Mechanochemical Synthesis and Thermal Behavior of Metastable Mixed Oxides in the CaO–Sb$_2$O$_3$–Bi$_2$O$_3$ System

V. V. Zyryanov

Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences,
ul. Kutateladze 18, Novosibirsk, 630128 Russia

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Abstract—The phase composition of crystalline mechanochemical synthesis products in the CaO–Sb$_2$O$_3$–Bi$_2$O$_3$ system was determined. Of the known phases in this system, only three could be prepared mechanochemically: Ca$_2$Sb$_2$O$_5$, CaSb$_2$O$_4$, and ~CaBiO$_2$$_5$ (fcc). A new metastable phase, δ$^\prime$-Bi$_2$O$_3$, with an orthorhombic structure close to that of the high-temperature, fluorite phase δ-Bi$_2$O$_3$, was obtained by mechanical processing at ~30°C. A number of new metastable fluorite solid solutions of binary and ternary oxides were obtained as single-phase powders by mechanochemical synthesis. The mechanochemical yield of primary crystalline products was shown to be several times higher than that of secondary products. A broad composition range was revealed in which perovskite and fluorite phases are in mechanochemical equilibrium. The composition dependence of the lattice parameter of the metastable fluorite phase Bi$_{2-x}$Sb$_x$O$_3$ was found to be the opposite of the one predicted by Vegard’s law. Metastable mixed oxides undergo phase transformations during heating (starting at 280°C in the case of the ternary perovskite phase). Bi$_{2-x}$Ca$_x$O$_3$–0.5Sb$_3$O$_5$ fluorite solid solutions experience a transformation at ~400°C, accompanied by oxygen loss. During heating in air, Sb$_2$O$_3$-containing fluorite phases partially stabilize owing to oxidation but, nevertheless, undergo structural transformations above 480°C. The transformation of Sb$_{2-x}$Ca$_x$O$_3$–0.5Sb$_3$O$_5$ metastable fluorite solid solutions near 500°C in air is accompanied by the formation of needle-like Sb$_2$O$_3$ crystals. A mechanism is proposed for the extremely rapid growth of such crystals: extrusion of the Sb$_2$O$_3$ resulting from fluorite decomposition in agglomerates through triple junctions of aggregates and through cracks in the surface layer of agglomerates.

INTRODUCTION

The engineering of nanocrystalline ceramic materials is an important field of research because the mechanical, magnetic, dielectric, and other physical properties of such materials differ markedly from those of conventional ceramics with a grain size above 1 μm [1–4]. One of the most promising methods for preparing powders less than 100 nm in particle size, necessary for producing nanocrystalline materials, is the mechanochemical ceramic method (MCM) [5, 6]. The MCM may involve only dry mechanical treatment and separation steps, which provide powders suitable for compaction and sintering. The high density and good sinterability of the green bodies prepared from such powders ensure a high density of the resulting ceramics and a small grain size even at mild sintering conditions [5–7]. The most important advantage of the MCM is that, in contrast to many other routes to metal-oxide nanopowders, it offers the possibility of preparing metastable compounds via mechanochemical synthesis from oxide mixtures [7–10]. To date, more than 50 new metastable ternary oxides have been prepared—as individual compounds or in mixtures [6–11]. However, mechanochemical processes in ternary systems are essentially unexplored, even though many materials of practical importance consist of three or more oxides.

The ternary system CaO–Sb$_2$O$_3$–Bi$_2$O$_3$ is of considerable scientific and technological interest. According to the model for the reaction zone described in [11, 12], the mechanochemical yield in binary oxide mixtures of this system must be high because the reagents have large molecular weights and are close in hardness. At the same time, in ternary mixtures of this system the yield would be expected to be much lower because of the small contribution of the roll mechanism to mass transfer in secondary impacts. Bi$_2$O$_3$-rich compounds in this system may be of interest as superionic conductors [13], while Sb$_2$O$_3$-rich compounds are potentially attractive as materials for proton conductors, gas sensors, and selective absorbents similar to antimonic acid [14, 15].

EXPERIMENTAL

All of the starting chemicals were of analytical grade: CaO calcined at 900°C immediately before synthesis to remove moisture and carbonate impurity, orthorhombic Sb$_2$O$_3$ (valentinite), and monoclinic Bi$_2$O$_3$ (bismite).
The techniques used were similar to those described previously [8, 9]. Powder mixtures were processed at 60 g in an AGO-2 planetary mill with water-cooled steel jars (2 × 150 cm³) and steel balls (9 mm diameter) [16]. The surfaces of the balls and jars were coated with the oxide mixture as described earlier [17]. Every 30 s of processing, the mill was shut off and positive mixing was performed. This procedure prevented contamination and improved the homogeneity of the powder. The ball load was 200 g and the sample weight was 15 g.

To assess the kinetics of mechanochemical synthesis, four or five 1-g samples were taken during the process. After 10 min of milling, the Fe content of the powder was within 0.02 wt %. Reducing the sample weight to 6 g and increasing the milling duration to 30 min (supplied energy of 100 MJ/kg) increased the amount of Fe contamination, which remained, however, not very high, about 0.2 wt %. Fe was present mainly in the form of coarse inclusions. The half-conversion energy $E_{1/2}$ was evaluated from conversion versus supplied energy data. Conversion was assessed from x-ray diffraction (XRD) data as the average over the starting reagents. The procedure we used, in conjunction with water cooling, allowed the jar temperature to be reduced to = 330 K, which prevented thermal annealing of metastable products.

XRD analysis was performed on a DRON-3M powder diffractometer (CuKα radiation). Thermal analysis (DTA + TG) was carried out in air using platinum crucibles (Paulik–Paulik–Erdey thermoanalytical system). The morphology of the decomposition products was examined on a JSM-T20 scanning electron microscope.

RESULTS AND DISCUSSION

Figure 1 shows a diagram (analogous to conventional phase diagrams) of mechanochemical synthesis products at supplied energies in the range 20–100 MJ/kg. The known ternary oxides (JCPDS PDF) are indicated outside the diagram. As seen, mechanical treatment yields only the stable tetragonal phase CaSb₂O₅ (PDF 29-0292), Ca₂Sb₂O₅ (PDF 20-0208, unindexed XRD pattern), and an fcc phase similar to the liquid-quenched phase Bi₁₀Ca₉O₅·₅₅ (PDF 40-0314). For simplicity, the metastable “phases” are assumed to have the same composition as the starting mixtures from which XRD single-phase samples were obtained. Actually, compounds prepared by mechanochemical synthesis do not fully satisfy the definition of a thermodynamic phase: they have neither sharp boundaries nor a definite composition, and their characteristics depend on processing conditions (in particular, on the supplied mechanical energy). The XRD patterns containing broad reflections from conventional crystal-