

Electronic Supplementary Information

Synthesis and photoluminescence of Eu³⁺-activated double perovskite NaGdMg(W, Mo)O₆— a potential red phosphor for solid state lighting

Le Zhang, and Qitu Zhang*

College of Materials Science and Engineering, Nanjing University of Technology, 5 Xinmofan Road, Nanjing, Jiangsu, P.R. China. Tel: +86-25-83587246; E-mail: njutzl@163.com.

Experimental

An improved citrate- EDTA complexing method was first used to synthesize double perovskite samples. The starting materials were Eu₂O₃ (99.99%), Gd₂O₃ (99.99%), Mg(NO₃)₂·6H₂O (AR), NaNO₃ (AR), (NH₄)₆Mo₇O₂₄·4H₂O (AR) and H₄₀N₁₀O₄₁W₁₂ (AR). EDTA(C₁₀H₁₆N₂O₈, AR) and citric acid (C₆H₈O₇, AR) are complexing agents and their mole ratios to the total metallic ions were 2.0 and 1.0, respectively.

Stoichiometric amounts of Eu₂O₃ and Gd₂O₃ were dissolved in HNO₃ under vigorous stirring. Then all nitrate were added in the deionized water and stirred homogenously (solution A, S_A). The ammonium molybdate was also dissolved in deionized water under the help of NH₃·H₂O (S_B). Then the citric acid was added in the mixed solution of S_A and S_B. After completely dissolved, the pH value of the solution was modulated to 6.0~7.0. At last, the solution of ammonium tungstate was added in the mixed solution. *A disordered addition should be avoided, or the unknown*

precipitation will easily appear. The heated temperature all above process was 30~50 °C. Then the mixed solution was heated to 60~70 °C and continuously stirred using a magnetic agitator for about an hour to obtain transparent solution. Moreover, it became transparent sol until removing the excess water. After then, the gel was put into an oven at 180~200 °C for 4 hours to suffer a combustion reaction. Finally, the precursor was pre-calcined at 600 °C for 4 hours to remove the organic elements and then calcined at 1100 °C for 6 hours. Series of $\text{NaGdMg}(\text{W}_{1-x}\text{Mo}_x)\text{O}_6$: Eu powders ($x=0.0, 0.1, 0.3, 0.5, 0.7, 0.9$) were prepared.

In addition, the commercial $\text{Y}_2\text{O}_2\text{S}$: $\text{Eu}_{0.05}$ and CaMoO_4 : $\text{Eu}_{0.3}$ phosphors were provided by (Changshu YaTai fluorescence material co., LTD, Jiang Su, China) to compare the photoluminescence properties with the as-synthesized red phosphor.

Characterization of samples

The crystalline phases of synthesized powders were determined by X-ray diffraction (XRD, D/Max2500, Rigaku, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) in the range of $5^\circ \sim 80^\circ$ with a step size of 0.02° . Crystal structure was refined using Rietveld method as implanted in GSAS software suite.^{1, 2}. Element contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Reflection spectra were recorded on a Shimadzu UV-3100 UV-Vis-NIR spectrophotometer with BaSO_4 as the reference. The photoluminescence spectra of the phosphors were measured using a fluorescent spectrophotometer (FL3-221, HOROBA, Jobin Yvon, France). The fluorescent quantum yields were measured using an integrating sphere (F-3018). Excitation light source: 450W xenon lamp; surface

coating of the integrating sphere: barium sulfate; data acquiring technology: single photo counting mode; excitation wavelength: 395 nm, 465 nm. All measurements were carried out at room temperature.

Reference:

- [1] A.C. Larson and R.B. Von Dreele, *Los Alamos National Laboratory Report LAUR*, 86-748 (1994).
- [2] B. H. Toby, *J. Appl. Cryst.*, 2001, **34**, 210-213.

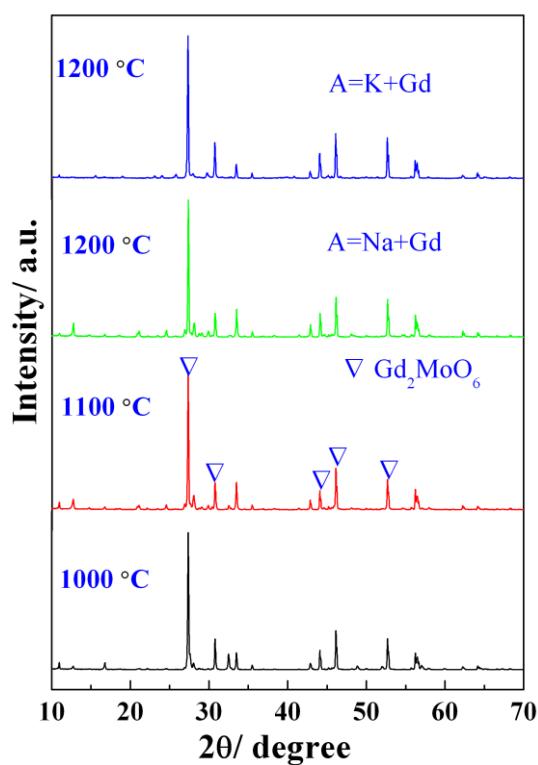


Fig. S1 XRD patterns of RGdMgWO₆:Eu(R=Na/K) under enhanced calcination temperatures

At present, AA'MgMoO₆ does not exist in the world. We have made many attempt to obtain this material including increasing the calcination temperatures and changing the combination of A+A' cations but still failed. Their XRD patterns are shown in Fig. S1 and are only indexed by Gd₂MoO₆ phase.