XANES and XEOL studies of Eu-doped calcium tungstate in silica synthesized by sol-gel method

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Abstract. Europium-doped calcium tungstate (CaWO₄:Eu) was synthesized by a modified
Pechini method. X-ray absorption near-edge structure (XANES) and X-ray excited optical
luminescence (XEOL) was employed to probe the chemical and luminescence properties of
CaWO₄:Eu. XANES results demonstrate that the chemical environment around calcium in the
doped CaWO₄ is similar to that of undoped CaWO₄. On the other hand, chemical environment
around oxygen is very different. Moreover, the results suggest that contributions to
luminescence in the sample are from both silica (from silica matrix) and CaWO₄. Using
XEOL, luminescence pathways and efficiency associated with the system can be identified.

1. Introduction
Calcium tungstate is well known for its use as a scintillator, and has been studied extensively for its
interesting luminescence properties [1, 2]. When scheelite materials, such as calcium tungstate (a
tetragonal body-centered crystal structure), are doped with rare earth element, they reveal non-
radiative pathway for energy transfer to the rare-earth activator, emitting red light [2]. Synthesis of
such materials is typically done using solid-state reaction [3] and Pechini sol-gel method [4, 5]. The
Pechini sol-gel method [6] has several advantages over solid-state reactions, such as better
homogeneity through mixing at the molecular level and milder synthesis conditions (i.e. low
calcination temperature and shorter processing time) [7].

The purpose of this study is to use X-ray Absorption Near-Edge Structure (XANES) and X-ray
Excited and X-ray Excited Optical Luminescence (XEOL) [8] to probe the chemical environment and
to understand the origin of luminescence from europium-doped calcium tungstate.

2. Experimental
Eu-doped CaWO₄ was synthesized by a modified Pechini sol-gel method using steps similar to those
reported by Grobelna et al [4]. Briefly, stoichiometric amounts of sodium tungstate and europium
chloride were each dissolved in water and warmed to about 60° C, then the two solutions were mixed
with stirring, and insoluble (1-x)CaWO₄·xEu was formed, where x=0.1. Next, EDTA was added to the

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mixture, which formed the stable complex of metal (Ca\(^{2+}\)) ion while tungstate remained solvated in the solution. To this solution, citric acid and polyethylene glycol were added with stirring and heating for 24 hours. Tetramethoxysilane (TMOS) was then added and a transparent gel was formed. Finally, the gel products were heated in air for three hours at 600° C, and a white powder of calcium tungstate doped with europium incorporated into silica (SiO\(_2\)) matrix was obtained. This sample is henceforth denoted CaWO\(_4\):Eu.

Ca L\(_{3,2}\) and O K-edge XANES and XEOL measurements were performed on the Spherical Grating Monochromator (SGM) beamline 11ID-1 (Energy range: 250-2000 eV, Resolution \(\Delta E/E < 2 \times 10^{-4}\)), and Ca K-edge XANES measurements were performed on Soft X-ray Microcharacterization Beamline (SXRMB) 06B1-1 (Energy range: 1.7-10 KeV, Resolution \(\Delta E/E: 1 \times 10^{-4}\)) at the Canadian Light Source (CLS). XANES were simultaneously collected in total electron yield (TEY), and photoluminescence yield (PLY). XEOL spectra were collected using a QE6500 Scientific-grade Spectrometer (Ocean Optics, Dunedin, FL), and a network CCD camera (Axis 2120).

3. Results and Discussions

Figures 1 shows the XANES spectra of CaWO\(_4\):Eu and standard CaWO\(_4\) power across the Ca L\(_{3,2}\)-edge (a), the Ca K-edge (b), and the O K-edge (c). PLY shows inversion at the Ca L\(_{3,2}\) and O K-edges, indicating a decrease in photoluminescence yield at the absorption edges. Inversion of PLY is further discussed later in this section. For Ca L\(_{3,2}\)-edge XANES, both Eu-doped and standard CaWO\(_4\) have main Ca L\(_{3,2}\) peaks, along with pre-edge shoulder peaks. However, peaks from the Eu-doped sample are much broader. In addition, post-edge shoulder peaks observed in the XANES of the standard powder are not clearly seen from the Eu-doped sample; rather, it seems the features are buried under the broad peaks. These peaks are sensitive to the local environment and the crystal field splitting (10Dq) [9]. From the Ca L\(_{3,2}\)-edge TEY, we infer that the chemical environment between the Eu-doped and standard samples are generally similar around Ca\(^{2+}\), but there is evidence (shoulders at 351.2 eV and 355.0 eV for the powder that diminish in the doped sample) that the local environment in the doped sample is closer to O\(_{h}\) symmetry. For the Ca K-edge XANES, there is a slight difference between the TEYs of CaWO\(_4\):Eu and standard CaWO\(_4\) powder, especially in the relative intensity of the whiteline; these features are more prominent in the TEY of standard CaWO\(_4\) powder. The general spectral pattern however, is still very similar. This suggests that the structure of the CaWO\(_4\) unit cell remains intact but the interface between the CaWO\(_4\) crystallite and SiO\(_2\) in the silica matrix and the presence of the dopant Eu has an effect on the Ca environment. Looking at O K-edge TEY, the spectral profile between the Eu-doped and standard samples differs markedly due to the presence of silica resulting from the decomposition of TMSO, forming the silica matrix which embeds the CaWO\(_4\). In fact, the O K-edge XANES of the Eu-doped sample looks very similar to that of SiO\(_2\) except for the region between 531-536 eV where contributions from the WO\(_4\) tetrahedra are noticeable. [10] From a difference spectrum between the spectra of the doped and undoped samples (not shown), we can quantify O K-edge-jump ratio of CaWO\(_4\):Eu/SiO\(_2\) to be 0.15. The PLY contains features of both the standard CaWO\(_4\), as well as those of SiO\(_2\). It is interesting to note that the WO\(_4\)-contribution (531-536 eV) makes a positive response (edge jump) in the PLY while the PLY is inverted but remains CaWO\(_4\) like when the SiO\(_2\) channel turns on at the O K-edge of SiO\(_2\). The switching from positive edge to inversion results from an abrupt drop of quantum efficiency (number of optical photons produced per photon or eV of excitation energy absorbed). In other word, compared to CaWO\(_4\), SiO\(_2\) is less efficient in converting the X-ray energy it absorbs to optical photons. This observation immediately indicates that CaWO\(_4\) makes a dominant contribution to the luminescence of the sample.
Figure 1. (a) Ca $L_{3,2}$-edge XANES spectra of CaWO$_4$:Eu and standard CaWO$_4$ (b) Ca $K$-edge XANES spectra of CaWO$_4$:Eu and standard CaWO$_4$ (c) O $K$-edge XANES of CaWO$_4$:Eu and standard CaWO$_4$

Figure 2 shows the XEOL spectra across the Ca $L_{3,2}$-edge of CaWO$_4$:Eu (a) and standard CaWO$_4$ powder (b). Looking at Figure 2a, there is a broad peak centred around 435 nm, as well as sharp peaks at 590 nm, 613 nm, 652 nm, and 700 nm. Sharp peaks (590 nm, 613 nm, 652 nm and 700 nm) can be attributed to Eu $f$-$f$ transition, $5D_{j} \rightarrow 7F_{j}$ (where $j = 1, 2, 3,$ and $4$ respectively) [4]. The broad peak at 435 nm can be explained as follows: When the sample is excited, there is enough energy for the valence electron of O $2p$ to be transferred to empty $5d$ orbital of W$_{6+}$ ($5s^25p^64d^0$), forming W$_{5+}$ ($5s^25p^64d^1$), which relaxes to the ground state resulting in the blue emission [2]. The broadness of the peak can be attributed to Jahn-Teller effect which influences degenerate excited states of the tetrahedron of WO$_4^{2-}$. Looking at the XEOL across the Ca $L_{3,2}$- and O $K$-edges (not shown, but spectral features are identical to XEOL across Ca $L_{3,2}$-edge), luminescence intensity is minimum at the absorption edges, as observed in the inverted PLY spectra. Inversion of PLY in general can be attributed to the fact that measurements were made in total absorption region, where attenuation length of the sample (~0.45 µm at Ca $L_{3,2}$-edge, and 0.50 µm at O $K$-edge) is significantly smaller than the thickness of the sample. Furthermore, decrease in luminescence at O $K$-edge can be attributed to the presence of the non-luminescent silica gel resulting from the synthesis (see above). Thus going across the O $K$-edge, the absorption cross-section increases abruptly as SiO$_2$ begins to compete with CaWO$_4$. If the silica gel is non-luminescent as is observed here, the luminescence intensity will drop since absorption of silica does not produce any efficient luminescence pathway.

Figure 2. XEOL spectra across Ca $L_{3,2}$-edge of CaWO$_4$:Eu (a), standard CaWO$_4$ powder (b)
From Figure 2a we can track the relative intensity of CaWO$_4$ versus Eu emission as a function of excitation energy. We see that the relative intensity is proportional to the absorption coefficient and there is no dramatic difference in the branching ratio. Finally it is interesting to note that the standard sample, Figure 2b, exhibits similar blue luminescence as a doublet at ~ 420 nm and 500 nm. The 500 nm emission is quenched in the CaWO$_4$:Eu sample. This observation suggests that there is likely a non-radiative pathway for energy transfer from this state to the Eu optical channels. It is also possible that difference in size between the doped and the undoped sample plays a role in the observed luminescence pattern.

4. Conclusions
Eu-doped CaWO$_4$ has been synthesized by a modified Pechini sol-gel method, and spectroscopic studies on the sample have been performed. From XEOL, peaks due to transitions related to relaxation processes after the sample has been excited by X-rays can be observed. XANES results suggest that the chemical environment around calcium is similar between the standard and the Eu-doped sample while doping and the SiO$_2$ matrix have some noticeable effect on the local symmetry of the Ca site and the optical properties in that one optical channel in CaWO$_4$ is quenched and red luminescence from Eu is observed.

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