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Local atomic structure of rare-earth doped $SrMoO_4$ phosphors by X-ray absorption spectroscopy

Alexei Kuzmin[1,*], Georgijs Bakradze[1], Inga Pudza[1], Andris Anspoks[1], Aleksandr Kalinko[2], Edmund Welter[2]

[1] Institute of Solid State Physics, University of Latvia, LV-1063 Riga, Latvia

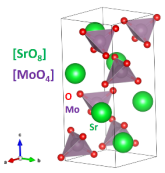
[2] Photon Science – Deutsches Elektronen-Synchrotron (DESY), 22607 Hamburg, Germany

*a.kuzmin@cfi.lu.lv

Introduction

Rare-earth (RE) doped tungstates and molybdates with a chemical formula $AW(Mo)O_4$ have a long history of practical applications because of their unique luminescence properties. Although it is generally accepted that RE(III) ions substitute A(II) ions, only a few experimental studies exist in the literature [1] on the location of dopant ions in the $AW(Mo)O_4$ crystal structure. The experimental difficulty arises from the low sensitivity of diffraction methods to small RE-dopant concentration. In this study, we used EXAFS spectroscopy combined with the reverse Monte Carlo (RMC) simulations to probe the local environment of the Nd(III), Eu(III), Ho(III), Er(III), and Yb(III) ions in microcrystalline $SrMoO_4$:0.3 mol%RE.

Crystallographic structure of $SrMoO_4$



Tetragonal (sheelite-type)
$I4_1/a$ **(No. 88)** ($Z = 2$)
a=b=5.403 Å, c=12.04 Å

Wyckoff positions:

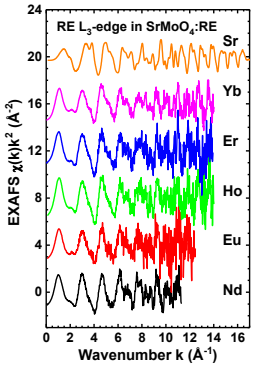
Mo	(4a)	(0, 1/4, 1/8)
Sr	(4b)	(0, 1/4, 5/8)
O	(16f)	(0.2318, 0.11359, 0.0463)

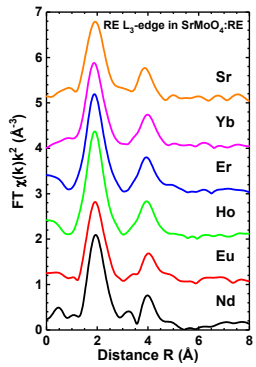
Mo-O = 1.74 Å **strong bond**
Sr-O = 2.62 Å **weak bond**

Ionic radii (Å):
Mo^{6+}(0.41) Sr^{2+} (**1.26**)
Nd^{3+} (1.109), Eu^{3+} (1.066), Ho^{3+} (1.015), Er^{3+} (1.004), Yb^{3+} (0.985)

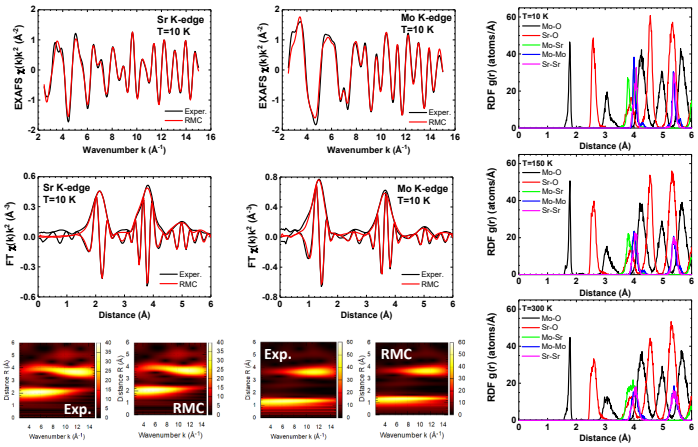
Experimental & Data Analysis

X-ray absorption spectroscopy experiments were performed at the PETRA-III P65 beamline [2] at the Sr and Mo K-edges and RE L_3-edges. The experimental EXAFS spectra were analyzed using the reverse Monte Carlo (RMC) simulations [3]. The EXAFS spectra were generated by the FEFF8.5L code [4]. The starting structural model was constructed based on the known crystallographic data obtained by diffraction for $SrMoO_4$ [5]. Atomic positions were relaxed to account for thermal disorder and static displacements till good agreement between the Morlet wavelets of the experimental and calculated EXAFS spectra was achieved. From the final atomic coordinates, a set of the partial radial distribution functions (RDFs) for different atomic pairs was obtained. RMC simulations were performed independently for undoped and RE-doped $SrMoO_4$.



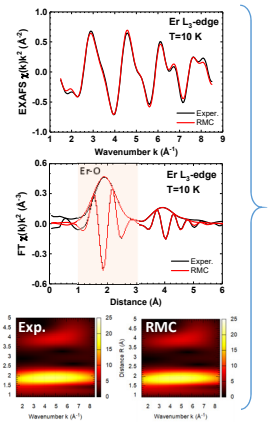


Multi-edge RMC analysis of the Sr and Mo K-edges



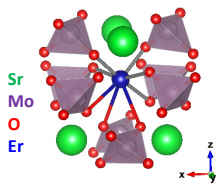
RMC simulations using 4x4x2 supercells and based on the XRD data [5] reproduce well the Sr and Mo K-edge EXAFS spectra of $SrMoO_4$. Calculated partial RDFs have weak temperature dependence in the range of 10-300 K.

RMC analysis of the RE L_3-edges

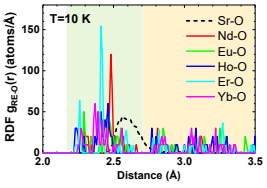


Example of the RMC simulation for $SrMoO_4$:0.3 mol%Er at 10 K. Similar results were found for other RE ions.

Final model



Local structure around RE ions



CONCLUSIONS

- RE(III) ions substitute Sr(II) ions but are located in the **off-center** position due to their smaller ion size.
- RE(III) ions are surrounded by 8 oxygen atoms which are divided into two groups: 5 atoms located in the range of 2-2.7 Å and 3 atoms located in the range of 2.7-3.5 Å.

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