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$La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheet phosphor and its multilayer films with enhanced host excitation-mediated photoluminescence

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ABSTRACT

$La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheets were achieved by exfoliating a layered compound $HLa_{0.90}Dy_{0.05}Nb_2O_7$. Multilayer films composed of the exfoliated nanosheets were prepared by a layer-by-layer deposition technology, which were subsequently heat-treated at 450 °C and exposed under ultraviolet light to obtain the polymer-free nanosheet films, respectively. The resulting $La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheet suspension and its films exhibit intense emission by the host excitation and negligibly low emission by the direct Dy^{3+} excitation, whereas the photoluminescence emissions of the bulk precursors are largely dominated by the direct Dy^{3+} excitation rather than the host excitation. The comparison between the excitation spectra and the bandgap absorption spectra indicates that the enhanced host excitation-mediated photoluminescence of $La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheet results from the efficient energy transfer from the O–Dy charge-transfer transition to Dy^{3+} within the nanosheet, and that the intensive emission of the multilayer films is attributed to the energy transfer from both of the O–Dy charge-transfer transition and the O–Nb network to Dy^{3+}. Dy^{3+} in the $La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheet and the nanosheet-based films gives two emission peaks at around 480 and 576 nm and the blue emission is prominent in the film form.

1. Introduction

In the past decades, two-dimensional nanosheets, prepared by delaminating layered oxides in a soft-chemical route, have been extensively explored [1–9]. An intriguing aspect of the exfoliated oxide nanosheets is their high crystallinity inherited from layered precursors, and an individual nanosheet can be considered as a two-dimensional single crystal with a thickness of subnano- to nanometer range and a lateral size of micrometers range. These oxide nanosheets were found to exhibit distinctive structure diversity, interesting photophysical and photochemical properties. Several studies demonstrated that the photoluminescence (PL) emissions from Ln (rare earth)-photoactivated oxide nanosheets in fluid suspensions are dominated by nanosheet host excitation rather than direct Ln photoactivator excitation, whereas the emissions from all their bulk precursors are dominated by direct Ln excitation [5,10–15]. For an Ln-containing phosphor with well-predictable mission wavelengths from the intra-4f transitions, its direct Ln excitation wavelength is often nontunable (corresponding to the characteristic f–f transitions of the Ln photoactivator), but its host excitation wavelengths can be tuned on the bias of the host absorption properties. Ozawa et al. reported the PL emissions of Eu^{3+}- and Sm^{3+}-doped $LaNb_2O_7$ nanosheets in fluid suspensions are predominated by the energy transfer from the oxide nanosheet hosts to the Ln photoactivators [12,13]. $LaNb_2O_7$ perovskite nanosheet can be considered as an ideal candidate host nanosheet for Ln-photoactivated phosphors. The absorption onset wavelengths of the Eu^{3+}- and Sm^{3+}-doped $LaNb_2O_7$ nanosheets and the Eu^{3+}-doped $KLaNb_2O_7$ bulk sample are around 370 nm [12,13,16], whereas the GaN-based solid state lighting requires phosphors that can be effectively excited in the 250–400 nm range [17]. Therefore, it is worthwhile to investigate the PL properties of Ln-doped $LaNb_2O_7$ nanosheets, shedding light on the new generation solid state lighting based on GaN.

Due to their negative charged nature, the exfoliated oxide nanosheets can be flocculated with positively changed species by the electrostatic self-assembly deposition (ESD) to form nanocomposites [1]. In particular, it is attractive to use them to fabricate multilayer composite films on a glass substrate through the layer-by-layer (LBL) assembly technology, based on the alternate adsorption with suitable polymeric cations [18–24]. After followed by ultraviolet light exposure or heat treatment, the organic cations will be decomposed completely, which leads to the formation of transparent polymer-free nanosheet multilayer films deposited on the substrate [22–24]. To the best of our knowledge, only the red Eu^{3+} and Sm^{3+} emissions of doped $LaNb_2O_7$ nanosheets in fluid suspensions have been reported [12,13], the assembly films of Ln-doped $LaNb_2O_7$ nanosheets have been unexplored so far. It is very

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interesting to evaluate the PL emissions of nanosheets in such solid state form for solid state lighting.

Among the Ln photoactivators, Dy^{3+} is particularly interesting due to its visible luminescence in the blue (470–500 nm, $^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow (570–600 nm, $^4F_{9/2} \rightarrow {}^6H_{13/2}$) wavelength regions. The latter one belongs to the hypersensitive transition, which is strongly influenced by the environment [25–27]. In the present paper, we report the preparation and PL properties of Dy^{3+}-photoactivated $La_{0.90}Dy_{0.05}Nb_2O_7$ perovskite nanosheet and its multilayer films. Their characterization results are compared with those of the bulk precursors $KLa_{0.90}Dy_{0.05}Nb_2O_7$ and $HLa_{0.90}Dy_{0.05}Nb_2O_7$.

2. Experimental

2.1. Reagents and materials

All reagents were of analytical grade and used without further purification. Milli-Q ultrapure water with a resistivity of 18.2 MΩ cm was used throughout the experiments. The host layered compound Dy^{3+}-doped $KLaNb_2O_7$, $KLa_{0.90}Dy_{0.05}Nb_2O_7$, was prepared by a conventional solid-state reaction of a mixture of K_2CO_3:La_2O_3:Nb_2O_5:Dy_2O_3 in the molar ratio of 1.15:0.90:2.00:0.05 at 1150 °C for 24 h in a corundum crucible, similar to the procedures of $KLa_{0.90}Eu_{0.05}Nb_2O_7$ and $KLa_{0.90}Sm_{0.05}Nb_2O_7$ analogs [12,13]. The 15% excess of K_2CO_3 was used in order to compensate for its loss by evaporation during the heating reaction. It was found that the single-phase stoichiometric bulk precursor $KLaNb_2O_7$/Dy^{3+} could not be synthesized. As reported in Refs. [12,28], the starting component amount Ln_2O_3 (Ln = La or Dy) had to be reduced from the stoichiometric one for $KLnNb_2O_7$ in order to avoid the coproduction of impurity phases like $LnNbO_4$. In case of 5% Dy^{3+} doping, 5% reduction of Ln was necessary to obtain the single-phase precursor $KLa_{0.90}Dy_{0.05}Nb_2O_7$.

The bulk layered compound was converted into its acid phase (designated as $HLa_{0.90}Dy_{0.05}Nb_2O_7$) by stirring vigorously a $KLa_{0.90}Dy_{0.05}Nb_2O_7$ suspension in 3 M HNO_3 solution at RT for 6 days. During the proton exchange reaction, the acid solution was replaced with a fresh one every 2 days. The resultant solid product was centrifuged, washed with deionized water and air-dried at room temperature for 24 h. The protonated powder was exfoliated into lanthanoniobate nanosheets in a tetrabutylammonium hydroxide (TBAOH) solution with a butylamine/H^+-niobate molar ratio of 2:1. In a typical reaction, 0.5 g $HLa_{0.90}Dy_{0.05}Nb_2O_7$ was added to 250 mL 15% TBAOH aqueous solution and ultrasonicated at RT for 2 h. Subsequent centrifugation at 4500 rpm for 30 min yielded an opalescent colloidal suspension of $La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheet with a concentration of about 10^{-3} M. Then the pH value of colloidal suspension was adjusted to 9.0 by 0.5 M HNO_3 carefully.

2.2. Preparation of flocculation and film

The flocculated nanohybrid PEI/$La_{0.90}Dy_{0.05}Nb_2O_7$ was performed by adding 20 mL polyethylenimine (PEI) solution (2.5 g L^{-1}, pH 9.0) into 200 mL as-prepared $La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheet suspension under vigorous stirring. Driven by electrostatic interaction between the negatively charged nanosheets and positively charged PEI, the mixing immediately resulted in a flocculated sludge. The sludge was separated by centrifugation at 3500 rpm, washed several times with ethanol–water mixed solvent (1:1 in volume) to remove excess PEI and other soluble products. The resulting product was dried under vacuum at 80 °C for 12 h. For comparison, a flocculated sample without PEI loading was prepared by acidizing the suspension and designated as e-$HLa_{0.90}Dy_{0.05}Nb_2O_7$.

Deposition of $La_{0.90}Dy_{0.05}Nb_2O_7$ nanosheets and PEI on Quartz glass was achieved by alternately exposing the substrate in the positively charged PEI and the negative nanosheets colloid through a LBL technique. Quartz glass substrates were cleaned by ultrosonication in acetone, followed by treatment in a bath of methanol/HCl (1:1 in volume) and then concentrated H_2SO_4 for 30 min each. The surface-cleaned substrate was first immersed in a PEI solution (25 g L^{-1}, pH 9.0) for 20 min. After being washed thoroughly with pure water and drying under a N_2 stream, the PEI-coated substrate was dipped into the nanosheet colloidal suspension (2×10^{-5} M, pH 9.0) for 20 min, followed by washing with copious water and drying under a N_2 stream. The above procedure was repeated n times to obtain a multilayer film of $(PEI/La_{0.90}Dy_{0.05}Nb_2O_7)_n$.

To obtain polymer-free phosphors, the as-prepared multilayer films were heated in air at 450 °C for 2 h with an increment of 2 °C min^{-1} and exposed under a 300 W low-pressure Hg lamp (λ_{max} = 254 nm) irradiation for 12 h, respectively. The resulting polymer-free phosphors were allowed to evaluate their PL properties.

2.3. Sample characterization

Powder X-ray diffraction (XRD) patterns were recorded at RT on a Bruker D8 Advance diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5406 Å) under the accelerating voltage of 36 kV at a scanning rate of 4° at 2θ min^{-1} from 2° to 50°. Elemental compositions of the as-prepared bulk compound were analyzed with a Leeman Prodigy ICP-OES analyzer. The surface topography of the films was examined using a Veeco Nanoscope 3D atomic force microscope (AFM) in the tapping mode with a silicon-tip cantilever (15 N m^{-1}). Simultaneous TG–DTA measurements were performed from RT to 900 °C at a rate of 10 °C min^{-1} on a Shimadzu DTG-60H thermalanalyzer in N_2 flow. UV–vis absorption spectra of the diluted nanosheet suspensions were measured on a Shimadzu UV-2450 spectrometer. Diffuse reflectance spectra were recorded on a Shimadzu UV-2550 spectrometer equipped with an integrating sphere 60 mm in diameter using $BaSO_4$ as a reference, and the reflectance spectra were converted to the absorption spectra by the Kubelka–Munk method. Both photoluminescence excitation and emission spectra were obtained on an Edinburgh FLS920 fluorescence spectrometer at RT. The excitation source is a 450 W Xenon lamp and the spectral resolution of the spectrofluorometer was 0.05 nm.

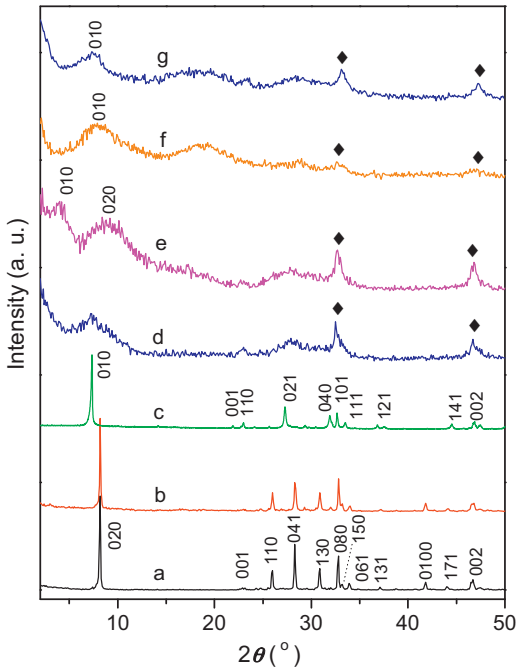

Fig. 1. Power XRD patterns of layered compounds $KLaNb_2O_7$ (a) and $KLa_{0.90}Dy_{0.05}Nb_2O_7$ (b), protonated $HLa_{0.90}Dy_{0.05}Nb_2O_7 \cdot nH_2O$ (c), restacked e-$HLa_{0.90}Dy_{0.05}Nb_2O_7$ (d), as-prepared PEI/$La_{0.90}Dy_{0.05}Nb_2O_7$ flocculation before (e), and after heat-treated at 450 °C (f) and after UV light exposure (g). Closed squares represent the in-sheet characteristic peaks of $La_{0.90}Dy_{0.05}Nb_2O_7$ sheets.

3. Results and discussion

3.1. Characterization of flocculation

Comparison of the XRD profiles between the layered lanthanoniobate $KLaNb_2O_7$ and its Dy^{3+}-doped phase $KLa_{0.90}Dy_{0.05}Nb_2O_7$ is documented in Fig. 1a and b. Their patterns are very similar and can be indexed to the orthorhombic cell with C222 space group and a = 3.9060, b = 21.6031, c = 3.8879 Å [28], which reflects that their structures consist of stacked single perovskite-type layers interspersed with K^+. The strong and sharp (0 2 0) diffraction of $KLa_{0.90}Dy_{0.05}Nb_2O_7$ at 8.16° with d-spacing of 1.08 nm indicates that the well-ordered layered structure was formed. The protonated bulk compound exhibits an intense reflection at around 7.28° (Fig. 1c). The corresponding d-spacing of 1.21 nm is close to the lattice parameter along the intersheet direction of the hydrated analogous protonated phase $HLaNb_2O_7 \cdot nH_2O$ [29]. In the undoped analogous phase $KLaNb_2O_7$, stacking of each sheet is shifted by 1/2 unit cell (perovskite unit) toward one of the intralayer directions, whereas no such shift of stacking layers was observed and the apical oxygen ions of the adjacent sheets are eclipsed in the case of its protonated form [28]. The unit cell of the as-prepared bulk compound contains two perovskite-type sheets along the intersheet direction (the b axis), whereas that of the protonated compound