CRYSTAL CHEMICAL PRINCIPLES OF
SELECTIVE SYNTHESIS OF
BISMUTH-CONTAINING PHASES WITH
PEROVSKITE-LIKE STRUCTURES

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Bismuth-containing phases with perovskite-like structures were systematized and assigned to 11 homologous series. For two phases differing in bismuth coordination, $Bi_2A'_kA''_kCu_{k+1}O_x$ and $Bi_2A'_kCu_{k+1}O_x$, crystallochemical principles of their formation are defined. The range of existence of these phases was found and confirmed by syntheses.

The structural type of perovskite is a parent structure for a general homologous series, in particular, $Bi_2A'_kA''_k'M_{k+1}O_x$ and $Bi_2A''_kA''_kCu_{k+1}O_x$. These phases are formed by several ($k$) blocks of perovskite $A''MO_x$ ($CNA'' = 12$, CP is cuboctahedron; $CNM = 6$, CP is octahedron; $CN$ and $CP$ are coordination number and coordination polyhedron, respectively). The blocks are combined with the layers: $Bi_2A''_kO_x$ in the former case ($CNBi = 5+1$, CP is distorted octahedron; $CNA' = 9$, CP is side-centered antiprism), and $Bi_2O_2$ in the latter ($CNBi = 4+4$, CP is tetragonal antiprism with Bi atoms shifted away from the center).

The phases of the $Bi_2A''_kM_{k+1}O_x$ homologous series are known in the literature as Aurivillius phases [1]. They generally have a formal charge (FC) of $4+$ or $5+$ on $M$ and $2+$ or $3+$ on $A''$. The phases of the $Bi_2A''_kA''_kM_{k+1}O_x$ series were obtained only recently [2]. They have FC of $3+$ on $M$ and $2+$ and $3+$ on $A'$ and $A''$. A distinctive feature of these structures is that at $k = 2n$ all $A''$ cations are shifted from the center of the cuboctahedron due to different effects of the surrounding polyhedra of various types, and at $k = 2n+1$ one $A''$ cation lies at the center of the cuboctahedron, through which the symmetry plane passes, while the other $A''$ cations are shifted from the center. The latter case suggests that the phases contain different types of $A''$ (e.g., $Bi^{3+}$ and $Ba^{2+}$, or $Bi^{3+}$ and $Sr^{2+}$), with one type of cation lying at the center of the cuboctahedron and another shifted from the center toward the cuboctahedron base.

With $M = Cu$, we have particular homologous series: $Bi_2A'_kA''_kCu_{k+1}O_x$ (A series) and $Bi_2A'_kCu_{k+1}O_x$ (B series). In these structures, the coordination polyhedra of $A'$ and $A''$ cations are tetragonal prism (CN8) and side-centered antiprism (CN9), respectively; for $Cu$ cations, tetragonal pyramid (CN5) and square (CN4). The coordination polyhedron of $Bi$ is the same as in analogous structures of the general homologous series. These phases, however, differ not only in structures but also in properties; the phases of the A series are superconductors in the range of $T_s$ (temperature of transition to the superconducting state) from 8 to 110 K depending on the value of $k$, whereas the phases of the B series are not.

The purpose of this work is to reveal the effects that govern the stability of these phases and determine the range of their existence.
EXPERIMENTAL

As starting reagents we used oxides and carbonates of the corresponding metals of “a” grade, previously calcined in air at 200°C to remove moisture. The phases were synthesized by a solid-phase reaction of the starting reagents in air in alundum crucibles placed in a horizontal tube furnace.

Samples of the Bi$_2$A$_{4-k}$Cu$_{1+k}$O$_x$ series were prepared in several stages with intermediate grinding and compacting in pellets. At each stage the reaction temperature was 800-860°C; the temperature was maintained within 10°C, reaction time 10 h. The samples were further cooled together with the furnace at an average rate of 40-50 °C/min. The Bi$_2$A$_{4-k}$Cu$_{1+k}$O$_x$ samples, including the particular case of M = Cu, were obtained at 850-860°C during 2-3 h with subsequent intense cooling by “air quenching.”

X-ray diffractograms of the samples were recorded on a DRON-2.0 diffractometer (CuK$_\alpha$ radiation, planar graphite monochromator). The X-ray diffraction data of the obtained phases were compared with those given in the ASTM card file and in original papers. The cell parameters of the main phases were determined from reflections, with 29 ranging from 2 to 70° and refined by the least squares method.

The temperature of transition to the superconducting state was determined by the standard procedure of measuring the electric resistance of samples as a function of temperature up to 4.2 K.

RESULTS AND DISCUSSION

The phases of the Bi$_2$A$_{4-k}$Cu$_{1+k}$O$_x$ homologous series were first reported in [3]; in [4] the crystal structure of Bi$_2$(Ca, Sr)$_3$Cu$_4$O$_x$ (2304) was given, which is presently the only member of this series with $k = 3$. The crystal chemical formula of this phase is Bi$_2$(Ca, Sr)Sr$_2$Cu$_4$O$_x$, i.e., the crystallographic positions occupied together by (Ca, Sr) and (Sr) cations are nonequivalent, despite the same form of coordination polyhedron: CN(Ca, Sr) = 8 ($d_{\text{A}-\text{O}} = 2.59$ Å, $d_{\text{A}-\text{O}}$ is the cation–anion interatomic distance) and $d_{\text{Sr}-\text{O}} = 4+4$ ($d_{\text{Sr}-\text{O}} = 2.64$ and 2.78 Å) [4].

The results of the syntheses are given in Table 1. From the Bi(Ca$_{0.7}$Sr$_{1-y}$)$_2$Cu$_2$O$_x$ charge at $0.33 < y < 1$ (1.12 Å $< r_{\text{vIII}} < 1.21$ Å; 2.465 Å $< d_{\text{A}-\text{O}} < 2.56$ Å; $r_{\text{vIII}}$ is the weighted mean radius of the A’ cation according to Shannon’s system [5]) the Bi$_2$CaSr$_2$Cu$_4$O$_x$ (2122) phase is predominantly formed, which belongs to the A series with $k = 1$. At $0.25 < y < 0.33$ (1.21 Å $< r_{\text{vIII}} < 1.225$ Å, 2.555 Å $< d_{\text{A}-\text{O}} < 2.57$ Å) Bi$_2$Sr$_2$Cu$_4$O$_x$ (2021) was obtained, also belonging to the A series with $k = 0$. The Bi$_2$(Ca, Sr)$_3$Cu$_4$O$_x$ (2304) phase of the B series with $k = 3$ was synthesized at $y = 0.25$ ($r_{\text{vIII}} = 1.255$ Å, $d_{\text{A}-\text{O}} = 2.57$ Å) (at $0 < y < 0.25$, phases with the superstructure of the Bi$_2$Sr$_2$Cu$_4$O$_x$ structure are formed). Hence the (A’O$_8$) tetragonal prism in the Bi$_2$CaSr$_2$Cu$_4$O$_x$ structure (A’ = Ca) is stable at $e_1 < r/R < e_3$, $e_1 = 0.732$, $e_3 = 0.910$ (e$_h$ and e$_l$ are the highest and lowest limits of polyhedron stability, respectively [6]). At $r/R > 0.910$ a coordination polyhedron with CN9 (4+4+1) is formed, and the 2122 structure is converted to 2304. At the interface between these two phases, the nonequilibrium 2304 phase is formed (judging by experimental data), where the A’O$_8$ (A’ = Ca, Sr) tetragonal prism is at the highest limit of its stability.

Such an increase in the size of the A’O$_8$ polyhedron should be accompanied by compression of the A”O$_9$ polyhedron and a tendency toward formation of the A”O$_{12}$ cubo-octahedron with equalization of distances in the BiO$_6$ octahedron (CN6) and simultaneous “decoupling” of the Bi$_2$O$_2$ layer. All this could lead to a phase with a Bi$_2$CaSr$_2$Cu$_2$O$_x$ (1122) structure (the Bi–O bond is directed along (100) or (hk0)). But this is possible only for Bi$_5^{3+}$ ($r_{\text{VIII}} = 0.76$ Å) or for a cation lying in the bismuth position with a higher formal charge and a smaller radius ($r_{\text{VIII}} = 1.03$ Å) than those of Bi$_3^{3+}$, needed for conjugation of all bonds and compensation of formal charges in the structure. The latter condition is satisfied by Pb$_4^{2+}$ ($r_{\text{Pb}} = 0.79$ Å); the 1122 phase was obtained with just this cation (Table 1, sample No. 22).

For Bi$_3^{3+}$, formation of a tetragonal antiprism with CN(4+4) is possible. In this case, A” (Sr) has CN(4+4) (A” $\rightarrow$ A’) (CPA’ is tetragonal prism), and a phase with a Bi$_2$(Ca, Sr)$_3$Cu$_4$O$_x$ structure is formed. Neither Pb$_2^{2+}$ nor Ti$_3^{3+}$ possess this ability (Table 1, samples No. 23, 26).