Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Warm white light generation from a single phase Dy^{3+} doped $Mg_2Al_4Si_5O_{18}$ phosphor for white UV-LEDs

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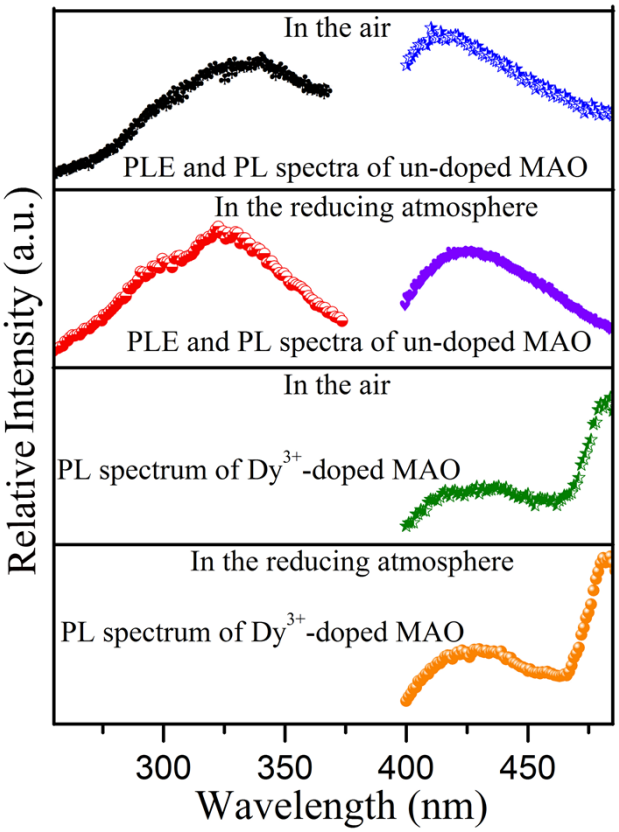

Figure S1 The PLE and PL spectra of un-doped MAO samples and PL spectra of Dy^{3+} doped MAO samples in the air and reducing atmosphere.

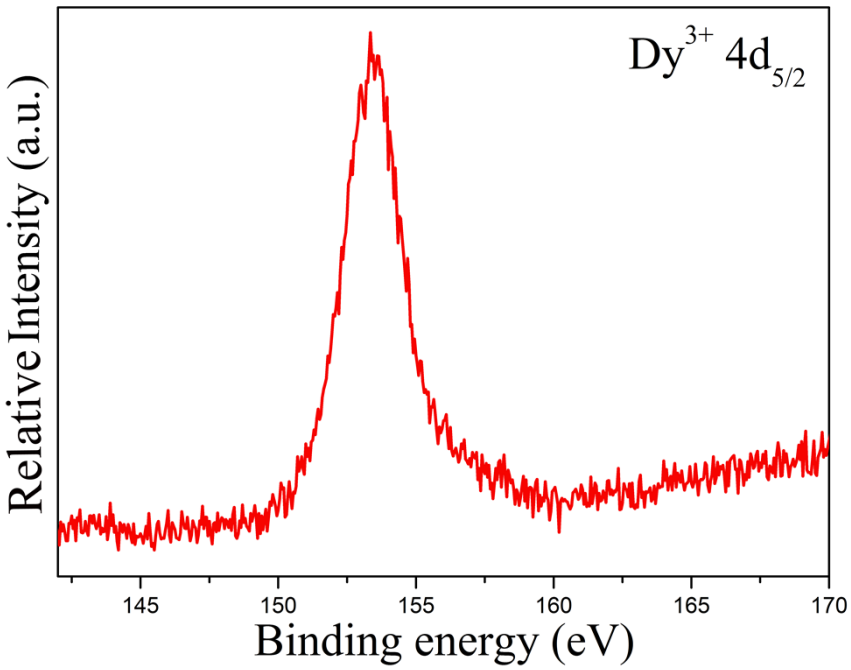

Figure S2 The Dy 4d XPS spectrum of the MAO: $0.18Dy^{3+}$ sample synthesized in the reducing atmosphere.

In Figure S1, the broad band centered at 425 nm is dominantly caused by the oxygen vacancies of the MAO host. The assumptions mainly base on the reasons as follows:

1) In figure S1, the un-doped MAO sample synthesized in the air shows a broad band emission centered at about 425 nm under the excitation of 325 nm. The Dy^{3+}-doped MAO samples present the strong characteristic emission of Dy^{3+} and a weak broad band centered at about 425 nm. The shape of broad band is very similar with that of un-doped MAO sample. The phenomenon implies that the broad band may originate from the MAO host.

2) As we known, the materials could easily produce the oxygen vacancies during the sintering process at a high temperature and the sintering atmospheres could seriously influence the concentration of oxygen vacancies of the products. Generally, the reducing atmosphere is conducive to the formation of oxygen vacancies. Therefore, we synthesized a serious of MAO: $x$$Dy^{3+}$ ($0 \leq x \leq 0.18$) samples in the reducing atmosphere. In Figure S1, under the excitation of 325 nm, the un-doped MAO sample synthesized in the reducing atmosphere also shows the broad emission band (~425 nm) with the similar shape compared with that of un-doped MAO sample synthesized in the air, but the intensity of broad band emission is sharply enhanced. Meanwhile, the samples synthesized in the air and reducing atmospheres is both single phase. Thereby, the broad band is likely caused by the oxygen vacancies of the MAO host. Further, the blue broad emission band of the MAO: Dy^{3+} samples synthesized in the reducing atmosphere also shows the similar shape with that of the un-doped MAO, which further prove the above assumptions.

3) Generally, Dy^{3+} is difficult to be reduced to Dy^{2+} in the process of synthesis and many researchers have reported that the Dy ion can be stabilized in the state of trivalence in many materials synthesized in the reducing atmosphere, such as $Sr_{(4-x-y)}Ca_xBa_yAl_{14}O_{25}$: Eu^{2+}, Dy^{3+}, $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, $Sr_3MgSi_2O_8$: Eu^{2+}, Dy^{3+}.[S1-S7]

4) The X-ray photoelectron spectroscopy (XPS) of MAO: $0.18Dy^{3+}$ synthesized in the reducing atmosphere are measured and shown in Figure S2. A symmetrical peak at 153.80 eV with the full width at half maximum 2.42 eV is observed and well matches

with the Dy^{3+} $4d_{5/2}$ peak reported by ref.S8 (The XPS data of Dy^{2+} are presently not available). The result further supports that the Dy ion in the MAO: $0.18Dy^{3+}$ synthesized in the reducing atmosphere exists only in the state of trivalence.

Based on the above analysis, we demonstrate that the broad band centered at 425 nm is caused by the oxygen vacancies of the MAO host.

Reference

S1. U. Caldiño, E. Álvarez, A. Speghini, M. Bettinelli, *J. Lumin.*, 2012, **132**, 2077.

S2. R. Martínez-Martínez, S. Rivera, E. Yescas-Mendoza, E. Álvarez, C. Falcony, U. Caldiño, *Opt. Mater.*, 2011, **33**, 1320.

S3. H.W. Kui, D. Lo, Y.C. Tsang, N.M. Khaidukov, V.N. Makhov, *J. Lumin.*, 2006, **117**, 29.

S4. H. N. Luitel, T. Watari, R. Chand, T. Torikai, M. Yada, H. Mizukami, *Mater. Sci. Eng., B*, 2013, **178**, 834.

S5. W. Pan, G. L. Ning, *Sensor Actuat A: Phys*, 2007, **139**, 318-322.

S6. L. L. Jiang, S. G. Xiao, X. L. Yang, X. A. Zhang, X. H. Liu, B. Y. Zhou, X. L. Jin, *Mater. Sci. Eng., B*, 2013, **178**, 123.

S7. P. Huang, Q. G. Zhang, C. Cui. J. Li, *Opt. Mater.*, 2011, **33**, 1252.

S8. Z. Kang, L. Li, Q. Wei, *Chem. Res. Chin. Univ.*, 1996, **12**, 281.