Supporting Information for:

"Charge compensations of Eu^{2+} and O_i^{2-} co-exist in Eu^{3+}: $CaMoO_4$ single-crystal fibers grown by micro-pulling-down method"

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Experimental Details:

Crystal quality

Figure S1 shows 1 at.% Eu^{3+} (a) and 1at.% Eu^{3+}– 1at.% Li^+ (b) doped $CaMoO_4$ SCFs with internal cracks. The 1% Eu^{3+}– 1% Li^+ SCF had less cracks than the 1% Eu^{3+} SCF. Figure S2 shows the good quality of 0.01 at.% Eu^{3+}:$CaMoO_4$ SCF tested by the X-ray Laue diffractometer.

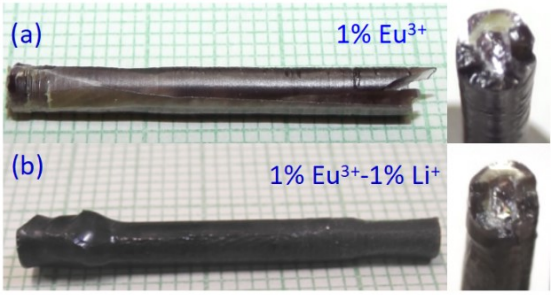

Figure S1: Two SCFs of $CaMoO_4$: 1% Eu^{3+} (a) and 1% Eu^{3+}-1% Li^+ (b) grown with a Pt wire in air atmosphere.

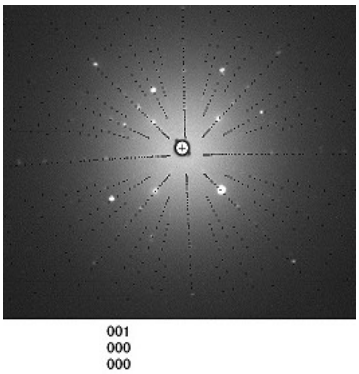

Figure S2: The good quality of 0.01 at.% Eu^{3+}:$CaMoO_4$ SCF tested by the X-ray Laue diffractometer.

Characterizations.

X-ray powder diffraction patterns were checked with a Bruker-AXS D8 ADVANCE X-ray diffractometer using Cu-Kα (λ = 1.5418 Å) radiation.

Absorption. Polarized absorption spectra in the range of 200-800 nm were performed using a Varian Cary 5000 spectrophotometer. The resolution was 1.5 nm. Low temperature (10 K、77 K) measurements were done with a closed cycle He cryostat.

Fluorescence. The fluorescence spectra were measured by exciting samples with a 395 nm LED or 532 nm solid state laser, focused by a 10 cm lens. The emission was chopped and focused on a monochromator equipped with a grating with 1200 g/mm, and synchronously detected by a Hamamatsu R943-02 photomultiplier. All spectra were corrected with the response of our detection system to a black-body lamp at 3000 K.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out on ESCALAB 250 XPS instrument (produced by ThermoFisher Scientific Ltd.) using Al Kα X-ray sources. The energies were calibrated with the peak of C 1s at 284.6 eV. The tests were centered on the polished surfaces.

Annealing. Two samples were cut from 0.01% Eu^{3+}: $CaMoO_4$ single crystal fiber. Before and after annealing, samples were polished and signed their thickness at two cut surfaces. Absorption measurements were centered on surfaces. Sample A was annealed at 1226°C for 24 h in air atmosphere. Sample B was annealed at 1000°C for 5 h in H_2 atmosphere (H_2:N_2=5:95). The absorption spectra were carried out by U-4100 spectrophotometer in the range of 350-800 nm. The resolution was 1.5 nm.

Calculated band gap

Figure S3 shows the band structure of pure $CaMoO_4$ and the (Eu^{2+}-O_i^{2-}):$CaMoO_4$. The Fermi level is located in the zero energy. The band gap of pure $CaMoO_4$ and the (Eu^{2+}-O_i^{2-}):$CaMoO_4$ are 3.1 eV and 1.5 eV, respectively.

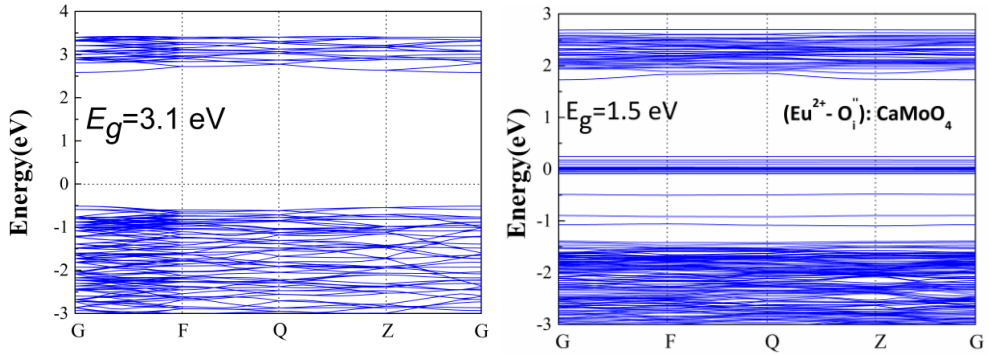

Figure S3: The Band structure of pure $CaMoO_4$ and the (Eu^{2+}-O_i^{2-}):$CaMoO_4$.

Raman spectrum

We have measured the Raman spectrum of the Eu^{3+}: $CaMoO_4$ SCF sample as shown in Figure S4. The wavelength range has been extended to 2000 cm^{-1}[1]. The maximum Raman shift of it is 879.3 cm^{-1}. The result is consistent with what others have reported about pure $CaMoO_4$. [2]

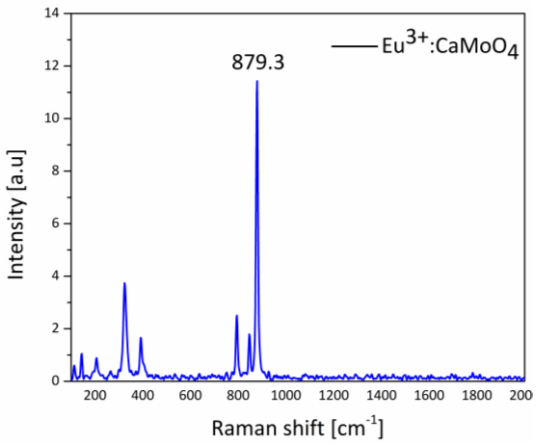

Figure S4: The Raman spectrum of the Eu^{3+}: $CaMoO_4$ SCF sample

XPS of Mo3d

Mo keeps the +6 valence state before and after annealing process as shown in Figure S5 and Figure S6. The Mo3d spectra composed of two peaks at 231.9 eV and 235.1 eV are ascribed to $Mo3d_{5/2}$ and Mo $3d_{3/2}$ of Mo^{6+}.[45-47]

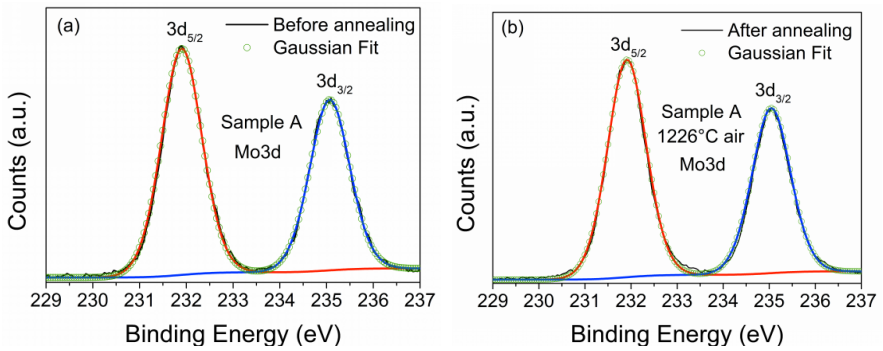

Figure S5: The Mo3d XPS of sample A before (a) and after (b) annealing in air atmosphere.

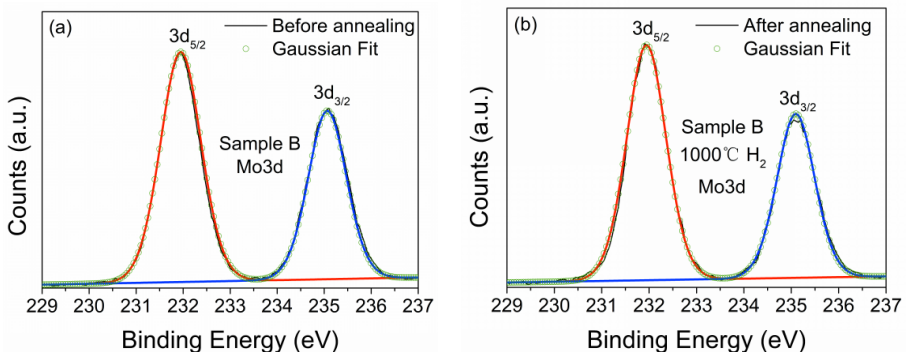

Figure S6: The Mo3d XPS of sample B before (a) and after (b) annealing in H_2 atmosphere.

References:

[1]. Hanuza, J. and V.V. Fomitsev, Journal of Molecular Structure, 1980. 66(SEP): p. 1-24.

[2]. Basiev, T.T., et al., Optical Materials, 1999. 11(4): p. 307-314.