The present paper describes the synthesis, characterization of mixed-valence bismuthates with three- or two-dimensional perovskite-like structures and structural criteria that influence superconductivity in these compounds.

Single-phase samples of Sr$_{1-x}$K$_x$BiO$_3$ were prepared for the broad range of K-content $0.25 \leq x \leq 0.65$. For these bismuthates the symmetry of the structure changes from monoclinic to orthorhombic and finally to tetragonal upon increasing the K-content thus resulting in the decrease of the Bi–O distances and reduction of the network distortions. Superconductivity with maximum $T_c = 12$ K exists in the narrow range $(x \approx 0.5$–$0.6)$ within the stability field of the tetragonal phase $(0.33 \leq x \leq 0.65)$, when the three-dimensional octahedral framework has close to the ideal perovskite structure arrangement.

The layered type (Ba,K)$_2$Bi$_2$O$_5$ and (Ba,K)$_2$BiO$_4$ bismuthates belonging to the $A_{x+1}B_xO_{3x+1}$ homologous series were investigated. Buckling of the (BiO$_3$) layers in the structure of the $n = 2$ member occurs due to the ordering of alkaline- and alkaline-earth cations between two independent positions. The formation of the one-layer bismuthate was revealed by Electron Microscopy and XRPD studies. Both types of compounds are considered to be possible candidates for new superconducting materials among bismuthates.

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1. Introduction

The discovery of superconductivity in Bi-based perovskite oxides has attracted significant attention to these compounds. Pioneering works by Sleight et al. (BaPb$_{0.75}$Bi$_{0.25}$O$_3$, $T_c = 12$ K) [1], Mattheis et al. [2] and Cava et al. (Ba$_{0.6}$K$_{0.4}$BiO$_3$, $T_c = 30$ K) [3] have inspired the further search for new superconductors among Bi-based oxides. More recently, Kazakov et al. (Sr$_{0.4}$K$_{0.6}$BiO$_3$, $T_c = 12$ K) [4] and Khasanova et al. (K$_{0.87}$Ba$_{0.13}$Bi$_2$O$_3$, $T_c = 10$ K and La$_{0.2}$K$_{0.8}$BiO$_3$, $T_c = 12$ K) [5,6] have discovered new Bi-containing superconducting perovskites with similar structures possessing a three-dimensional framework of BiO$_6$ octahedra.

The $T_c$'s record holder among Bi-based superconductors is Ba$_{1-x}$K$_x$BiO$_3$ ($x \approx 0.4$) with a perovskite structure. Superconductivity exists in the most symmetric cubic phase near metal-insulator transition associated with the phase transition from cubic to orthorhombic phase when the potassium concentration decreases [7]. An increase of the potassium content in cubic Ba$_{1-x}$K$_x$BiO$_3$ leads to the decrease of $T_c$ till complete suppression of superconductivity at $x \approx 0.75$ [8]. Sr$_{1-x}$K$_x$BiO$_3$ exhibits superconductivity ($T_{c_{\text{max}}} = 12$ K) in the narrower range of composition ($x \approx 0.5$–$0.6$) with the Bi valence close to $+4.6$, while the optimally doped
(x = 0.4 as for Ba-based bismuthate) tetragonal phase is not superconducting. The goal of our work was to synthesize Sr_{1-x}K_xBiO_3 in the wide range of compositions, investigate the structure-properties correlations and the factors influencing superconductivity in Sr_{1-x}K_xBiO_3, possessing three-dimensional crystal structure.

At the same time an investigation of layered bismuthates is certainly worthwhile; both for searching new superconductors as well as for attempting to understand the influence of dimensionality on the physical properties of mixed Bi-based oxides. The structures of layered plumbates and bismuthates belong to the Ruddlesden-Popper homologous series Ba_{n+1}(Pb_{1-n}Bi_n)_{3n+1}O_3n+1 and can be described as an alternate stacking of perovskite and rock-salt blocks along the c-axis (Fig. 1a and b). Among the plumbates the first three members were identified, and their transport properties change from semiconducting to metal-like upon n increase. Though these compounds can be doped to an electron concentration of about 0.25 per (Bi,Pb), which is optimal for superconductivity in BaPb_{1-x}Bi_xO_3 they do not become superconductors [9].

In contrast to the plumbates, only the n = 2 member of the A_{n+1}Bi_xO_{3n+1} family was obtained so far. Ba_{1.7}K_{1.3}BiO_7 can be obtained electrochemically [10] while Sr_{1.6}K_{1.4}Bi_2O_7 is prepared at elevated oxygen pressure [11]. According to band structure calculations the layered bismuthates should be more promising for superconductivity than the plumbates because of an increased binding energy of the atomic Bi (6s) level. In contrast to semiconducting Ba_{2-y}Pb_2O_7, a metallic behaviour and possible superconductivity is predicted for Ba_{2-x}K_{1+x}Bi_2O_7 at appropriate Ba/K ratio [12].

The absence of superconductivity in Ba_{1.7}K_{1.3}BiO_7 and Sr_{1.6}K_{1.4}Bi_2O_7 was explained by the high oxidation state of Bi (+4.65 and +4.7, respectively). Conditions under which this oxidation state could be reduced to more favorable value for superconductivity (about +4.4 as in the Ba_{0.6}K_{0.4}BiO_3) were not found so far. Since the possibility remains that these compounds would exhibit superconducting properties, the investigation of layered bismuthates was made.

2. Sample preparation

Samples of Sr_{1-x}K_xBiO_3 (0.2 ≤ x ≤ 0.65) were synthesized using high pressure high temperature technique at 700–900 °C and 20–50 kbar for 20–60 min. Appropriate amounts of SrO, KO_2 (96%) and Bi_2O_3 were mixed in a dry box filled with argon and placed into gold or platinum capsules. The role of oxygen stoichiometry in the initial mixtures should be emphasized. These syntheses require very oxidizing conditions, insufficient oxygen content in the starting compositions strongly affects on the samples final phase purity. In these experiments an excess of KO_2 was used as a source of extra oxygen.

It was shown earlier that in the Ba(K)–Bi–O system the conventional calcination in air at temperatures 800–950 °C using different precursors resulted in formation of three-dimensional perovskite phases without any sign of layered compounds. The previous studies demonstrate that synthesis at low temperatures (400–500 °C) might be successful if more reactive starting materials (such as alkali and alkali-earth oxides) are chosen. The high chemical activity of KO_2 and BaO, as well as the volatility of KO_2 require synthesis in closed vessels. The initial operations were performed in a glove box filled with purified Ar, and the syntheses were carried out in a sealed quartz ampoule or a closed steel container. Considering the volatility of KO_2, several starting mixtures with an excess of KO_2 were prepared.

3. The three-dimensional Sr_{1-x}K_xBiO_3 bismuthates

3.1. The evolution of the Sr_{1-x}K_xBiO_3 crystal structure by a variation of K-content

Four single-phase Sr_{1-x}K_xBiO_3 samples having different K-concentration (x = 0.24, 0.33, 0.43 and 0.6) were selected to study an influence of structure parameters on superconducting properties in this family.

The distorted perovskite-like structures can be derived from the parent cubic perovskite ABO_3 by applying a combination of distortions: such as a tilt of BO_6 octahedra along different axes and shift of an anion along the B–O–B bond (breathing-mode distortion).

[Fig. 1. Crystal structures of the n = 2 (a) and n = 1 (b) member of the (Ba,K)_{n+1}Bi_3O_{3n+1} family. Bi atoms are placed in the octahedra.]
These distortions could occur both separately and together giving rise to the large number of distorted perovskite structures. Using the Glazer’s approach for the Sr1–xKxBiO3 compounds following tilt distortions of the framework could be considered: tetragonal $a^0d^0c^-$ (I4/mcm), $d^0d^0c^+$ (P4/mmm); orthorhombic: $a^{-a^{-}c^+}$ (Pnma), $a^{-a^{-}c^{-}}$ (Imma); rhombohedral: $a^{-a^{-}a^{-}}$ (R3c) and monoclinic: $a^{-a^{-}c^{-}}$ (12/a).

The crystal structure of Sr0.76K0.24BiO3 was refined from X-ray powder diffraction data. Initially, the structure of Sr0.4K0.6BiO3 was proposed as a starting model. However, the XRD patterns contain number of weak reflections forbidden in the I4/mcm space group (011, 111, 210, 131). Therefore, the choice of space groups was limited to tetragonal P4/mmm and orthorhombic Pnma. Moreover, the (011) reflection can exist only in the latter space group, which was used for the structure refinement. The crystal structure of Sr0.76K0.24BiO3 shown in Fig. 2a is strongly distorted perovskite-like one with two successive tilts of BiO₆ around the [1 1 0]p and [0 0 1]p axes. There is only one position for Bi cations in flattened BiO₆ octahedron. Three pairs of Bi–O distances are present: the short one at 2.138(2) Å and two longer ones at 2.19(2) Å and 2.20(2) Å. Alkaline-earth/alkali cations occupy a strongly distorted cubooctahedron cavity inside the BiO₆ octahedral framework.

The XRD patterns of Sr0.67K0.33BiO3 and Sr0.57K0.43BiO3 do not contain any extra reflections compared to that one for Sr0.6K0.4BiO3 therefore the refinements were made in the I4/mcm space group. These compounds have distorted perovskite structures with octahedral tilt around the [0 0 1]p axis (Fig. 2b). An increase of the potassium content in Sr0.67K0.33BiO3, Sr0.57K0.43BiO3 and Sr0.6K0.4BiO3 results in the decrease of the BiO₆ octahedron distortion and tilt angle (Fig. 3). In the structure of Sr0.67K0.33BiO3 there are two short apical (2.115(2) Å) and four long equatorial (2.175(3) Å) Bi–O distances. Successive increasing the potassium content leads to a monotonic shrinkage of the equatorial Bi–O distances while apical ones practically do not change. The octahedron distortion and tilt angle are minimal in the superconducting Sr0.6K0.4BiO3 structure.

The increase of the potassium content in Sr1–xKxBiO3 causes the successive increase of the symmetry of the unit cell from monoclinic (SrBiO3) via orthorhombic (Sr0.76K0.24BiO3) to tetragonal (Sr0.67K0.33BiO3) to Sr0.4K0.6BiO3. Structure transformation (Pnma → I4/mcm) is accompanied by decreasing the distortion of the octahedral framework. The orthorhombic structure exhibits two octahedral tilts along the [1 1 0]p and [0 0 1]p axes ($a^{-a^{-}c^+}$ in Glazer’s notation). The octahedral tilt along [1 1 0]p is completely vanished when the structure transformation from orthorhombic (Sr0.76K0.24BiO3) to tetragonal (Sr0.67K0.33BiO3) occurs. However, in the tetragonal phase two adjacent (BiO₆)₃ layers are rotated along the c-axis in opposite direction (anti-phase tilt $c^-$), while in the orthorhombic phase the in-phase tilt ($c^+$) takes place. Within the range of the tetragonal phase the distortion of the octahedral framework tends decreasing with increasing K-content.

### 3.2. Superconductivity in three-dimensional bismuthates

Superconductivity in the Ba1–xKxBiO3 system appears at the boundary of metal–insulator transition associated with structural phase transition to the phase with maximum symmetry. The superconducting range ($x \approx 0.5–0.6$, $T_c,max = 12$ K) in the Sr1–xKxBiO3 solid solution is significantly smaller than the stability field of the tetragonal phase at ambient conditions. The Fig 4 represents the dependence of $T_c$ vs. bismuth valence for different Bi-based oxide superconductors. Increasing bismuth valence in Ba1–xKxBiO3 results in the decrease of $T_c$ till suppression of superconductivity at $x \approx 0.75$ [8]. In Ba0.45K0.55BiO3 ($T_c = 17$ K) and Ba0.34K0.66BiO3 ($T_c = 7$ K) the values of Bi valence are +4.55 and +4.66, respectively. These valences are very close to those ones in superconducting Sr0.4K0.6BiO3 and La0.3K0.8BiO3, which have close values of $T_c$. The crystal structures of Ba- and La-containing bismuthates are cubic, while superconducting perovskite with Sr has the tetragonal crystal

![Fig. 2. The crystal structures of Sr0.76K0.24BiO3 (a), Sr0.67K0.33BiO3 and Sr0.6K0.4BiO3 (b).](image-url)
structure. Therefore, one can conclude that carrier concentration in the conducting band (formal Bi valence) is a key factor for $T_c$ in three-dimensional bismuthates.

According to the theoretical calculations of the optimal carrier concentration for superconductivity in bismuthates, the conducting band filling should be as close as possible to the half-filled band condition for a maximum electron-phonon interaction (Bi valence should be close to +4). The maximum $T_c$ is observed for Ba$_{6.3}$K$_{0.37}$Bi$_3$O$_7$ ($\nu$(Bi) ≈ +4.4), while at the lower K-content structure transforms to the distorted orthorhombic one, which does not exhibit superconductivity. One can assume, that the distortions of the octahedral framework affect $T_c$ in Sr$_{1-x}$K$_x$Bi$_2$O$_4$, Sr$_{0.67}$K$_{0.33}$Bi$_2$O$_4$, and Sr$_{0.57}$K$_{0.43}$Bi$_2$O$_4$, with Bi valence close to that one in superconducting Ba-analogue do not exhibit any sign of superconductivity. The proximity of the average Bi-O bond distances ($d_{\text{Bi-O}} \approx 2.15$ Å) in these compounds with the same K-content indicates that the Bi valence is about the same in Sr- and Ba-bismuthates. However, in the structures of Sr-containing bismuthates the octahedral framework is strongly distorted ($\angle\text{Bi-O-Bi} = 152.6(2)^\circ$) in contrast to the ideal one in Ba$_{6.3}$K$_{0.37}$Bi$_3$O$_7$ ($\angle\text{Bi-O-Bi} = 180^\circ$). Moreover, the distortions of the octahedron in Sr$_{0.67}$K$_{0.33}$Bi$_2$O$_4$ could be another reason for the change of the band structure leading to charge localization and suppression of superconductivity.

4. Layered bismuthates: (Ba,K)$_{n+1}$Bi$_n$O$_{3n+1}$ ($n = 1$ and 2)

According to preliminary investigations the layered bismuthate, (Ba,K)$_3$Bi$_2$O$_7$, can be obtained in the temperature interval 300–475 °C. Synthesis at 400–450 °C was found to be optimal, while no (Ba,K)$_3$Bi$_2$O$_7$ was detected at higher temperatures. The composition of the samples depends on the heating regime and the starting composition. Since we were particularly interested in the (Ba,K)$_3$Bi$_2$O$_7$ phase with the higher Ba-content (i.e. with the appropriate lower oxidation state of Bi), mixtures with a high Ba-concentration were prepared. For “stochiometric” initial mixtures, the formation of (Ba,K)$_3$Bi$_2$O$_7$ was observed when the samples were placed in a hot furnace. These samples were ill crystallised, that resulted in broadened XRD peaks, and contained small amounts of impurities. The (Ba,K)$_3$Bi$_2$O$_7$ phase is formed for both heating regimes, when the starting mixtures contain an excess of KO$_2$. However these samples always contained impurity phases, furthermore their amount increased with increasing Ba/Bi ratio. These impurities were identified as a perovskite related phase (Ba,K)$_3$Bi$_2$O$_7$ (with $a_0 = 4.29$–4.30 Å, and the excess of potassium was detected as KOH on the XRD spectrum. Diffraction patterns of the (Ba,K)$_{3}$Bi$_{2}$O$_{7}$ phase were indexed in the tetragonal 14/mmm space group with $a = 4.25$ Å and $c = 21.8$ Å as should be expected for the $n = 2$ member of the Ruddlesden-Popper series (Ba,K)$_{n+1}$Bi$_n$O$_{3n+1}$.

The structural parameters for this phase refined from XRD powder data are consistent with those reported by Cava et al. [10]. In the structure of (Ba,K)$_3$Bi$_2$O$_7$ (Fig. 1a) the 12-coordinated position inside the perovskite block is filled by Ba only, while the 9-coordinated site is occupied by Ba and K in a ratio 0.43:0.57. This corresponds to a chemical composition Ba$_{1.36}$K$_{1.14}$Bi$_2$O$_7$ and agrees well with the results of the EDX analysis performed on individual crystallites (the average Ba/K ratio was found to be 1.91(1)/1.2(2)/1.9(1)). According to the structure refinement of (Ba,K)$_3$Bi$_2$O$_7$ the octahedral coordination of Bi is slightly distorted. The Bi–O distances within the BiO$_2$ layer are 2.148 Å, but the Bi atoms are shifted out of this plane resulting in buckling of the BiO$_2$ layers and the occurrence of two different apical Bi–O distances (2.091 and 2.182 Å).

ED patterns of this phase were completely indexed on the base of an 1-centred tetragonal space group with $a = 4.25$ Å and $c = 21.8$; no superstructure reflections were detected. Fig. 5 represents a high-resolution image taken along the [0 1 0] orientation. Image simulations are in good agreement with the experiment. Other samples containing the (Ba,K)$_3$Bi$_2$O$_7$ phase were also studied by TEM, but no deviation from the 1-centred space group was observed. The (Ba,K)$_3$Bi$_2$O$_7$ phase however is unstable under the electron beam and decomposes fast.

Magnetic measurements were performed for the number of samples containing the (Ba,K)$_3$Bi$_2$O$_7$ phase. No diamagnetic effects were observed down to 5 K in any of them. For resistance measurements one sample was washed in methanol, pressed into a pellet and heated at 400 °C for 20 h in an ampoule filled with O$_2$. The temperature dependence of the resistance exhibits a semiconducting behaviour.
A HREM investigation revealed also the presence of stacking defects corresponding to the existence of the $n = 1$ member in a matrix of $(\text{Ba}, \text{K})_3 \text{Bi}_2 \text{O}_7$, moreover in some crystallites the appearance of these defects is quasiregular (Fig. 6). These observations indicated that under appropriate synthesis conditions the $n = 1$ member of the $(\text{Ba}, \text{K})_{n+1} \text{Bi}_n \text{O}_{3n+1}$ series might be stabilized.

To synthesize the $(\text{Ba}, \text{K})_2 \text{BiO}_3$ phase mixtures with a Ba/Bi ratio > 1 were prepared. The formation of a perovskite related phase with $a_0 = 4.34$ Å was observed when syntheses were carried out in ampoules filled with oxygen. This large value of the perovskite parameter reflects the occupation of the B-site by Bi together with Ba, as it was shown in [13]. The formation of this perovskite, $(\text{Ba}, \text{K})_2 \text{BiO}_3$, is competitive to the formation of the $(\text{Ba}, \text{K})_2 \text{BiO}_4$ layered phase, which has a close cation composition. It looks reasonable to assume that a low annealing temperature would favor the latter reaction due to a decrease of the entropy contribution.

Careful examination of the X-ray diffraction data revealed that samples prepared in a steel container or in ampoules filled with Ar contained a phase that can be assigned to the $n = 1$ member of the $(\text{Ba}, \text{K})_{n+1} \text{Bi}_n \text{O}_{3n+1}$ series. Investigation by TEM allowed to isolate single crystallites of the $(\text{Ba}, \text{K})_2 \text{BiO}_4$ phase. The ED patterns, shown in Fig. 7, were completely indexed on the base of an I-centred tetragonal space group with $a \sim 4.3$ Å, $c \sim 13.2$ Å. X-ray powder diffraction patterns were indexed using these parameters. The amount of the $(\text{Ba}, \text{K})_2 \text{BiO}_4$ phase in these samples was evaluated as 20–25%, while the major phase was perovskite related. For one sample the local cation composition, as determined by EDX analysis, corresponds to Ba1.3(1)/K0.7(2)/Bi1.0(1). This phase was found to be very unstable under the electron beam that strongly hampered HREM observations (Fig. 8). The low stability of $(\text{Ba}, \text{K})_2 \text{BiO}_4$ could explain the unsuccessful attempts to synthesize the phase in a pure form. It should be noticed that due to the symmetry reason for the I-centred unit cell of $(\text{Ba}, \text{K})_2 \text{BiO}_4$ buckling of the BiO$_2$ layer and partial ordering of the Ba and K cations are absent in contrast to those observed in $(\text{Ba}, \text{K})_3 \text{Bi}_2 \text{O}_7$. This makes the $n = 1$ member, containing an isolated (BiO$_2$) layer,
promising for further search of superconductivity among layered bismuthates.

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