

o.m2.p3 Neutron and X-ray powder diffraction study of the antiferromagnet-ferromagnet and insulator-metal transitions in the $\text{TbBaCo}_{1.9}\text{Fe}_{0.1}\text{O}_{5.5}$ perovskite. D.D. Khalyavin¹, I.O. Troyanchuk¹, A.N. Pirogov², ¹Institute of Solids and Semiconductors Physics, NAS, P. Brovki str. 17, 220072 Minsk, Belarus. ²Institute for Metal Physics, Ekaterinburg.

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It has been recently found that oxygen deficient orthocobaltites $(\text{Gd,Tb})\text{BaCo}_2\text{O}_{5.5}$ with crystal structure similar to the 112 type perovskite structure where oxygen vacancies are ordered exhibit first order phase transitions antiferromagnet-ferromagnet (AF-F) at $T_i \approx 250$ K and insulator-metal (M-I) at $T_M \approx 340$ K^{1,2}. The AF-F transition is accompanied by a jump of conductivity and giant magnetoresistance. Above T_i the value of the spontaneous magnetization M_S is $\sim 0.18 \mu_B$. This value M_S is too low for ferromagnetic ordering of magnetic moments of Co^{3+} ions in the case of the intermediate or high spin states. In order to explain this fact authors of the work³ suppose that $\text{TbBaCo}_2\text{O}_{5.5}$ undergoes transition from antiferromagnetic into weak ferromagnetic state. In this work results are reported for the neutron and X-ray powder diffraction study of phase transitions at T_i and T_M for $\text{TbBaCo}_{1.9}\text{Fe}_{0.1}\text{O}_{5.5}$. We have established that small ($\sim 10\%$) substitution of Co ions by Fe ones leads to decreasing T_i down to 195 K and increasing the temperature of the magnetic ordering T_N up to 305 K. This enables to carry out investigation of the AF-F phase transition by the neutron diffraction method (since $T_i \ll T_N$). According to our results obtained for $\text{TbBaCo}_{1.9}\text{Fe}_{0.1}\text{O}_{5.5}$ the neutron diffraction picture caused by magnetic superlattice does not change due to phase transition at T_i . This fact is argument in favour of the assumption made in work³. The temperature X-ray diffraction study has shown that M-I transition is accompanied by the crystal structure transformation resulting from the change of the unit cell parameters without change of orthorhombic symmetry. In the work³ by analogy with the $\text{SrFeO}_{3-1/n}$ ⁴ it was suggested that the first order phase transition at T_M results from oxygen vacancies ordering. On the base of this assumption it is impossible to explain the invariance of the orthorhombic symmetry of the crystal structure above T_M since in the case of random distribution of the vacancies the symmetry should be rather tetragonal than orthorhombic. In contrast with AF-F phase transition the M-I one is not accompanied by any crystal structure transformations. In this way the anomaly of conductivity at T_i is not connected with modification the energy-bond structure due to a crystal structure transition.

o.m2.p4 Preparation and structure of a new perovskite-like ternary oxide Sr_3ReO_6 . K.G. Bramnik^a, A.M. Abakumov^b, H. Fuess^a, ^aDepartment of Materials Science, University of Technology Darmstadt, D-64287, Darmstadt, Germany. ^bDepartment of Chemistry, Moscow State University, 119899 Moscow, Russia

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A new ternary Sr_3ReO_6 oxide has been synthesized using ceramic technique in an evacuated silica tube under controlled partial oxygen pressure $p(\text{O}_2) = 4.6 \times 10^{-15}$ bar at 740°C. To control partial oxygen pressure a mixture of metallic Ni and NiO was used. The preliminary structure investigation of the Sr_3ReO_6 complex oxide was carried out using X-ray powder diffraction data ($R_1 = 0.077$, $R_p = 0.135$). Its cation composition was determined by EDX analysis. The Sr_3ReO_6 oxide has a monoclinic cell with $a = 8.1177(8)$ Å, $b = 5.9103(6)$ Å, $c = 5.9422(6)$ Å, $\beta = 90.47(1)^\circ$ (S.G. I 2/m) and adopts a distorted perovskite structure with Sr and Re ordered on the B-sites in "rock-salt" manner. Formally the Sr_3ReO_6 formula can be written as $\text{Sr}_2\text{SrReO}_6$. The Sr_3ReO_6 complex oxide could be considered as a $\text{Ba}_2\text{SbBiO}_6$ type of perovskite structure distortion¹. The ReO_6 and SrO_6 octahedra are cooperatively rotated about $[011]_{\text{perovskite}}$ and tilted with respect to $a^*b^*c^*$ Glazer notation². The A-sites in a perovskite cell are occupied by the rest of Sr atoms. This compound is stable in the narrow range of partial oxygen pressure of 4.6×10^{-17} – 2.3×10^{-15} bar only. At the higher partial oxygen pressure the Sr_3ReO_6 oxide decomposes to a mixture of SrO and $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ compounds. The formal Re valence in the Sr_3ReO_6 increases from +6 to +6.5 due to a formation of cation vacancies in the A-sublattice, that leads to changing the coordination number of the Sr atoms in the B-sublattice from 6 to 8. The further increasing of a partial oxygen pressure to 1.1×10^{-3} bar leads to decomposition of the $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ compound to $\text{Sr}_5\text{Re}_2\text{O}_{12}$ ⁴ and SrO. In this case the rest of the Re atoms with the oxidation state +6 in the $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ oxidizes to the Re^{+7} and vacancies in the B-sublattice are formed. This oxidation sequence could be considered as a stepwise increase of the amount of cation vacancies in the A- and B-sublattices from $\text{Sr}_6\text{Re}_2\text{O}_{12}$ through $\text{Sr}_{5.5}\text{Re}_2\text{O}_{12}$ to $\text{Sr}_5\text{Re}_2\text{O}_{12}$. Further structure investigations of the Sr_3ReO_6 are in progress now.

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