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Effect of Surface Melting on the Formation and Growth of Nanocrystals in the Bi_2O_3–Fe_2O_3 System

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Abstract—Formation of nanocrystals in the Bi_2O_3–Fe_2O_3 system prepared by the co-precipitation of bismuth and iron hydroxides has been studied. The temperature of onset of the $BiFeO_3$ and $Bi_2Fe_4O_9$ nanocrystals formation is correlated with the melting point of the non-autonomous phases. The optimal temperature of $BiFeO_3$ and $Bi_2Fe_4O_9$ nanoparticles synthesis is 460–520 and 500–550°C, respectively.

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Materials, including nanostructured ones, based on the compounds formed in the Bi_2O_3–Fe_2O_3–$BiFeO_3$ system ($Bi_2Fe_4O_9$ and γ-Bi_2O_3) are interesting due to the combination of magnetic, electrical, optical, and chemical properties [1–4]. The preparation of such materials, for instance, macrocrystalline and nanocrystalline $BiFeO_3$, revealed several complications [5]. One of the problems is the preparation of pure $BiFeO_3$, free of admixtures of other compounds existing in the Bi_2O_3–Fe_2O_3 system [5–7]. Despite numerous attempts to prepare nanocrystalline $BiFeO_3$ described in the literature, the reasons for obtaining the multiphase products have remained unclear [5, 7]. In view of this, the elucidation of the factors influencing the rate of formation and growth of the crystals in the Bi_2O_3–Fe_2O_3 system is an important task.

The data on the phases formation in the Bi_2O_3–Fe_2O_3 system revealed that upon dehydration of bismuth hydroxide the nanoparticles of sillenite (γ-Bi_2O_3) appeared, the rate of their formation being the highest at about 480°C (Fig. 1). These conditions corresponded to the liquefying of the particles surface [8–10], or, in other words, to melting of the non-autonomous phase based on bismuth oxide (at 460±40°C according to [10]), favoring the mass transfer along the grains boundaries. In the same temperature range, the formation of $BiFeO_3$ nanocrystals started (Fig. 1), their growth being activated at 520–540°C (Fig. 2). The latter temperature range was well correlated with the calculated melting point of the non-autonomous phase based on $BiFeO_3$ (520±40°C [10]). Again, the growth of $BiFeO_3$ crystal grains was accelerated due to the active mass transfer along the $BiFeO_3$ grain boundaries. The onset of the $Bi_2Fe_4O_9$ nanocrystals formation was observed at about 500°C; in the 500–550°C range, the fraction of $Bi_2Fe_4O_9$ phase and its crystal grains size were nearly constant (Fig. 1). The increase of the $Bi_2Fe_4O_9$ phase fraction and the steep increase in its crystal grains size occurred at 560–600°C (Figs. 1 and 2). Again, the latter temperature range was in agreement with the calculated melting point of the non-autonomous phase based on $Bi_2Fe_4O_9$ (550±50°C [10]).

Thus, the data on the phase fractions and the crystal grains size reported in Figs. 1 and 2 in general demonstrated good correlations of the temperature conditions of the efficient formation and growth of the nanocrystals with the respective melting points of the surface non-autonomous phases [8–10]. The possibility of such correlation was indicated in the papers on the solid-phase chemical reactions and the grain growth in the polycrystalline systems [11, 12].

The analysis of temperature effect of annealing the coprecipitated bismuth and iron hydroxides showed the decisive role of the non-autonomous phases melting in the formation and growth of nanocrystals in the Bi_2O_3–

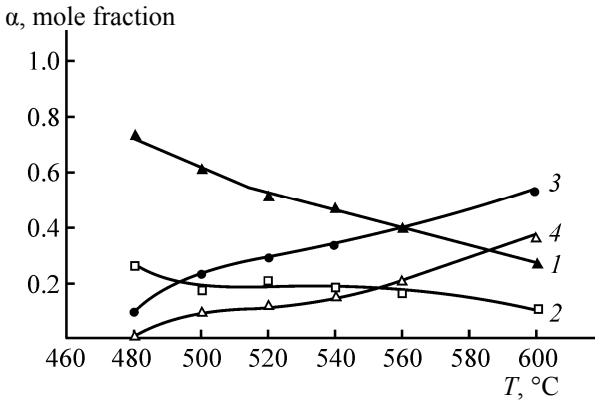

Fig. 1. Molar fraction of the phases as a function of isothermal annealing temperature. (*1*) γ-Bi_2O_3, (*2*) X-ray amorphous Bi_2O_3, (*3*) $BiFeO_3$, and (*4*) $Bi_2Fe_4O_9$.

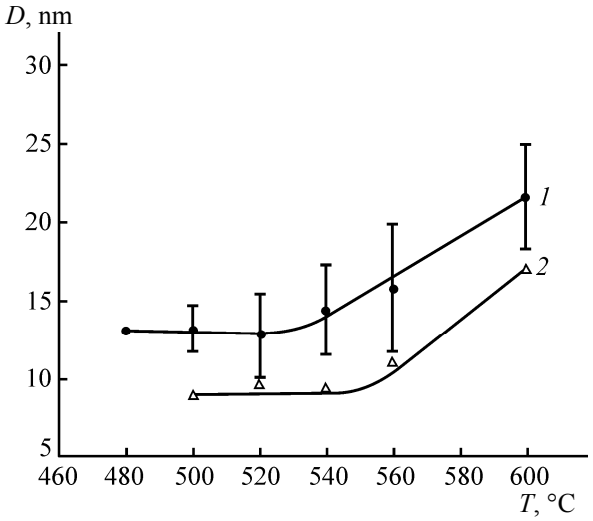

Fig. 2. Crystal grain size as a function of isothermal annealing temperature. (*1*) $BiFeO_3$ and (*2*) $Bi_2Fe_4O_9$.

Fe_2O_3 system. Thus, we concluded that the optimal temperature of the $BiFeO_3$ nanoparticles formation from the coprecipitated hydroxides was 480–520°C. The lower preparation temperature of the $BiFeO_3$ nanoparticles was only possible in the case of initial composition with significantly enhanced surface contact of the components; at the preparation temperature above the optimal range, the annealing time should be decreased in order to preserve the nanometer size range of the crystalline product. The optimal temperature of the $Bi_2Fe_4O_9$ nanocrystals preparation at the annealing the coprecipitated hydroxides was 500–550°C. At higher temperature, above the melting point of the non-autonomous $Bi_2Fe_4O_9$ phase, the grains growth was accelerated due to enhanced rate of the mass transfer along the grain boundaries.

EXPERIMENTAL

$BiFeO_3$ nanoparticles were prepared by thermal annealing of the hydroxides, obtained in turn by co-precipitation of bismuth nitrate (extra pure grade) and iron(III) nitrate (analytically pure grade) from 0.05 mol/L solution in diluted nitric acid with 25 wt % solution of NH_4OH. The hydroxides precipitate was washed with distilled water till ammonium ions were absent. Thermal annealing was performed at 480–600°C by stepwise heating with 30 min isothermal incubation at each step.

Elemental composition of the precipitated hydroxides (as determined by means of microanalysis with FEI Quanta 200 scanning electron microscope equipped with EDAX attachment) revealed that the [Fe] : [Bi] = 1.1±0.1 ratio corresponded to the $BiFeO_3$ stoichiometry. The fractions of the elements in the crystalline phases of the Bi_2O_3–Fe_2O_3 system were determined by X-ray diffraction analysis using XRD-7000 Shimadzu diffractometer equipped with HTK–1200N (Anton Paar) high-temperature attachment. The fraction of X-ray amorphous bismuth oxide was calculated from the reaction system mass balance. The crystal grains size was estimated using the Scherrer equation taking into account the broadening of X-ray diffraction lines. The lines broadening not associated with the particle size was corrected using the α-Al_2O_3 reference sample.

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