NEW COBALTITES AND CHROMITES WITH A DISTORTED K_2NiF_4 TYPE OF STRUCTURE

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Oxometalates *R*Ca*M*O_4 and *R*Sr*M*O_4 (*R* = rare earth, *M* = transition metal) with the structures related to K_2NiF_4 display very interesting phase and structural behaviour both at low and high temperatures and exhibit a rich variety of physical properties, which are potential for the further application [1–3]. Recently, four new *R*Ca*M*O_4 phases were found in the R_2O_3–CaO–M_2O_3 quasi-ternary systems [4]. Starting from the mixture of the respective oxides and $CaCO_3$, the cobaltites $EuCaCoO_4$ and $TbCaCoO_4$ were obtained by solid state reaction in air at 1470 K, whereas chromites $TbCaCrO_4$ and $ErCaCrO_4$ were synthesized by arc melting in Ar atmosphere. The phase and structural behaviour of these compounds in the temperature range of 298–1200 K was examined *in situ* by high-resolution X-ray synchrotron powder diffraction and using DTA technique. X-ray absorption spectroscopy was applied for the estimation of the valence state of terbium, chromium and cobalt. $EuCaCoO_4$ and $TbCaCoO_4$ are isotypic with the respective samarium and gadolinium cobaltites (La_2CuO_4 structure type, space group *Bmab*) and posses orthorhombically distorted K_2NiF_4 type of structure. Both compounds undergo structural phase transitions to the tetragonal structure at the temperatures of 440 K and 970 K, respectively. At ambient conditions $ErCaCrO_4$ structure is also isotypic with La_2CuO_4. In contrast, weak reflections in the powder X-ray diffraction diagram of $TbCaCrO_4$ obtained at room temperature indicate a primitive orthorhombic lattice. The structure was found to be isotypic with $La_{0.8}Sr_{1.2}InO_{3.9}$ (space group *Pbca*). High temperature powder X-ray diffraction examination of $TbCaCrO_4$ revealed structural changes at around 720 K to the base-centered La_2CuO_4 type of structure. Further phase transition into the tetragonal K_2NiF_4 type of structure was predicted for $TbCaCrO_4$ at 1560 K by the extrapolation of the unit cell parameters *a* and *b* of the orthorhombic phase. Structural peculiarities and thermal behaviour of the newly prepared cobaltites and chromites are discussed with the related *R*Ca*M*O_4 compounds (*M* = Fe, Co, Ni, Cr, Al, Ga).

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