

PREPARATION OF $Ba_{0.6}K_{0.4}BiO_3$ PURE SUPERCONDUCTING POWDER

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Abstract

Propionate precursors have been used for the preparation of superconducting phase. The formation of perovskite phases has been studied under inert gas and oxygen during heat treatment. X-ray diffraction and magnetic susceptibility measurements have been carried out at different stages of the three steps process of synthesis. $BaBiO_3$ with unreacted Bi_2O_3 and $KBiO_2$ appears under oxidizing treatment near 700 °C. Perovskite intermediate phases $Ba_{0.87}K_{0.13}BiO_3$ (cubic; $a = 4.322 \text{ \AA}$) and $Ba_{0.6}K_{0.4}BiO_{2.3}$ (tetragonal; $a = 4.292 \text{ \AA}$, $c = 4.539 \text{ \AA}$) are observed during second step under neutral gas. These compounds are not superconducting. Final annealing under oxygen at 400 °C leads to superconducting phase. Grain surface area is related to the reaction speed. Pure superconducting $Ba_{0.6}K_{0.4}BiO_3$ powder has been prepared.

1. Introduction

When the superconductivity in $BaPb_{0.75}Bi_{0.25}O_3$ was discovered [1], the T_c onset = 12 K was considered remarkable for a non-metal compound. After discovery of high T_c superconductivity by Bednorz and Müller [2] in lanthanum barium copper oxide the research on superconductive oxide ceramics has been more appreciated and arose again. In 1988 the superconductivity was discovered in the Ba-K-Bi-O system by Mattheiss et al. [3]. Cava [4] has found the composition $Ba_{0.6}K_{0.4}BiO_3$ with T_c onset = 29.8 K. This is an oxide ceramic without copper having the T_c onset higher than 23 K, the highest T_c of any metallic alloys.

The structure of $Ba_{0.6}K_{0.4}BiO_3$ is related to the structure of $BaBiO_3$ and $BaPb_xBi_{1-x}O_3$. It is a perovskite ABO_3 structure which consists of a regular array of BO_6 octahedra sharing by all corner oxygens with neighbouring equivalent octahedra with 180° B - O - B angle. The A atom, in our case Ba and K, lies in the dodecahedral oxygen site. This ideal ABO_3 lattice has a simple cubic symmetry.

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The synthesis of the superconducting $Ba_{0.6}K_{0.4}BiO_3$ consists of several stages. The first stage is heating of the precursor under oxygen at 720 °C which results in the formation of the $BaBiO_3$ and KO_2 . During the following stage, heating in the inert gas flow at 720 °C, potassium oxide reacts with $BaBiO_3$, and $Ba_{0.6}K_{0.4}BiO_{3-x}$ is formed. After annealing in oxygen at 400 °C the superconducting $Ba_{0.6}K_{0.4}BiO_3$ is formed.

The formation of perovskite phases has been studied by Hinks et al. [5] and Pei et al. [6] using neutron diffraction in situ. They have shown fully oxygenated $Ba_{1-x}K_xBiO_3$ for $x > 0.1$, including the superconducting composition, to be metastable and the creation of oxygen vacancies to be necessary to allow the substitution of K^+ for Ba^{2+} . They have found that, on heating in 1% O_2 , the cubic $Ba_{0.6}K_{0.4}BiO_3$ decomposes into $Ba_{1-x}K_xBiO_3$ with $x < 0.4$ and $KBiO_2$. Further increase in temperature leads to the reincorporation of potassium into the perovskite structure. At 720 °C, the sample is again single - phase perovskite with $x = 0.4$ containing a large concentration of oxygen vacancies.

Our research has been focussed on the characterization of the phase which arose during the heating in the inert gas flow.

2. Preparation

Sol-gel method is used for ceramic oxides preparation. This method enables us to prepare the samples with a high level of homogeneity. $BaCO_3$, K_2CO_3 , $Bi_2O_2(CO_3)$ and propionic acid are used as starting materials [7]. The carbonates are gradually dissolved in the propionic acid. The propionic acid excess is removed by vaporization until a sticky resin appears. This liquid is cooled and results in a resinic precursor. It is heated from room temperature to 500 °C for organic compounds decomposition. At this step, precursor is free of organics but no crystalline structure is observed. This product is ground and used as precursor for further annealing.

The superconducting sample $Ba_{0.6}K_{0.4}BiO_3$ is prepared by following way:

1. Oxidizing treatment at 720 °C: Yellow precursor is heated at 720 °C for 4 hours under oxygen atmosphere.

2. Inert gas treatment at 720 °C: Argon flow takes place for 4 hours at this temperature.

In order to follow the chemical process we built a device which enables us to prepare sample at different stage of reaction. The yellow precursor is placed in six silver crucibles hanging on wires in a closed quartz tube. Precursor is heated at 720 °C for 4 hours in the oxygen gas flow. At this point oxygen is replaced by argon and crucibles are lifted up into cooled zone after different time intervals (10, 20, 40 minutes, 1, 2, 4 hours). These samples are used for phase analysis measurement. After pulling out the last crucible, the samples are left in argon atmosphere. Reduced phase is very unstable and it tends to decompose to Bi_2O_3 , $BaCO_3$ and K_2CO_3 in air. All following operations and preparations for physical measurements are done in inert atmosphere in a glove bag.

3. Oxidizing annealing at 400 °C: Samples are cooled in argon until 400 °C. Then the oxygen annealing follows at 400 °C for 12 hours. Superconducting $Ba_{0.6}K_{0.4}BiO_3$ is formed during this period.

3. Physical measurements

3.1 X-ray diffraction

X-ray diffraction measurement has been used for phase analysis and also for lattice parameters determination.

Two devices have been used : a Guinier - de Wolff chamber focalization with photorecording on film and a vertical diffractometer Siemens KR 500.

The Guinier de Wolf chamber has been used for samples which are air and moisture sensitive, because the sample holder enables to protect the powders from

moisture, oxygen and CO_2 during the measurement. The Fe-anode radiation of the wave length $\lambda (FeK\alpha_1) = 1.93604 \text{ \AA}$ has been used with a monochromator.

Vertical diffractometer is equipped with Co anode and Fe filter. Radiation wave length $\lambda (CoK\alpha_{1,2}) = 1.79021 \text{ \AA}$.

Lattice parameters were fitted by the least square refinement method.

3.2 Magnetic susceptibility measurement

A MANICS Faraday type magnetic balance has been used for magnetic susceptibility measurement. The device accuracy is 10^{-7} uemcgs. The mass of the measured sample has been between 10 and 500 mg. The amount of the superconducting phase in the sample has been estimated from the Meissner effect.

4. Results.

4.1 Phase analysis

4.1.1. Oxygen heating at 720 °C

At the end of oxidizing treatment at 720 °C, the phase analysis points out the presence of $BaBiO_3$ and Bi_2O_3 .

4.1.2. Inert gas heating at 720 °C

X-ray diffraction phase analysis shows the presence of $Ba_{0.87}K_{0.13}BiO_3$ cubic phase ($a = 4.322 \text{ \AA}$), tetragonal phase ($a = 4.292 \text{ \AA}$, $c = 4.539 \text{ \AA}$), $BaBiO_3$ and Bi_2O_3 . The concentration of present phases are time dependent.

The cubic phase content increases during the first 40 minutes and then decreases while tetragonal phase ($a = 4.292 \text{ \AA}$, $c = 4.539 \text{ \AA}$) concentration continuously increases. At the same time $BaBiO_3$ and Bi_2O_3 disappear continuously.

4.1.3. Oxygen annealing at 400 °C

The tetragonal phase seems to be the precursor of superconducting $Ba_{0.6}K_{0.4}BiO_3$ phase. In order to verify this assumption each sample is submitted to oxygen annealing at 400 °C for 12 hours. Their magnetic susceptibility is measured by zero field cooling procedure. The amount of the superconducting phase is estimated from the diamagnetism in relation with Meissner effect. Figure 1 gives magnetic susceptibility measurement of the sample heated for 20 min, 1 h and 4 h in argon at 720 °C and annealed 12 hours at 400 °C in oxygen.

Because the amount of superconducting phase gradually increases, the tetragonal phase ($a = 4.292 \text{ \AA}$, $c = 4.538 \text{ \AA}$) seems to be the reduced precursor of superconducting phase $Ba_{0.6}K_{0.4}BiO_3$.

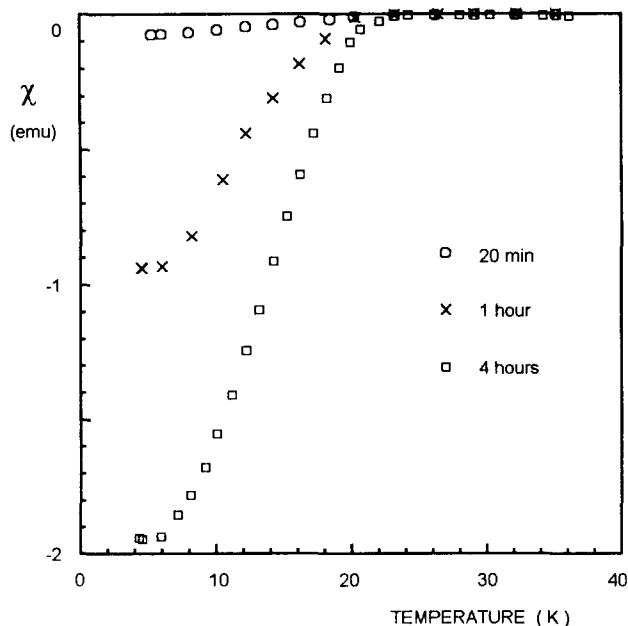
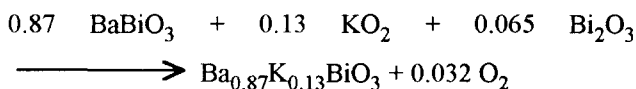


Figure 1. Mg. susceptibility measurement.

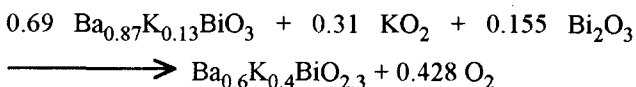
5. Discussion

From the results it can be concluded that process comprises three stages. At the first step, oxidizing treatment under oxygen at 720 °C, we have seen the formation of $BaBiO_3$, Bi_2O_3 grains and KO_2 melted phase covering grains. At second step, two stage can be observed: first stage - reaction between $BaBiO_3$ and potassium compound and second stage - formation of tetragonal phase. At first stage, a cubic phase appears with assumed composition $Ba_{0.87}K_{0.13}BiO_3$, $a = 4.322 \text{ \AA}$ according to the following scheme



This intermediate phase reaches its maximum amount after 40 minutes. This composition has been described by Wignacourt et al. [8].

After additional heating in argon flow potassium continues to react with cubic phase and tetragonal phase is formed. This tetragonal phase ($a = 4.292 \text{ \AA}$, $c = 4.538 \text{ \AA}$) is the reduced phase of the superconducting $Ba_{0.6}K_{0.4}BiO_3$ phase.



Similar phenomenon was also observed during the heating of $BaBiO_3$ under the inert gas [9,10].

Tetragonally distorted perovskite type structure ($Ba_{0.6}K_{0.4}BiO_{2.3}$) has brown-red colour. It is unstable in air being quickly decomposed into $BaCO_3$, K_2CO_3 and Bi_2O_3 .

It is noticed that the superconducting phase is created at first on the shell of grain and the core remains non-superconducting. Explanation of this phenomenon is evident from the reaction kinetics. Formation of the $Ba_{0.6}K_{0.4}BiO_{2.3}$ reduced phase depends on oxygen release from the structure. Because of solid phase - gas type reaction, surface of grain plays the great role. Powders are highly sintered after oxidizing heating. In order to show the influence of grain surface at inert gas treatment two attempts were made.

Two samples (yellow precursor) have been simultaneously heated at 720 °C under oxygen for 4 hours. After oxygen heating, one of them was well ground in the inert atmosphere. Then both samples were heated to obtain the superconducting phase (4 hours argon 720 °C, 12 hours O_2 400 °C). After this procedure, the X-ray diffraction analysis and magnetic susceptibility measurement were done.

Figure 2 shows the comparison of X-ray diffraction patterns.

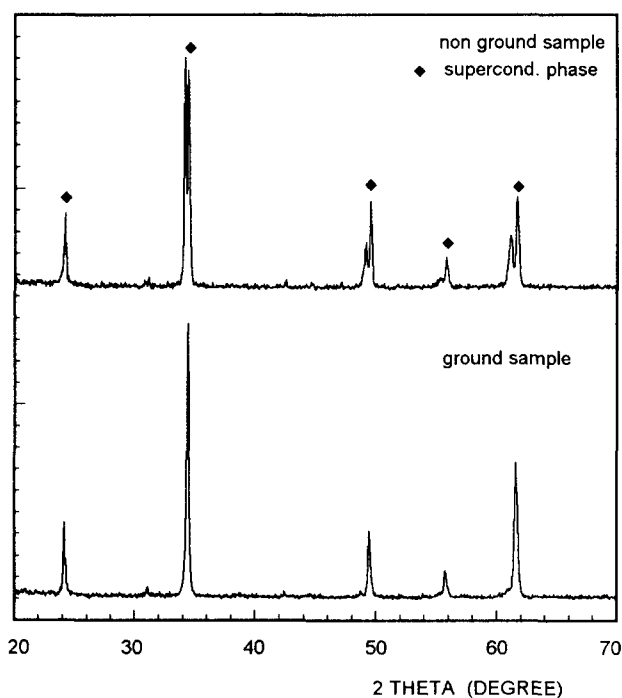


Figure 2. Compared X-ray diffraction patterns

From the results it is obvious that the grain surface plays a role in the reaction kinetics. Pure phase can be obtained by intermediate regrinding of sample.

Oxygen leaves the $BaBiO_3$ structure by inert gas heating. Bi^V is formally reduced to Bi^{III} and anion vacancies arise in the structure and enable the dissolution of KO_2 in structure. Cubic $Ba_{0.87}K_{0.13}BiO_3$ ($a = 4.322 \text{ \AA}$) was noticed as the first stage of KO_2 incorporation. After further heating more oxygen leaves the structure. Perovskite cubic structure increases in the c -axis direction and tetragonal phase appears. This tetragonal structure is the final step of the potassium oxide and bismuth incorporation into structure. The completely reduced perovskite - like tetragonal phase $Ba_{0.6}K_{0.4}BiO_{2.3}$ ($a = 4.289 \text{ \AA}$, $c = 4.538 \text{ \AA}$) with oxygen vacancies is formed. These results rather correspond with the mechanism of $BaBiO_3$ reduction described by Beyerlein et al. [9]. They observed tetragonal structure of fully reduced $Ba_2Bi_2O_{5.1}$ ($a = 8.784 \text{ \AA}$, $c = 8.977 \text{ \AA}$). In our case, potassium substitution, the tetragonal distortion in the c -axis direction is even greater than in $Ba_2Bi_2O_{5.1}$.

After additional oxygen annealing, the superconducting cubic phase $Ba_{0.6}K_{0.4}BiO_3$ ($a = 4.289 \text{ \AA}$) is formed. The formal charge of Bi is 4.4. This would mean, that 70% of Bi would have formal valence V and 30% formal valence III. But all the Bi atoms are equal, which is obvious from the primitive perovskite type structure (Pm3m).

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