doi:10.1017/S1431927620014452
Microsc. Microanal. 26 (Suppl 2), 2020

Comparison of Cathodoluminescent Emission from Scheelite and Wolframite Structured Electrospun Tungstate Nanofibers

Caressia Edwards, Candyce Collins, Jacob Hayes, Gibin George, Daryush Ila and Zhiping Luo

Fayetteville State University, Fayetteville, North Carolina, United States

Tungstate with the general formula AWO_4 is promising optical material with a characteristic blue-green emission under UV irradiation, originating from ligands [1]. The A-site in AWO_4 compositions are occupied by divalent metal ions such as Ba, Ca, Sr, Zn, Mg, etc. Based on the ionic size of A-site cations, AWO_4 materials adopt two different crystal structures, and they are called as scheelites and wolframites, respectively. The scheelite structure is composed of a three-dimensional framework of vertex sharing AO_8 polyhedra and BO_4 tetrahedra [2] resulting in a tetragonal symmetry, as shown in Fig. 1(a). Scheelites are formed when elements occupy the A-site with a large ionic radius, especially alkaline earth metals (Ca^{2+}, Ba^{2+}, Sr^{2+}, etc.). The wolframites adopt a monoclinic crystal structure composed of AO_6 and WO_6 octahedra as shown in Fig. 1(b), and the wolframite structures are formed when the A-site is occupied by smaller ions, mainly transition metals (Co^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, etc.) [3]. In this work, representative scheelite and wolframite AWO_4 (A = Sr and Mg) nanofibers doped with RE^{3+} ions are fabricated using sol-gel assisted electrospinning technique. The cathodoluminescent (CL) emission from these nanofibers is compared to understand the effect of structure and the RE^{3+} dopants on the CL emission. The nanofibers are fabricated through a sol-gel assisted electrospinning process [4]. The process involves two steps; in the first step, the precursor composite nanofibers are fabricated using an electrospinning process, and later, the fibers are calcined at a high temperature. The electrospinnable precursor solution for the fabrication AWO_4 nanofibers is prepared by dissolving 0.07 M ammonium metatungstate and 0.07 M metal acetate salt in a 20 mL 20/40/40 mixture of H_2O/ethanol/N,N-dimethylformamide solvent solution. Then 2.0 g of polyvinylpyrrolidone (PVP) (molecular weight ~1,200,000 g/mol) was added to the above solution and stirred vigorously for 12 h to ensure uniform mixing. The electrospinning was conducted at atmospheric conditions with an applied voltage of 18 kV, a flow rate of 300 mL/h, and a spinneret to collector distance of 17 cm. The xerogel fibers obtained through the electrospinning process were subsequently calcined at 700 °C in air for 5 h at a ramp of 2 °C/min to obtain the tungstate nanofibers. Samples were coated with carbon and analyzed in a JEOL field-emission JXA-8530F EPMA, which was equipped with an SDD X-ray energy-dispersive spectrometer (EDS) and xCLent cathodoluminescence (CL) spectrometer. Fig. 1 (c, d) shows SEM images of AWO_4 nanofibers after calcination. One can observe the high aspect ratio of the nanofibers with an average size of < 150 nm. The EDS analysis, as shown in Fig. 1(e, f) confirms that the composition of the obtained fibers has significant peaks arising from the respective A, W, and O elements. On comparing the CL emission from the nanowires in Fig. 2(a, b), the scheelite structured nanofibers exhibit emission characteristics to the RE^{3+} ions. However, the emission from the wolframite nanofibers is from their lattice. The RE^{3+} dopant ions are not occupying the expected A-site in the lattice of wolframite nanofibers due to the large mismatch of the A-site and RE^{3+} ionic sizes. The strong emission of CL enables these materials for high-energy radiation detection [5, 6].

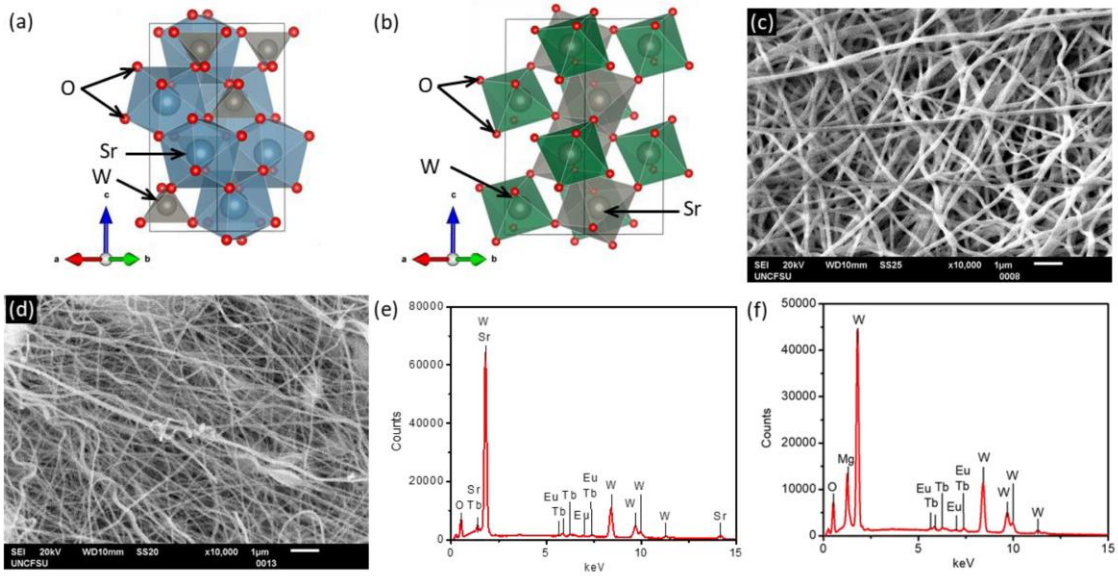

Figure 1. (a) and (b) Crystal structure, (c) and (d) SEM images, and (e) and (f) EDS spectra of scheelite and wolframite structured nanofibers.

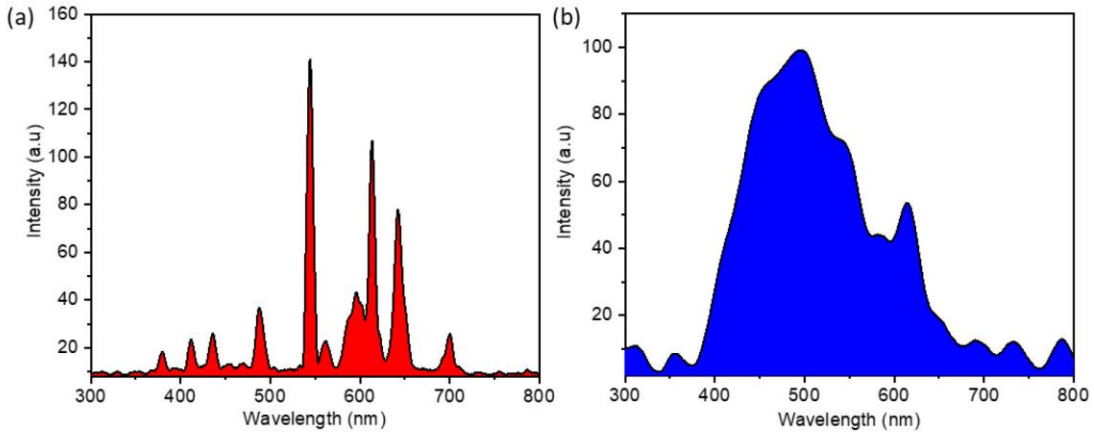

Figure 2. Cathodoluminescence spectra of (a) scheelite structured and (b) wolframite structured nanofibers.

References
[1] G. George, et al. J. Mater. Chem. C **7** (2019), p. 14949.
[2] V. Morozov, et al. Chem. Mater. **30** (2018), p. 4788.
[3] G. Benoît, et al. Solid State Sci. **13** (2011), p. 460.
[4] G. George, et al. Curr. Nanosci. **15** (2020), doi: 10.2174/1573413715666190112121113.
[5] Z. Luo, et al., Curr. Nanosci. **13** (2017), p. 364
[6] This work was supported by Army Research Office (ARO), contract no. W911NF1810469. The EPMA was funded by ARO W911NF-09-1-0011, and CL by NSF MRI Program DMR 1626376.

https://doi.org/10.1017/S1431927620014452 Published online by Cambridge University Press