonal sheets and are crystallized well.

The PL excitation and emission spectra of pure and doped $LaKNaTaO_5$ single crystal at room temperature are shown in Fig. 4. Fig. 4(a) demonstrates the excitation spectrum of the pure sample. There are two broad bands at around 294 and 362 nm (monitored at 472 nm). When the excited wavelength is 362 nm, the most intense emission band of the compound has at 472 nm. It has been reported that compounds such as $KTaO_3$ [22], $Sr_2Ta_2O_7$ [23] and anhydrous $K_2La_{2/3}Ta_2O_7$ [24] displayed an intense luminescence peak at around 440 nm when the excited wavelength is around 290 nm. This is attributed to the charge-transfer transitions within the octahedral tantalate groups. Likewise, the emission band at around 472 nm here can be resulted from the charge-transfer transitions within the TaO_5 pyramids.