Rare Metal Materials and Engineering
Volume 38, Issue 4, April 2009
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2009, 38(4): 0583–0586.

ARTICLE

Preparation of $Ba_{1-x}K_xBiO_3$ by Molten Salt Method and Thermostability of $Ba_{0.6}K_{0.4}BiO_3$

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Abstract: $Ba_{1-x}K_xBiO_3$ (BKBO) samples with $0.315 \le x \le 0.6$ were synthesized at a relatively low temperature of 260 °C by molten salt method. The superconductivity was tested in the whole range of x value, the highest superconducting transition temperature T_c = 30.6 K at x = 0.4. X-ray Diffraction patterns reveal that small amount of impurity phase of $BaCO_3$ were detected in BKBO which is attributed to the reactions between $Ba(OH)_2 \cdot 8H_2O$ and CO_2 in air. The plate-like morphology of BKBO was observed from SEM images. For comparison, sol-gel method was also used in synthesizing $Ba_{0.6}K_{0.4}BiO_3$ sample, but no single phase of BKBO was obtained. For the sample of $Ba_{0.6}K_{0.4}BiO_3$ prepared by molten salt method, the thermostability was investigated by thermogravimetric analysis (TGA) and annealing treatment, and the sample was decomposed at 400 °C . The result showed that $Ba_{0.6}K_{0.4}BiO_3$ was thermally unstable above 400 °C.

Key words: $Ba_{1-x}K_xBiO_3$; molten salt method; superconductivity

Since the superconductivity in $Ba_{1-x}K_xBiO_3$ (BKBO) samples was discovered in 1988[1,2], lots of experimental and theoretical researches about this kind of bismuthate have been carried out. The superconducting transition temperature of $Ba_{0.6}K_{0.4}BiO_3$ reaches 31 K which was considered to be the highest at that time. BKBO superconductor received great attention for its several predominant properties, such as the absence of transition metal elements, three-dimensional perovskite structure and the isotropism, which is more convenient to explore the superconducting mechanism in this system. Low sintering temperatures or some special preparation techniques are needed because of instabilities of BKBO samples at high temperatures. Up to now, electrochemical growth from melts process[3,4], high temperature high pressure technique[5], the sputtering method (film)[6], molecular beam epitaxy (MBE) techniques (film)[7], pulsed-laser deposition (film)[8], thermal evaporation[9], direct precipitation from KOH melt[10,11] and molten salt method[12] are extensively used in preparing BKBO superconductors. In this paper, the superconducting samples of BKBO will be prepared adopting both sol-gel method[13] and molten salt method. The effects of preparing conditions on the crystal structures and microstructures will be studied by XRD and SEM measurement. Although many references pointed out the instabilities of BKBO superconductor, there is still lack of concrete analysis, so the thermal analysis of DSC-TGA will be also carried out to reveal the stabilities of $Ba_{0.6}K_{0.4}BiO_3$ samples.

1 Experiments

Adopting molten salt method, raw materials, $Ba(OH)_2 \cdot 8H_2O$, Bi_2O_3 and $NaBiO_3 \cdot 2H_2O$, were dissolved into liquid KOH in a Teflon crucible at 260 °C in air. The KOH here would act as both the source of K and molten salt. To obtain the crystals with various contents of potassium, the mole ratio of $NaBiO_3 \cdot 2H_2O$ toBi_2O_3 had to be accommodated. Detailed synthesis procedures of $Ba_{0.6}K_{0.4}BiO_3$ samples are as follows:

Firstly, 20 g KOH was held at 260 °C for 0.5 h in a Teflon

Received date: April 22, 2008; Revised manuscript received date: February 17, 2009
Foundation item: 2007 Innovation Fund for Ph.D. Student of Southwest Jiaotong University and China National Funds for Distinguished Young Scientists (50588201)
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crucible. Then 1.85 g $Ba(OH)_2 \cdot 8H_2O$, 1.11 g $NaBiO_3 \cdot 2H_2O$ and 0.68 g Bi_2O_3 were mixed well in the agate mortar, and dissolved into the melted KOH. After maintained at 260 °C for a certain time, the liquid KOH in the crucible was poured out while the crystal was kept. Cooling to room temperature, the samples were washed 5-10 times using distilled water, and twice using ethanol. Finally, the wet powder samples were dried at about 75 °C for 24 h in air.

Adopting sol-gel method processes, $BaCO_3$, K_2CO_3 and Bi_2O_3 were weighed in the stoichiometric proportion of Ba:K:Bi = 0.6:0.4:1. Then they were gradually dissolved into the heated propionic acid and mixed steadily. The excess of propionic acid was removed by vaporization until a sticky resin appeared. This liquid was cooled down, resulting in a resinic precursor. It was heated from room temperature to 500 °C for 5 h to decompose the organic compounds. At this step, the precursor was free of organic compounds, and no crystalline structure was observed. The product was ground and used as precursor for further annealing. The precursor of $Ba_{0.6}K_{0.4}BiO_3$ was then treated in oxygen and Ar atmosphere for 10 h at 720 °C, respectively. After cooling, the powders were reground and pressed into pellets with 2-3 mm in thickness and 10 mm in diameter, and then treated again in Ar atmosphere for 10 h at 720 °C, followed by the finial annealing at 400 °C for 10 h in oxygen atmosphere.

A Philips X'Pert MRD X-ray diffractometer with CuKα radiation was used for XRD patterns. The morphology of BKBO was determined by an environmental scanning electron microscope (ESEM). The magnetic properties were examined in the temperature range between 5 K and 50 K by SQUID magnetometer (Quantum Design MPMS) in an applied magnetic field of 3980 A/m.

2 Results and Discussions

Fig.1 shows the XRD patterns of BKBO samples prepared for different sintering time. In Fig.1a, the main phase can be indexed by the cubic perovskite structure in the samples synthesized for between 5 h and 25 h. Impurity phase of $BaCO_3$ can also be observed which formed from the $Ba(OH)_2 \cdot 8H_2O$ and CO_2 in air at low temperatures around 75 °C. At 260 °C, it was hard to decompose and finally remained in the products. The magnified view of the diffraction patterns for (110) peaks are displayed in Fig.1b. (110) peak shifts towards higher diffraction angles with time prolonging, indicating a decrease of the lattice constants of BKBO and an increase of the K content in BKBO. The high-purity $Ba_{0.6}K_{0.4}BiO_3$ sample which we supposed to synthesize is obtained when the sintering time reached 19 h. The samples sintered for 5, 15, 25 h are proved to be $Ba_{0.685}K_{0.315}BiO_3$, $Ba_{0.685}K_{0.315}BiO_3$ and $Ba_{0.534}K_{0.466}BiO_3$, respectively. A further increasing of the sintering time such as 32 h would lead to the volatilization of KOH and the decomposition of BKBO. In this case, Bi_2O_3 and $BaCO_3$ become the main phases and only a small amount of BKBO

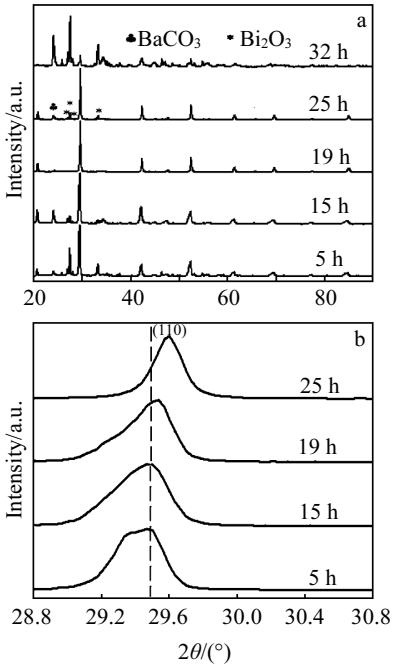

Fig.1 XRD patterns of the BKBO samples for different sintering time: (a) 20°≤2θ≤90° and (b) 28.8°≤2θ≤30.8°

phase can be detected.

The magnetic measurement data shown in Fig.2 confirms the successful synthesis of BKBO samples sintered for 5-32 h, showing bulk nature of superconductivity. The highest superconducting transition temperature is 30.6 K in the sample of x = 0.4. These results are consistent with those obtained by Y. Nagata *et al*[14].

A typical SEM image for $Ba_{0.6}K_{0.4}BiO_3$ sample is displayed in Fig.3. Homogeneous crystal grain with layered structure can be recognized to be general microstructures in BKBO samples obtained by molten salt method. The average particle size for $Ba_{0.6}K_{0.4}BiO_3$ is around 700 nm.

In the samples of BKBO superconductors synthesized by molten salt method, the content of potassium is related to the

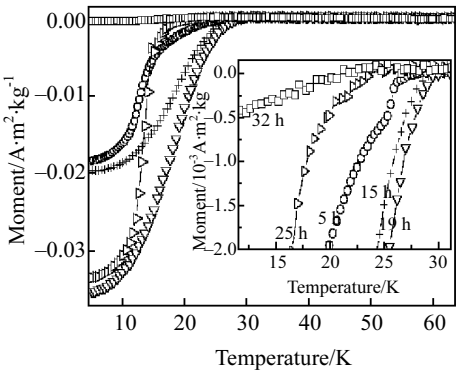

Fig.2 Temperature dependence of magnetization for the BKBO samples, and insert shows magnified view of the superconducting transition

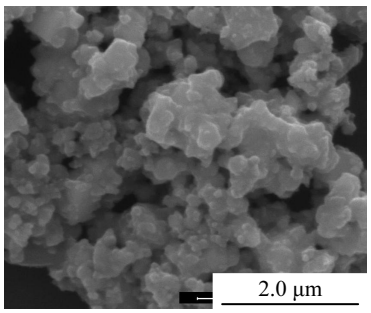

Fig.3 Typical SEM image for $Ba_{0.6}K_{0.4}BiO_3$ sample

relative quantities between $Ba(OH)_2 \cdot 8H_2O$ and KOH, the mole ratio of $NaBiO_3 \cdot 2H_2O$ to Bi_2O_3 in the raw materials and the sintering time. Single phase BKBO samples with $0.315 \le x \le 0.6$ can be received by accommodating the influencing factors mentioned above.

Except for the molten salt process, many other methods can be applied in preparing BKBO superconductors. L F Mattheiss *et al*[1] successfully synthesized superconducting BKBO compounds by solid state reaction at 900 °C. For the volatilization of K_2O, extra amount of K was added in the raw materials. Even in this case, the compound was proved to be multi-phases whereas the transition temperature was 22 K and only 4% volume fraction displayed Meissener effect.

In this paper, we tried to prepare BKBO using sol-gel method and Fig.4 shows the *M-T* curve of this sample. Although its transition temperature displays to be higher than that prepared using molten salt method, the diamagnetic signal is nearly several thousand times smaller. Analyses together with the X-ray diffraction patterns suggest that single-phase BKBO can not be obtained in this process. Accommodations of sintering temperature, atmosphere and time are explored for future investigation. It is still impossible to prepare single phase BKBO by sol-gel method. Two main reasons should be taken into account for the failure: the volatilization of potassium oxide and the instability of BKBO at high temperature. R. J. Cava *et al*[2] modified the solid state reaction and succeeded in synthesizing $Ba_{0.6}K_{0.4}BiO_3$. Their process was as follows: the raw materials were sealed in the silver tube with an additional excess of KO_2, sintered at 675 °C for 3 d, and then annealed the product at 475 °C in O_2 atmosphere. Compared with our molten salt method, this process is more complicated.

The investigations about the stability of $Ba_{0.6}K_{0.4}BiO_3$ synthesized by molten salt method were also carried out. Fig.5 displays the DSC and TGA curves of $Ba_{0.6}K_{0.4}BiO_3$ powder. Endothermic changes appeared at 57.3 °C and 71.3 °C accompanied with great mass change. This part corresponds to the evaporation of water in the sample. A slow endothermic process can be observed at the temperature range from 250 °C to 550 °C. Steady and sharp weight loss happened at 250-400 °C and 400-500 °C respectively. In this process, $Ba_{0.6}K_{0.4}BiO_3$ slightly decomposed between 250 °C and 400 °C, and further increasing of temperatures lead to a rapid decomposition.

Annealing at 400 °C and 500 °C was carried out to make a confirmation of these results. Fig.6 shows the XRD results for the annealed and unannealed samples. Annealing at 400 °C would not change the compositions of the compounds. But the main phase changes to $Ba_{0.9}K_{0.1}BiO_3$ for the sample annealed at 500 °C (see the magnified views in Fig.6) and the impurity of $BaCO_3$ diminishes almost to vanishing point in this process. These results mentioned above prove the instability of the $Ba_{0.6}K_{0.4}BiO_3$ sample at the temperature higher than 400 °C.

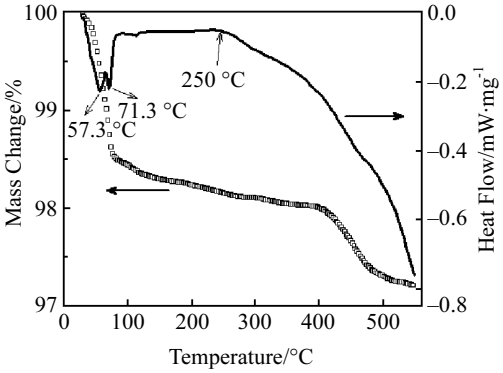

Fig.5 DSC and TGA curves of $Ba_{0.6}K_{0.4}BiO_3$ powder

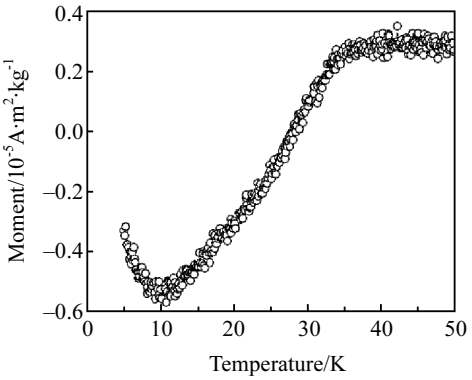

Fig.4 Temperature dependence of magnetization for the BKBO sample prepared by Sol-Gel

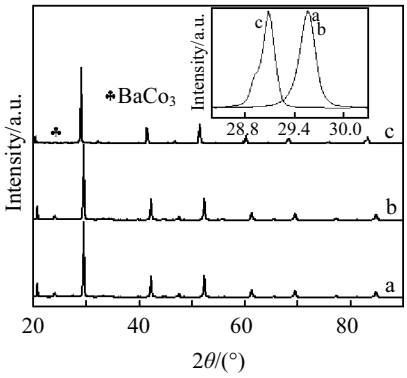

Fig.6 XRD patterns of $Ba_{0.6}K_{0.4}BiO_3$ samples: (a) unannealed, (b) annealed at 400 °C, and (c) annealed at 500 °C

Another method was also used to confirm the stability of $Ba_{0.6}K_{0.4}BiO_3$ prepared by molten salt method. The so prepared sample was kept in the open air for one month at room temperaure, and its superconductivity maintained still the same. The result proves that the BKBO sample prepared by molten salt method is stable at low temperatures.

3 Conclusions

1) Superconducting BKBO samples can be synthesized at a relatively low temperature by molten salt method. The compounds show great superconductivity in the range of $0.315 \le x \le 0.6$. However, in the process, impurity phase of $BaCO_3$ appears in most of the samples. The elimination of the impurity can be realized under the protection of oxygen atmosphere. This molten salt method can be accomplished at one step, in short time and at low temperatures which is more favorable to synthesizing of BKBO samples.

2) The sample of $Ba_{0.6}K_{0.4}BiO_3$ is thermally unstable at the temperaures higher than 400 °C.

References

1 Mattheiss L F, Gyorgy E M, Johnson D W. *Phys Rev B*[J], 1988, 37(7): 3745

2 Cava R J, Batlogg B, Krajewski J J *et al*.. Nature[J], 1988, 332: 814

3 Shiryaey S V, Barilo S N, Ustinovich S N *et al*. *J Crystal Growth*[J], 2000, 211(1-4): 471

4 Klinkova L A, Uchida M, Matsui Y *et al*. *Phys Rev B*[J], 2003, 67(14): 140 501

5 Kim D C, Baranov A N, Kim J S *et al*. *Physica C*[J], 2003, 383(4): 343

6 Sato H, Tajima S, Takagi H *et al*. *Nature*[J], 1989, 338: 241

7 Yamamoto H, Aoki K, Tsukada A *et al*. *Physica C*[J], 2004, 412-414(1): 192

8 Mijatovic D, Rijnders G, Hilgenkamp H *et al*. *Physica C*[J], 2002, 372-376(2): 596

9 Utz B, Wiest F, Prusseit W *et al*. *IEEE Trans Appl Supercond*[J], 1995, 5(2): 1351

10 Jones N L, Parise J B, Flippen R B *et al*. *J Solid State Chemistry*[J], 1989, 78: 319

11 Zhao L Z, Yin B, Zhang J B *et al*. *Physica C*[J], 1997, 282-287(2): 723

12 Liu S F, Fu W T. *Mater Res Bull*[J], 2001, 36(7-8): 1505

13 Rrhspringer J L, Niznansky D. *J Alloys Compd*[J], 1993, 195: 73

14 Nagata Y, Mishiro A, Uchida T *et al*. *J Phys Chem Solids*[J], 1999, 60(12): 1933

熔盐法制备 $Ba_{1-x}K_xBiO_3$ 超导体及 $Ba_{0.6}K_{0.4}BiO_3$ 的稳定性

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摘　要：利用熔盐法在 260 °C 的低温下制备出了单相 $Ba_{1-x}K_xBiO_3$ (BKBO, $0.315 \le x \le 0.6$)样品。磁性测量结果表明，在 x 值整个范围内的 BKBO 样品都表现出超导电性，x=0.4 时，超导转变温度达到最高值（T_c=30.6 K）；粉末 X 射线衍射结果表明，所有样品中均含有少量的 $BaCO_3$ 杂相，它是由于反应过程中 $Ba(OH)_2 \cdot 8H_2O$ 和空气中的二氧化碳反应造成的；扫描电镜观察 BKBO 微观形貌为片状。为与熔盐法作比较，利用溶胶-凝胶法制备 $Ba_{0.6}K_{0.4}BiO_3$，发现此法难以制备出单相 BKBO 样品。利用热分析和退火处理来研究熔盐法制备 $Ba_{0.6}K_{0.4}BiO_3$ 的热稳定性，发现样品大约在 400 °C 开始分解，表明 $Ba_{0.6}K_{0.4}BiO_3$ 在 400 °C 以上是不稳定的。

关键词：$Ba_{1-x}K_xBiO_3$；熔盐法；超导电性

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