

**EFFECT OF CATION COMPOSITION ON THE STABILITY AND PROPERTIES OF FLUORITE-TYPE HIGH-ENTROPY FLUORIDES***Iarushina D.V., Mariappan Anandkumar, Zaitseva O.V., Trofimov E.A.*

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The concept of high-entropy materials, originally developed for metallic alloys, has been actively extended to ceramic compounds over the past decade. A key role in the stabilization of such complex multicomponent systems is played by the configurational entropy of mixing, which makes it possible to obtain single-phase solid solutions even from components that do not exhibit mutual solubility under ordinary conditions. Despite advances in the synthesis of high-entropy oxides and carbides, research on high-entropy fluorides (HEFs) is still in its initial stages. From a thermodynamic perspective, it is critically important to understand how variations in the cationic composition affect the stability of the crystal lattice, the defectiveness of the structure, and, consequently, the macroscopic properties of the material. The aim of this work was to establish the fundamental “composition – structure – property” relationship for novel HEFs with a fluorite-type structure.

In this study, three compositions of high-entropy fluorides were synthesized using the co-precipitation method followed by annealing with  $\text{NH}_4\text{F}$  as a flux: HEF1 ( $\text{CaSrBaPbCeF}_{11}$ ), HEF2 ( $\text{CaSrBaPbLaF}_{11}$ ), and HEF3 ( $\text{CaSrPbCeLaF}_{12}$ ). X-ray diffraction analysis showed that all samples crystallize into a single-phase cubic fluorite structure (space group  $\text{Fm-3m}$ ), despite significant differences in the ionic radii of the elements.

It was found that the composition of the cation sublattice significantly affects the lattice parameters, with  $\text{Pb}^{2+}$  making the dominant contribution to the formation of the framework, as its lattice parameter is the closest to the obtained values. The most interesting and thermodynamically significant result is a sharp decrease in the band gap  $E_g$  of the synthesized materials compared to the dielectric binary fluoride constituents. Furthermore, the cationic composition directly determines the morphology and surface energy of the particles, which range from nanoporous to dense micron-sized structures.

Thus, the ability to purposefully tune the band gap and morphology by varying the cationic composition opens up broad prospects for the thermodynamic design of novel functional materials. The obtained HEFs may find applications as visible-light photocatalysts, sensitizers in solar cells, and active supports or coatings in heterogeneous catalysis, where controlled porosity plays a key role.

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