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$Ba_{2.1}Bi_{0.9}(O, F)_{6.8-\delta}$: A new ordered anion-excess fluorite

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Abstract

The anion-excess ordered fluorite-related phase $Ba_{2.1}Bi_{0.9}(O, F)_{6.8-\delta}$ has been synthesized by a solid state reaction of BaF_2, BiF_3 and Bi_2O_3 at 873 K with subsequent short annealing at 573 K. The crystal structure of the new phase has been solved using electron diffraction and X-ray powder diffraction ($a = 9.5372(1)$ Å, $c = 18.1623(3)$ Å, space group $I4/m$, $R_I = 0.025$, $R_P = 0.029$). Interstitial anions in the fluorite-based structure are considered to form isolated cuboctahedral 8:12:0 clusters. The structural relationship between the oxyfluoride phase $Ba_{2.1}Bi_{0.9}(O, F)_{6.8-\delta}$ and similar rare-earth-based fluorides is discussed.

Keywords: A. Fluorides; C. X-ray diffraction; C. Electron diffraction; D. Crystal structure

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1. Introduction

The interest of compounds with a fluorite-derived structure in systems containing Bi(III) increased because of their prospects as ionic conductors at rather low temperatures (below 800 K) [1]. Nevertheless, compared with similar systems with rare-earth cations, Bi-based fluorites are not well studied [2]. A detailed investigation of such compounds is probably hampered by the synthesis difficulties: fluorine-containing Bi-based compounds are prone to pyrohydrolysis and easily decompose to metallic Bi at reductive conditions. It concerns not only the bismuth fluorides, but also the generally more stable bismuth oxyfluorides. Only a few of the Bi^{3+}-based fluorides and oxyfluorides are structurally characterized: $BiZr_3F_{15}$ [3], $MBiF_4$ (M = K, Rb) [4], $CsBi_2F_7$ [5], $Bi(O, F)_{2.45}$ [6], $Bi_7F_{11}O_5$ [7], $Ba_4Bi_3F_{17}$ [8].

For anion-excess fluorides and oxyfluorides with the fluorite-type structure the hypothesis on an association of anionic defects (clustering) is commonly used for establishing the ‘‘composition-structure-properties’’ relationship. A detailed description of known types of anionic clusters along with the notation system is given in refs. [9,10]. For example, the cuboctahedral 8:12:0 or 8:12:1 clusters are commonly considered as strongly affecting the ionic transport properties. The anionic clustering approach is well developed for the ordered and disordered fluorite-like rare-earth-based compounds [11,12] and can also be used for the Bi-containing phases [8]. The most solid direct proof for cluster formation is usually obtained by structural analysis of the ordered fluorite-like phases with chemical composition

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close to that of the disordered solid solutions. For example, in the BaF_2–BiF_3 system near the disordered $Ba_{1-x}Bi_xF_{2+x}$ solid solution ($x < 0.45$ at 973 K [13] or $x < 0.28$ at 873 K [14]) the ordered $Ba_4Bi_3F_{17}$ compound is observed; it contains isolated cuboctahedral clusters, as evidenced by electron and X-ray powder diffraction [8]. The homogeneity areas are described for the $M^{II}{}_4M^{III}{}_3F_{17}$-based phases with variable cation M^{II}/M^{III} and anion F^-/O^{2-} ratio [2,8,13,15].

The investigation of the BaF_2–Bi_2O_3–BiF_3 system revealed a formation of a new tetragonal fluorite-like phase [14]. This new, most probably oxyfluoride phase forms at slow cooling of the disordered BaF_2-based cubic solid solution $Ba_{1-x}Bi_xO_zF_{2+x-2z}$ and probably belongs to the fluorite family with an ordered arrangement of anionic defects. The formation of this phase explains a non-monotonic temperature dependence of the ionic conductivity of the $Ba_{1-x}Bi_xO_zF_{2+x-2z}$ fluorite-like solid solutions. In the present contribution, we describe the chemical composition and the crystal structure of this new ordered fluorite-like phase as determined by X-ray powder diffraction and electron diffraction (ED).

2. Experimental

The preparation of $Ba_{1-x}Bi_xO_zF_{2+x-2z}$ solid solutions was described in detail in ref. [14] and will be only briefly summarized here. The mixed powders of BaF_2, BiF_3 and Bi_2O_3 ($x = 0$–0.40, $z = 0$–0.25 with step of 0.05 for $Ba_{1-x}Bi_xO_zF_{2+x-2z}$) were pressed into pellets and heated in sealed Ar-filled copper tubes at 873 ± 10 K for 24 h, subsequently cooled down to 573 K with a rate of 1.5 K/min and annealed at 573 K for 4 days and quenched in icy water. In order to get better quality of the samples of the new ordered fluorite-like phases, different modifications of the synthesis procedure were also tried: quenching from 873 K to room temperature, solid state reaction at 573 K for 8 days, slow cooling down to room temperature after annealings at either 873 K or 573 K.

X-ray powder diffraction analysis was performed with a focusing Guinier camera FR-552 (Cu $K\alpha_1$ radiation) using germanium as an internal standard. X-ray powder diffraction data for the structure refinement were collected on a STADI-P diffractometer (Cu $K\alpha_1$ radiation, curved Ge monochromator, foil transmission mode, linear PSD). The JANA2000 program package was used for Rietveld refinement of the crystal structure [16].

Samples for transmission electron microscopy were made by crushing the crystals in ethanol and depositing fragments on a holey carbon grid. Electron diffraction and energy-dispersive X-ray (EDX) analysis were carried out using a Philips CM20 microscope with a LINK-2000 attachment.

3. Results and discussion

The new tetragonal phase was reproducibly obtained in different oxygen-containing $Ba_{1-x}Bi_xO_zF_{2+x-2z}$ samples, but was never observed in the samples with $z = 0$ (i.e. without oxygen). In all samples the tetragonal phase was present along with some amount of admixtures of the fluorite-like solid solutions based on the BaF_2 and $Ba_4Bi_3F_{17}$ structures. It should be noted that the preparation of this material is strongly depends on the conditions of the thermal treatment. The tetragonal phase is absent in the samples quenched from 873 K, as well as in the samples annealed for longer time (8 days) at 573 K and slowly cooled or synthesized at this temperature from the initial materials. Since the structural investigation described below reveals that this new tetragonal phase belongs to an ordered variant of the anion-excess fluorites, one can expect that the anion ordering is strongly influenced by even small deviations in the heating and cooling regime, so that other competing fluorite phases with different anion ordering patterns are always present in the sample. The largest abundance of the new tetragonal phase was observed in a sample with nominal composition $Ba_{0.7}Bi_{0.3}O_{0.1}F_{2.1}$ synthesized at 873 K, cooled down to 573 K and annealed at this temperature for 4 days.

Aside from the tetragonal main phase, the oxyfluoride solid solutions based on the $Ba_4Bi_3F_{17}$ and BaF_2 phases were found as admixtures. Hence, one can assume that this tetragonal ordered phase either has narrow temperature field of stability or is not an equilibrium product and should be absent on the phase diagram of the BaF_2–Bi_2O_3–BiF_3 system. Since it is not possible to determine the exact anion composition of the admixture phases, the composition of the main phase can be deduced as $Ba_{0.7}Bi_{0.3}O_xF_{2.3-2x}$ according to the results of the EDX analysis (see below) and the electroneutrality requirement (assuming Bi in the oxidation state +3). The