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LETTERS TO THE EDITOR

Solid State Reaction of Preparation of Chromium and Iron Niobates with the Structure of Double Perovskite

A. A. Selyutin, A. Yu. Shirkin, I. A. Kasatkin, and N. P. Bobrysheva

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: n_bobrysheva@mail.ru

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Double perovskites Sr_2ANbO_6 (where A = Fe, Cr) are extensively studied as materials for magneto-electronics, which is due to their unusual physico-chemical properties [1–3]. In particular, the change in the character of exchange interactions and appearance of the state of the spin glass in the course of the temperature variation are observed for Sr_2FeNbO_6 and Sr_2CrNbO_6. For double perovskites the presence of several different transformation patterns depending on the temperature and conditions of the synthesis of the samples is also noted [6], to date, however, the character of location of the *p*- and *d*-elements in A-positions and generated type of the structure are still under discussion. To clarify the data available, we carried out the synthesis of Sr_2CrNbO_6 and Sr_2FeNbO_6 by the conventional ceramic method and performed a parallel study of thermal transformations of the stoichiometric mixture of the starting reagents for the synthesis by the method of thermal analysis.

The synthesis was performed by annealing the mixture at 1450°C for 50 h without intermediate stages of additional grinding of samples. The heating of the furnace up to 1450°C was performed at the rate 60 deg/min.

According to data of the X-ray diffraction analysis, complex oxides Sr_2CrNbO_6 and Sr_2FeNbO_6 with the ordered *Fm*-3*m* cubic structure were obtained. Parameters of the unit cell were as follows: *a* 7.8756, 7.9375 Å for oxides of chromium and iron, respectively.

The thermal behavior of the stoichiometric mixture of the initial reagents for the synthesis has been investigated by the method of the thermal analysis allowing to identify the range of the mass changes of the analyzed sample in the heat treatment process, as well as to quantitatively determine the percentage of the weight loss or increase.

The samples synthesized and samples of the mixture for the synthesis were studied. No mass changes for the complex oxides prepared were observed in the whole range of temperatures. Under heating the initial mixture a series of distinct effects of mass changes occurred, under cooling these effects were already absent.

When considering the segment of heating the close nature of the temperature changes in the curves of TG and DTG for Sr_2FeNbO_6 and Sr_2CrNbO_6 should be noted, which are a sharp two-step mass loss of the samples in the temperature range of 400–1050 and 1150–1300°C. These stages are associated with thermal transitions of strontium carbonate and niobium oxide as similar components of the mixture to obtain both oxides. On DTG curves two stages of mass loss correspond to each segment apparently related to the simultaneous realization of two interacting processes: the decomposition of strontium carbonate and the reversible transition of niobium oxide in phases of the various non-stoichiometric composition.

The theoretical calculation of the mass loss on the stoichiometric reaction in case of the decomposition of

the carbonate is 17.5%. This is close to the experimental total value of 17.3% in case of Sr_2FeNbO_6 and 16.3% for Sr_2CrNbO_6. In addition, in both cases there is a slight increase in the mass of samples in the range of 1100–1200°C, which may be associated with the beginning of the formation of a complex oxide.

Synthesis of complex oxides was performed by annealing stoichiometric mixture of corresponding starting reagents $SrCO_3$, Nb_2O5, Fe_2O_3, Cr_2O_3 of the "pure for analysis" grade.

A carefully ground mixture was pressed into tablets and annealed in a muffle furnace Nabertherm HTC 03/15 at 1450°C for 50 h. Strontium carbonate was previously annealed at the temperature of 800°C to remove adsorbed water and carbon dioxide.

The samples obtained were studied using X-ray powder diffraction (XRD) analysis on an 2D Phaser Bruker benchtop diffractometer using CuK_α = 1.5406 Å and CoK_α = 1.7890 Å radiation. The measurements were carried out in the range of angles 2θ = 15–120°C with the step of 0.02°. The XRD data were analyzed by the method of Ritfeld using full-profile applications in the program Topas 4.2.2.

The thermal analysis was carried out in the air flow of 40 mL/min on the installation Setsys Evolution (Setaram) with a platinum-platinum rhodium thermocouple at heating from 25 to 1300°C at the rate of 15 deg/min and cooling from 1300 to 25°C at the same rate. A sample with the mass of 90 mg was placed in an open corundum crucible.

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