

Cathodoluminescence of alkaline earth hexafluorometallate nanowires

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¹Fayetteville State University, United States, ²Fayetteville State University, Fayetteville, North Carolina, United States, ³Argonne National Laboratory, United States, ⁴Argonne National Laboratory, Lemont, Illinois, United States, ⁵Fayetteville State University, FAYETTEVILLE, North Carolina, United States

Cathodoluminescence of alkaline earth hexafluorometallate nanowires Jacob I. Hayes, aCaressia S. Edwards, aGibin George, a Lei Yu, bJianguo Wen, bZhiping Luo a* a Department of Chemistry, Physics, and Materials Science, Fayetteville State University, Fayetteville, USA. b Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439, USA * Corresponding author: zluo@uncfsu.edu Hexafluorometallates with the general formula ABF₆ (A=Ba, Sr, Ca etc. and B=Si, Ge, Sn, Ti etc.) are widely studied as potential red-emitting phosphors by doping with Mn⁴⁺ transition metal ions [1-3]; however the cathodoluminescence from Mn⁴⁺ doped phosphors are poor. The class of materials mentioned above is also identified as potential host lattices for rare-earth (RE³⁺) dopants [4, 5]. In general, alkaline earth metal fluorides are well-known for their consistent luminescence from the dopant ions and they are promising candidates for inorganic scintillators, due to their high chemical stability and low lattice phonon energy [6, 7]. Materials with ABF₆ arrangement crystallizes with rhombohedral symmetry with corner-sharing BF₆ octahedra with a coordination number of 6 with fluorine atoms and the A-site ion at the body center is coordinated to 12 fluorine atoms, as shown in Fig. 1a. In this work, representative single-crystal ABF₆ nanowires doped with Ce³⁺ and Tb³⁺ ions are synthesized using a reverse micelle solvothermal method and their cathodoluminescent (CL) emission properties are evaluated for radiation detection [8]. Nanowires were synthesized using a reverse-micelle solvothermal process using cyclohexane as the solvent. Cetyltrimethylammonium bromide (CTAB) and 1-pentanol were used as the surfactant and co-surfactant, respectively. In the typical synthetic procedure, two identical solutions of 25 mL cyclohexane, 1 mL of 1-pentanol, and 2 g CTAB were prepared to form the solvent medium. 1.2 mL of a 1M solution of the corresponding tetravalent element in 20% HF was delivered dropwise to one of the two above solvent mixtures and 1.2 mL of 1M barium chloride (BaCl₂) was delivered to the other under vigorous stirring at a speed of 700 rpm. For the preparation of RE³⁺ doped nanowires, the BaCl₂ precursor solution was added with varying percentages of CeCl₂ and TbCl₂, in order to produce the desired dopant percentages. After 30 min of stirring at 700 rpm, the two mixtures were mixed and stirred well for another 30 min at a rate of 900 rpm. The solution was then sealed in an autoclave reactor vessel lined with Teflon and heated at 120°C for 12 h, after which the autoclave cooled naturally to room temperature. The resulting nanowires were separated from the solution and washed several times using water and ethanol and dried overnight at 80°C. 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. For TEM analysis, the nanowires are dispersed in pure ethanol solutions by sonication for 30 min and then dropped on carbon-film supported grids. The grids were observed in FEI Talos F200X TEM/STEM instrument at 200 kV. Fig. 1b&c shows the morphology of the solvothermally synthesized nanowires obtained using SEM and TEM analysis, respectively. Both the above images reveal that the nanowires uniform with an average diameter of ~100 nm. The EDS spectra in Fig. 1d reveal the characteristic peaks originating from Ba, Sn and F elements of the synthesized ABF₆ nanowires. In Fig. 2, the CL emission from the pure and rare-

earth-doped ABF6 nanowires are compared. The RE³⁺ doping significantly affects the CL emission from the pure nanowires. The pure nanowires exhibit a broad CL emission spanning in the entire visible-spectrum, whereas the RE³⁺ doped nanowires exhibit an emission characteristic to the energy bands of the RE³⁺ ions. The broad emission observed in the pure nanowires can be attributed to the 2p F- $\rightarrow$ 5p Ba²⁺ cross-over transition of electrons [9, 10].

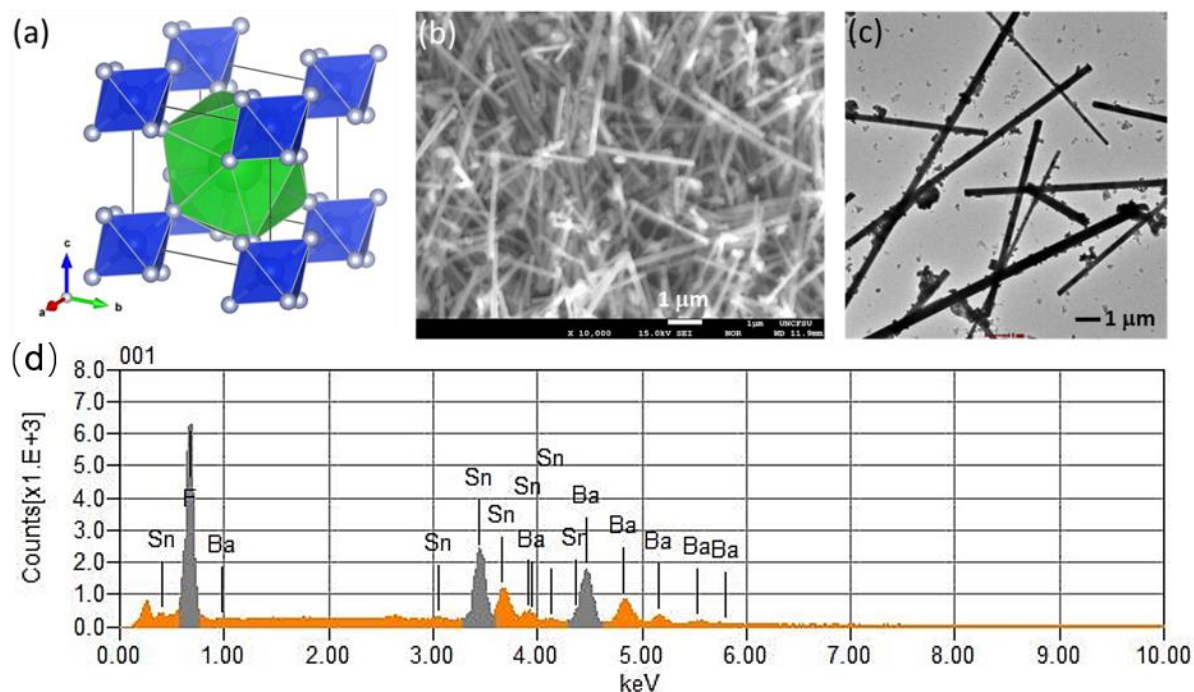


Figure 1. Figure 1. (a) Crystal structure; (b) SEM image; (c) TEM image; (d) EDS of synthesized ABF6 nanowires.

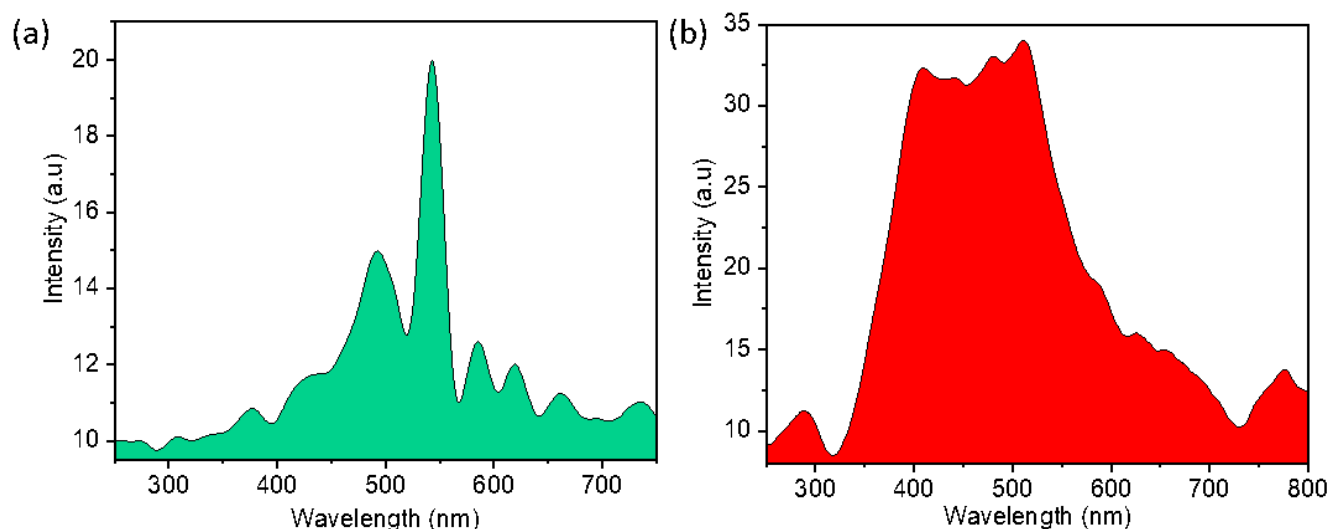


Figure 2. Figure 2. Comparison of CL spectra of pure and RE³⁺ doped representative ABF6 nanowires.

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