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Supporting Information

Detection of oxide-ion and oxygen vacancy swapping via upconversion luminescence in $La_2Mo_2O_9:Yb^{3+},Er^{3+}$

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Upon a 976 nm laser diode excitation, the LMOEY sample exhibits strong UC luminescence at room temperature that can be easily seen by the naked eyes. Figure S1 shows the power-dependent UC emission spectra of LMOEY. The intensities of the three peaks increase with the increment of pumping powers. The power-dependent integrated UC emission intensities on a log-log scale, shown in the inset of Figure S1, reveals that the three UC emission processes of Yb^{3+}-Er^{3+} in this system are two-photon processes upon the excitation of a 976 nm laser beam.

In order to exclude the effects of temperature-dependent $Yb^{3+}\rightarrow Er^{3+}$ energy transfer on the UC emissions of Er^{3+}, temperature-dependent Stokes luminescence of Er^{3+}-singly doped LMO under the excitation of 379 nm xenon lamp light is measured and the result is presented in Figure S2. It can be seen that the variation of the lognormal integrated intensity ratios versus 1/T, presented in Figure S2d, is similar to that of Figure 3b. It convinces that the variations of the UC emission peaks in Figure 3 are originated from the intrinsic structural change at Er^{3+} site rather than the temperature-dependent $Yb^{3+}\rightarrow Er^{3+}$ energy transfer efficiency.

The UC mechanism of the LMOEY is described in Figure S3. Under the excitation of a 976 nm laser, Yb^{3+} ions absorb photons and are excited to the $^2F_{5/2}$ levels (black dashed arrow). They could transfer photon energy to Er^{3+} ions and populate the $^4I_{11/2}$ level (G_1, R_1). There are generally two seperated pathways after this step. One is that the electrons partly decay to the $^4I_{13/2}$ level (R_2). Then through excited state absorption (ESA, R_3), the $^4F_{9/2}$ level is populated with the following red emission (R_4). The other is that when the populated $^4I_{11/2}$ level of Er^{3+} is excited by the

sequential energy transfer from another Yb^{3+} ion, it would result in the population of $^4F_{7/2}$ level (G_2). Then, the radiative transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (525 nm) and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (550 nm) would take place (G_4) after relaxation.

Figure S4 presents the plot of the bulk conductivity as function of $1/T$ for dense ceramic of LMOEY in the temperature range of 200–700 °C. It shows that the conductivity increases with the temperature. The abrupt increase at ~500°C is owed to the phase transformation of monoclinic α-$La_2Mo_2O_9$ to cubic β-$La_2Mo_2O_9$.

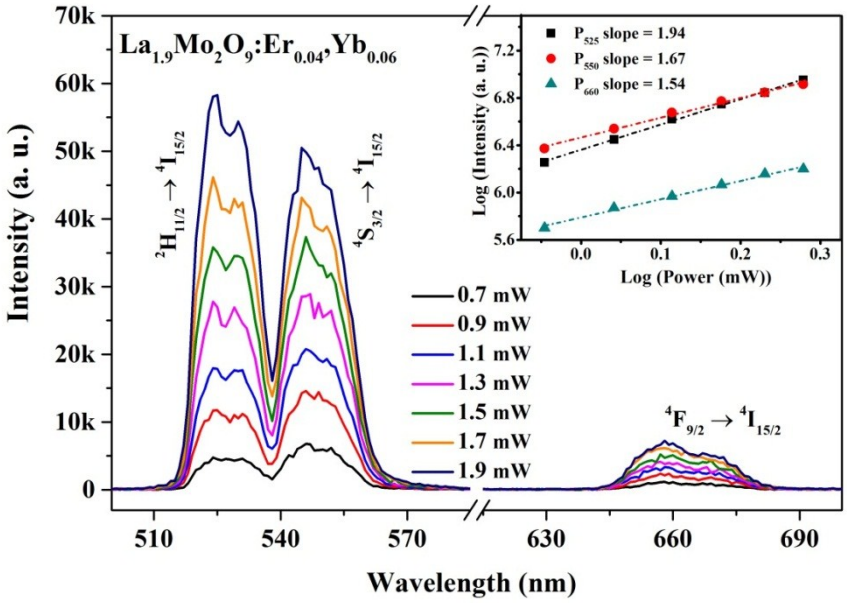

Figure S1. UC luminescence spectra of $La_{1.9}Mo_2O_9:Er_{0.04},Yb_{0.06}$(LMOEY) under excitation of a 976 nm laser beam with different pumping power. Inset is the intensity dependence of different UC emission peaks (integrated intensity) on different pump power (in Log-Log plot).

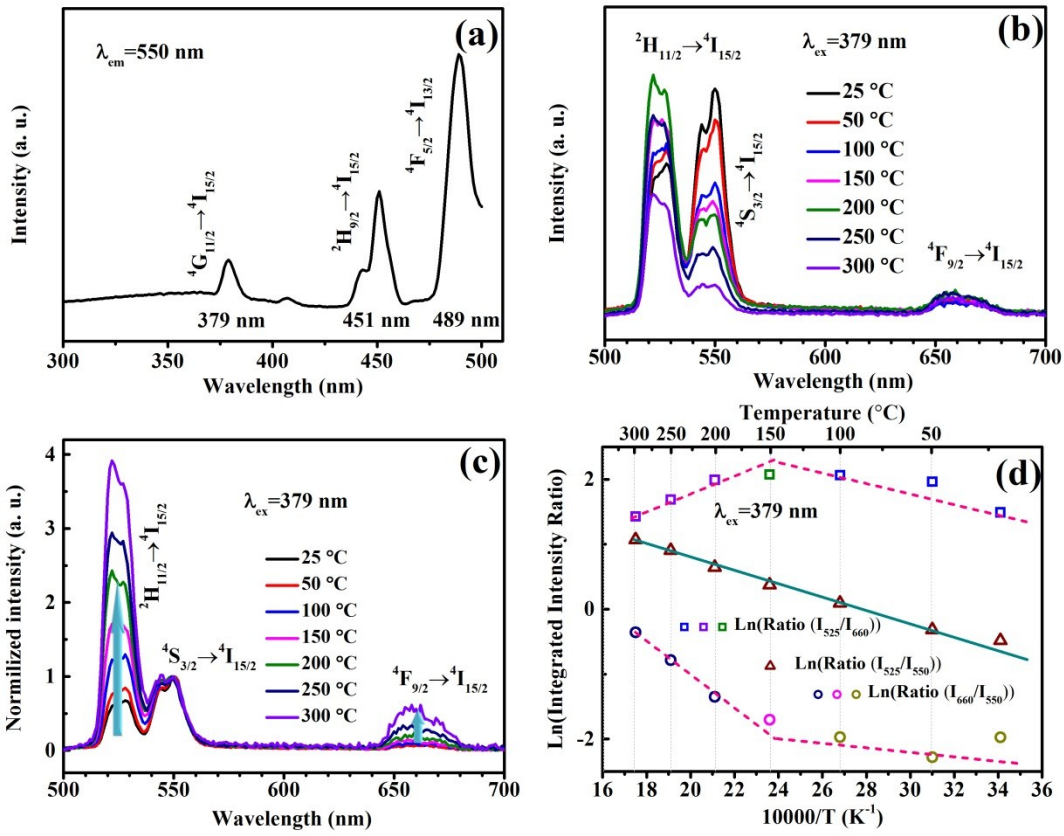

Figure S2. (a) Excitation spectrum of $La_{1.96}Mo_2O_9:Er_{0.04}$ (λ_{em}=550 nm). (b) Temperature-dependent Stokes emission spectra of $La_{1.96}Mo_2O_9:Er_{0.04}$ under excitation of 379 nm xenon lamp light from room temperature to 300 °C. (c) All the spectra are normalized at ~550 nm. (d) Lognormal plot of the intensity ratio of I_{525}/I_{550} (Ln(Ratio (I_{525}/I_{550}))), I_{660}/I_{550} (Ln(Ratio (I_{660}/I_{550}))) and I_{525}/I_{660} (Ln(Ratio (I_{525}/I_{660}))) as a function of inverse absolute temperature. Solid dark cyan line is the fitted line of the lognormal ratio (I_{525}/I_{550}) while the pink dashed lines are to guide the eye.

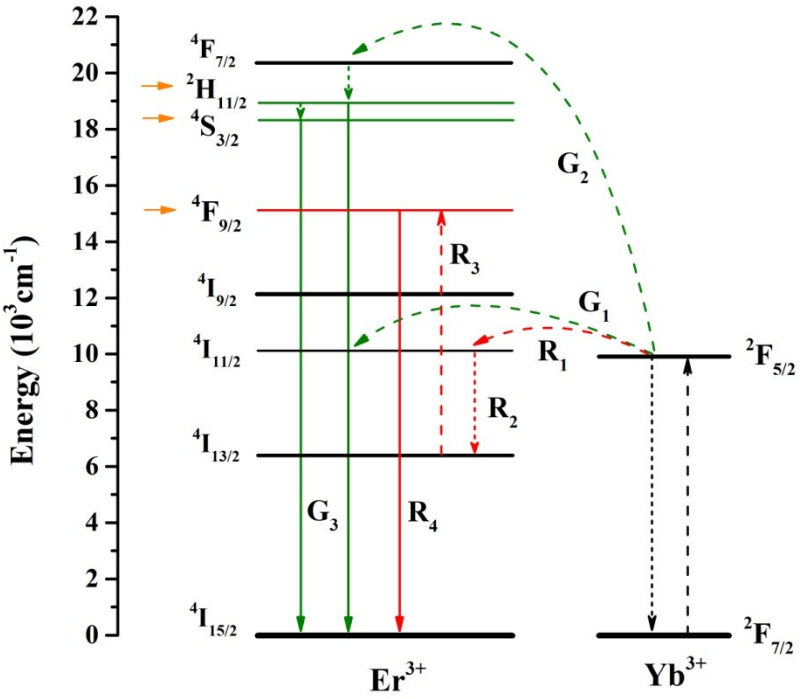

Figure S3. Sketch of UC emission model of Yb^{3+}-Er^{3+} in LMOEY. R_1~R_4 denote the process of red emission, and G_1~G_3 denote the process of the green emissions.

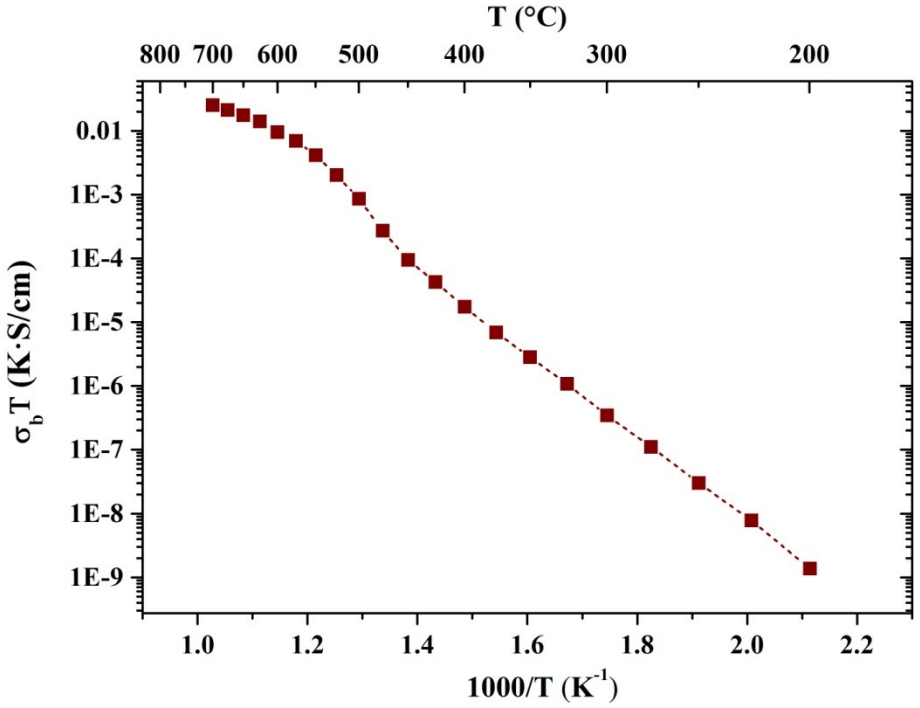

Figure S4. Temperature dependency of the bulk conductivity (σ_b) measured in air on dense ceramic of the LMOEY.