

**PHASE EQUILIBRIA, STRUCTURE, AND PROPERTIES OF COMPLEX OXIDES IN THE  $\text{Eu}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  SYSTEM AT 1373 K IN AIR***Legonkova V.S., Aksenova T.V., Cherepanov V.A.*

Ural Federal University

620002, Ekaterinburg, Mira st., 19

The aim of this work is a systematic study of phase equilibria, determination of the homogeneity ranges, and investigation of the structural features of complex oxides in the quasi-quaternary system  $\text{EuCoO}_3 - \text{SrCoO}_{3-\delta} - \text{SrFeO}_{3-\delta} - \text{EuFeO}_3$ .

A series of samples with the composition  $\text{Eu}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  with  $0.1 \leq x \leq 0.9$  and  $0.1 \leq y \leq 0.9$  was synthesized by a glycerol-nitrate technique, followed by final annealing at 1373 K in air and subsequent quenching to room temperature. The phase composition and crystal structure were studied by X-ray diffraction and the Rietveld full-profile analysis.

An isobaric-isothermal section of the phase diagram of the quasi-quaternary system  $\text{EuCoO}_3 - \text{SrCoO}_{3-\delta} - \text{SrFeO}_{3-\delta} - \text{EuFeO}_3$  at 1373 K in air has been constructed. It was found that depending on the strontium ( $x$ ) and iron ( $y$ ) content the solid solutions  $\text{Eu}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  crystallize in one of three perovskite structures: cubic (sp. gr.  $Pm\bar{3}m$ ), tetragonal (sp. gr.  $I4/mmm$ ), or orthorhombic (sp. gr.  $Pbnm$ ). The cubic phase is stable for compositions enriched in strontium and iron ( $x = 0.9$  and  $0.1 \leq y \leq 0.9$ ;  $x = 0.8$  and  $0.2 \leq y \leq 0.9$ ;  $x = 0.7$  and  $0.5 \leq y \leq 0.9$ ). The tetragonal superstructure  $2a_p \times 2a_p \times 4a_p$ , characterized by an ordered arrangement of Eu and Sr cations in the A-sublattice, observed for  $x = 0.8$  and  $y = 0.1$ ; for  $x = 0.7$  and  $0.1 \leq y \leq 0.4$ ; for  $x = 0.6$  and  $0.1 \leq y \leq 0.3$ , while the orthorhombic structure is characteristic of europium-rich oxides with  $x = 0.1$  and  $0.1 \leq y \leq 0.9$ . The unit cell parameters exhibit a linear dependence on composition upon substitution of europium by strontium in the A-site and of cobalt by iron in the B-site obeying Vegard's rule.

Thermogravimetric analysis of the oxides  $\text{Eu}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  ( $0.6 \leq x \leq 0.9$  and  $y = 0.3$ ;  $x = 0.8$  and  $0.3 \leq y \leq 0.8$ ) showed that all of them are oxygen-deficient. The oxygen content, determined by iodometric titration and reduction in a hydrogen stream, decreases with increasing temperature and increasing strontium and cobalt contents in the samples. Charge compensation upon substitution of  $\text{Eu}^{3+}$  by  $\text{Sr}^{2+}$  occurs through the formation of oxygen vacancies and an increase in the average oxidation state of 3d-metals.

The nonlinear temperature dependence of relative thermal expansion of  $\text{Eu}_{1-x}\text{Sr}_x\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$  ceramic samples ( $x = 0.6, 0.7$ ) in the range of 300–1373 K in air is caused by thermal and chemical factors. The latter is associated with the release of oxygen from the lattice at  $T > 600$  K and a change in the oxidation state of 3d-metals. The increase in LTEC with increasing strontium content correlates with the increase in the oxygen nonstoichiometry.

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