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LETTERS
TO THE EDITOR

Mass Spectrometric Control of High-Temperature Synthesis of the System $SrO–Mn_2O_3–Al_2O_3–Sb_2O_5$

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The ceramic method, which includes a stage of the high-temperature calcination of the starting components mixture, is the most common approach to prepare various mixed antimonates at controlled stoichiometric ratio of the components. Deviation from the stoichiometric ratio leads to distortions of the product crystal structure and, consequently, to undesired changes of physico-chemical properties of the product.

Generally, mixed antimonates based on oxides of strontium, aluminum, and *3d*-elements are obtained by annealing the stoichiometric mixtures of strontium carbonate, Sb_2O_5, Al_2O_3, and oxides of *3d*-elements. Duration of the synthesis strongly depends on the temperature that can be varied within the 900–1770 K range [1]). Under such conditions, losses of the most volatile component of the system, antimony(V) oxide, are possible; Sb_2O_5 is known to eliminate oxygen in vacuum at as low as 700–800 K, transforming into Sb_2O_3 [2]. At 600–700 K, antimony(III) oxide, in turn, passes into the gaseous phase in the form of Sb_4O_6, Sb_2O_3, Sb_2O_2, and SbO. Data on Sb_2O_5 behavior in the course of the synthesis is nearly absent in the available literature.

In this work, we studied vaporization of the mixed oxide $Sr_2Mn_{0.01}Al_{0.99}SbO_6$ (applied in magnetoelectronics) and of the corresponding initial mixture containing the components in the stoichiometric ratio, using mass spectrometry method. According to the X-ray diffraction data, homogeneous samples can be obtained by isothermal annealing of the oxides mixture at 1173 K during 200 h. Noteworthily, the Sr_2MnSbO_6 mixed oxide can be prepared via 90 h calcination, other conditions being the same.

In the experiment, the oxides mixture was placed in one of the cells of dual effusion chamber, and the same mass of the mixed oxide $Sr_2Mn_{0.01}Al_{0.99}SbO_6$ was put into the other cell for comparative observation.

At about 1200 K, mass spectrum of the vapor over the oxides mixture contained peaks assigned to Sb^+, Sb_2^+, and SbO^+. The same peaks were observed in the spectrum of the vapor over the mixed oxide sample at about 1500 K. At 1900-1950 K, Sr^+ ions were detected in the mass spectra, whereas Al^+, Al_2O^+, and AlO^+ ions appeared at above 2000 K. Appearance energies of the mentioned ions corresponded to the ionization energies of Sb, Sb_2, SbO, Sr, Al, Al_2O, and AlO, respectively [3].

To summarize, at 1500–1600 K the vapors over both the oxides mixture and the mixed oxide consisted of atomic antimony, its dimer, and monoxide. Strontium oxide started to vaporize at higher temperature (about 1900 K), and aluminum oxide was only found in the vapor at above 2000 K. Fraction of manganese oxide in the samples was negligible, therefore, Mn^+ ions were not detected in the vapor mass spectra.

In this work we used effusion chambers made of molybdenum, allowing a sample to be evaporated completely. It would be more correctly to use inert platinum chambers, but it was impossible to perfectly clean them of strontium, manganese, and aluminum oxides after the experiment. Molybdenum acted as reducing agent interacting with antimony oxide; therefore, we observed products of the high-temperature antimony reduction in the vapor. Nevertheless, as the reducing action of molybdenum on the both specimens was identical, we could conclude on the evaporation features basing on the intensities of ionic currents.

At the initial stage of evaporation (1500 K), intensities of Sb^+, Sb_2^+, and SbO^+ ionic current in mass spectra of the vapor over the oxides mixture were 20–25 times higher than in those over the mixed oxide sample. Hence, in course of the mixed oxide preparation via ceramic method from the corresponding oxides, antimony oxide activity is considerably reduced due to formation of a solid solution or new chemical compounds. The latter possibility cannot be excluded, as the acid-base properties of strontium and antimony oxides are noticeably different. Even quailtatively, it is obvious that the antimony oxide activity in the mixed oxide is much lower than its molar fraction, which is typical of formation of thermally stable chemical compounds. After the equilibrium has been established, partial pressures gradually decrease due to selective evaporation of antimony oxide and reduction of its molar fraction in the condensed phase.

All the measurements were performed in vacuum; it is not easy to extrapolate the obtained results to the case of annealing in air. On the one hand, the observed oxygen loss suggests that the products vaporization in air should occur at higher temperature. On the other hand, data reported in [3] reveal that temperature of antimony oxide vaporization is much lower than the temperature used in our experiments. Evidently, to avoid antimony oxide losses, synthesis of the mixed oxides $Sr_2Mn_xAl_{1-x}SbO_6$ from the corresponding oxides should be run longer at sufficiently low temperature.

The experiments discussed herein were performed taking advantage of high-temperature mass spectrometry method with the MS-1301 mass spectrometer, energy of ionizing electrons being of 25 eV. The specimens were evaporated from a dual molybdenum effusion chamber heated up by electron bombardment. Temperature was measured with the EOP-66 optical pyrometer with accuracy of ±5 K at 1200–1850 K. The instrument was calibrated against the vapor pressure of CaF_2 prior to the experiment [4].

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