The Mechanism of $BiFeO_3$ Hydrothermal Synthesis

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The perovskite bismuth ferrite $BiFeO_3$ is a multiferroic material – ferroelectric (T_C = 1103 K) and antiferromagnetic (T_N = 643 K) – exhibiting weak magnetism at room temperature. Since the spins in this material take the form of a long-wavelength (62 nm) the spiral linear magnetoelectric effect averages to zero. One of the ways to recover the linear effect is by thin-film epitaxial constraints [1]; so we expected the same effects in nanostructured $BiFeO_3$. The phases appearing in the hydrothermal reaction in the Fe–Bi–O system were investigated, with the aim to study the conditions for the synthesis of nanostructural bismuth ferrite.

For the hydrothermal reactions a series of precipitations, with various molar ratios of iron and bismuth ions, were carried out. The solution of iron and bismuth salt was co-precipitated with a strong hydroxide to high pH values. The hydrothermal treatments were performed for 6 h at 200 °C in a stainless-steel Teflon-lined autoclave. The phase composition of the samples was studied by micro-Raman spectroscopy (RS) and was compared with X-ray powder diffraction (XRD) results. To avoid laser-induced thermal effects on the samples during the recording of the Raman spectra the laser power was carefully optimized. The morphologies and nanostructures of the different phases were determined using high-resolution transmission electron microscopy (HRTEM) and/or scanning electron microscopy (SEM). The chemical composition at the nanoscale was determined with energy-dispersive X-ray spectroscopy (EDXS).

$BiFeO_3$ was detected only in the samples with a higher content of Bi^{3+} ions, while in the case of the lower content of Bi^{3+} ions only the iron oxide and/or the iron-hydroxide phases with different Bi-doping were observed. Raman spectroscopy was used to clarify the possible existence of metastable maghemite or magnetite [2] in the samples with 3.5 and 5 mol% of bismuth, since it is difficult or impossible to distinguish between these two phases just from the XRD results. In the samples with 7.5 and 10 mol% of Bi^{3+} ions in the reactions, the hematite phase dominated. We observed that the bismuth ferrite did not form at these low Bi^{3+} concentrations and was detected only for contents above 30 mol%. However, at 20% of Bi^{3+} content a poorly crystalline, nanosized phase appeared during the sintering. This phase implies a formation step between the doped iron oxide/hydroxide phases and the $BiFeO_3$. RS, XRD and HRTEM results have to be combined for a proper and complete meaningful evaluation. In spite of the difficulties in synthesizing pure $BiFeO_3$ [3], this was achieved in a hydrothermal reaction with 50 mol% Bi^{3+}. The mechanism of the $BiFeO_3$ synthesis will be discussed in terms of the observed stable and metastable phases.

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[3] J.-T. Han, Y.-H. Huang, X.-J. Wu, C.-L. Wu, W. Wei, B.o Peng, W. Huang and J. B. Goodenough Adv. Mater. 18 (2006) 2145, and the references therein.