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Superconducting properties of Ba(Pb, Bi)O_3 single crystals and melt-processed (Ba, K)BiO_3

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Abstract

Single crystals of the superconductor $BaPb_{1-x}Bi_xO_3$ with nominal compositions of $x=0.25$, were grown by cooling from the melt using an excess of PbO. The superconducting transitions have been measured on the grown crystals as a function of oxygen annealing and sharp transitions with T_{conset} at 12 K have been observed. The related perovskite $Ba_{1-x}K_xBiO_3$ superconductor ($x=0.4$) has been synthesized by a new melt-processing technique using an infra-red image furnace. The melt-processed material on post annealing, is superconducting with $T_{conset} \sim 25$ K. The superconducting properties of these two families of superconductors are presented.

1. Introduction

Ba(Pb,Bi)O_3 and (Ba,K)BiO_3 belong to the perovskite family of oxide superconductors. Their parent compounds $BaBiO_3$ and $BaPbO_3$ are also interesting compounds in their own right and have been well studied in the past [1,2]. These perovskite superconductors are three-dimensional and hence offer themselves as useful comparisons with the layered cuprate superconductors. Superconductivity in Ba(Pb,Bi)O_3 over a composition range $0.1 < x < 0.3$, was discovered in 1975 by Sleight et al. [3]; a maximum T_c of ~ 13.5 K is observed for $x \sim 0.25$–0.3, close to the metal–insulator transition. Superconductivity in the (Ba,K)BiO_3 was discovered by Mattheis et al. in 1988 [4]. A maximum T_{conset} of ~ 29 K was found for the composition $Ba_{0.6}K_{0.4}BiO_3$. This is the highest T_c for an oxide superconductor without copper [5]. The compound which has the optimum T_c has a cubic structure.

This paper describes the crystal growth of the compounds $BaBiO_3$, Ba(Pb,Bi)O_3 and the superconducting properties of the Ba(Pb,Bi)O_3 crystals produced. We also present the results of a new method of melt processing for (Ba,K)BiO_3 using an infra-red image (IR) furnace to produce high-density material. The measurements of the superconducting properties of this material are also presented.

2. $BaBiO_3$ single crystals

Before attempting the crystal growth of the superconducting compounds, the single-crystal growth of the parent compound $BaBiO_3$ was carried out, to ascertain in particular if it is possible to use the floating zone method for producing aligned material or crystals of this compound. For the growth of $BaBiO_3$ single crystals, two different methods were adopted:

(1) cooling slowly from the melt and

(2) the floating zone method using an IR furnace.

For both these methods, large quantities of single-

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phase $BaBiO_3$ were prepared prior to the crystal growth by the solid-state reaction of $BaCO_3$ and Bi_2O_3.

2.1. Melt growth

About 30 g of $BaBiO_3$ powder was placed in an alumina crucible, heated up to 1100°C, then slowly cooled at a rate of 2°C/h down to 900°C; at this temperature the furnace was switched off. A layer of golden and shiny crystals was found on the top surface of the molten material in the crucible, crystalline to a depth of about 2 mm. From this portion, single-crystal pieces of about 5 mm×5 mm×1 mm were cut out for characterization by X-ray Laue patterns. The crystals were found to be of good quality with their "*c*"-axis perpendicular to the plane of the plates.

2.2. Crystal growth by the floating zone method

This procedure was carried out using an IR furnace, the details of the furnace used and the floating zone method are described in Ref. [6]. The pre-reacted powder was pressed in the form of rods (~80 mm long, ~7–10 mm dia) and used as the "feed" and the "seed" rods. The crystal growth was carried out by passing the molten zone through the rods at a rate of ~5 mm/h, in 1 atm of oxygen gas, with a gas flow of about 1 l/min. The rods were counter-rotated at 20 rpm during the growth.

The rod of $BaBiO_3$ processed in such a way showed plate-like crystals on the surface and when cleaved longitudinally, showed a stacking of needle-like crystals along the growth (and rod) axis. This is similar to what is found in the case of the Bi-2212 superconductor grown by the same method, at growth rates higher than 2 mm/h and is promising for future work. Such a growth of $BaBiO_3$ may produce crystals with larger faces if the growth is carried out at a much slower rate.

3. $BaPb_{1-x}Bi_xO_3$ single crystals

Single-crystal growth of $Ba(Pb,Bi)O_3$ has been carried out in the past by what is essentially a flux growth, using various flux materials. In some cases, molten KCl has been used as flux and the growth was carried out by employing a temperature gradient across the crucible [7]. Other methods used involve the use of an excess of the components, PbO, Bi_2O_3 or PbO_2 in the starting compositions as flux in the melt growth [8]. In all cases, a good control of the growth parameters has been essential in producing homogeneous crystals. We describe below our attempts to grow good-quality single crystals by two methods, one of which was successful in producing homogeneous crystals using an excess of one of the starting materials, PbO, as flux and without the need for excessively rigid control of the parameters during growth.

3.1. Crystal growth by the floating zone method

Crystal growth by the floating zone method was attempted using rods of the superconducting composition, $BaPb_{0.75}Bi_{0.25}O_3$ synthesized by the usual solid-state reaction method. Unfortunately these attempts failed because of the loss of Pb due to the decomposition of the compound, as it does not melt congruently. To overcome the problems associated with the incongruent melting of this composition, it was decided to start with a mixture containing excess of the constituents which might act as a flux or solvent [9]. Therefore a mixture of $BaCO_3:PbO:PbO_2:Bi_2O_3 = 2:4:2:1$ was pressed into rods and the experiment was repeated in the IR furnace, using these rods. This again proved unsuccessful, there was considerable loss of PbO thus making it difficult to maintain a stable molten zone. More experiments are necessary to arrive at a suitable composition for the feed and the solvent rods, which would allow a molten zone to be formed.

3.2. Crystal growth from melt

Crystal growth of $BaPb_{1-x}Bi_xO_3$ was then attempted by conventional methods, i.e. cooling from the melt. Single crystals were successfully grown by fast cooling of the melt of different starting compositions. Excess of PbO was used in the starting compositions to act as the flux. Three different mixtures of $BaCO_3$, PbO and Bi_2O_3 for the superconducting composition $BaPb_{0.75}Bi_{0.25}O_3$ with 7.5%, 5%, 2.5% excess of PbO were taken. The mixtures were heated to 1100°C in covered alumina crucibles to lower the

loss of Pb and then cooled down rapidly to 800°C.

Crystals were obtained for all compositions, typically bluish black and plate-like with edge lengths of about 4 mm×4 mm. X-ray Laue patterns of the individual crystals showed that the crystals were of good quality (see Fig. 1), and the correct symmetry for the orientation of the crystals, the "*c*"-axis is perpendicular to the plane of the platelet. The size and the T_c of the crystals obtained depended on the excess of PbO in the starting composition. Fig. 2(a) shows the measurement of T_c by DC magnetization on the crystals obtained from the three different growths, showing a gradual change in T_c with different starting compositions of the melt. The best results were obtained for the 7.5% excess PbO starting composition (Fig. 2(b)). As with polycrystalline material, it was found that the superconducting properties could be optimised by oxygen-annealing of the crystals after growth. The resistive transitions of the oxygen-annealed crystals was found to be sharper than that of the as-grown crystals. The resistance measurement on an oxygen-annealed crystal of the optimum Pb concentration, exhibiting a sharp superconducting transition is shown in Fig. 3. The sharpness of the transition indicates that the crystals are homogeneous in composition.

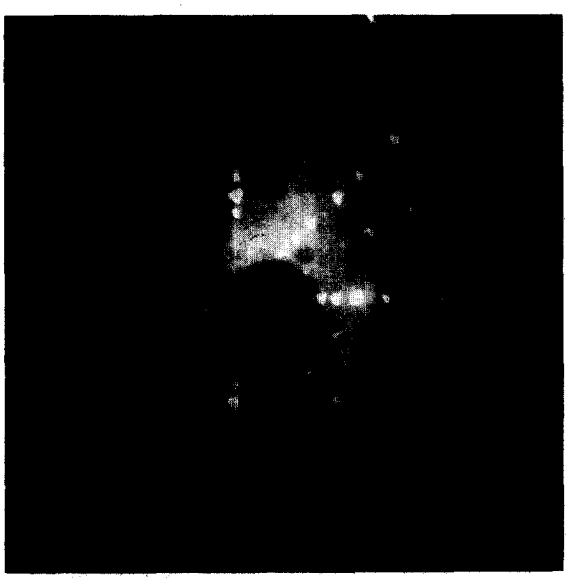

Fig. 1. X-ray Laue back-reflection photograph of a single crystal of $BaPb_{0.75}Bi_{0.25}O_3$. The "*c*"-axis of the crystal is perpendicular to the plane of the platelet (and out of the paper).

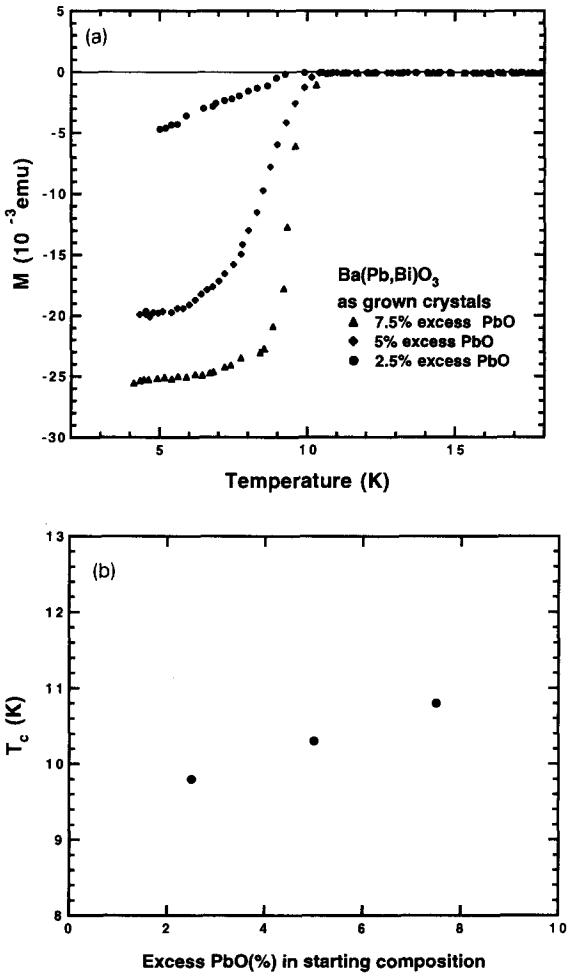

Fig. 2.(a) Superconducting transitions of the crystals of $BaPb_{0.75}Bi_{0.25}O_3$ grown by fast cooling from the melt using different excesses of PbO, measured using a VSM, $H=10$ G, zero field cooled. (b) This figure shows the influence of the excess of PbO in the starting composition on the T_c of the as-grown crystals of $BaPb_{0.75}Bi_{0.25}O_3$.

The compositions of the crystals grown were analysed using the scanning electron microscope (EDAX) and the results of the analysis are shown in Table 1. There is a systematic correlation between the starting compositions of PbO and the resulting composition of the crystals. The crystals grown with 7.5% excess PbO, for example, showed a ratio of Pb:Bi ~ 3:1, which is the composition with the highest T_c.

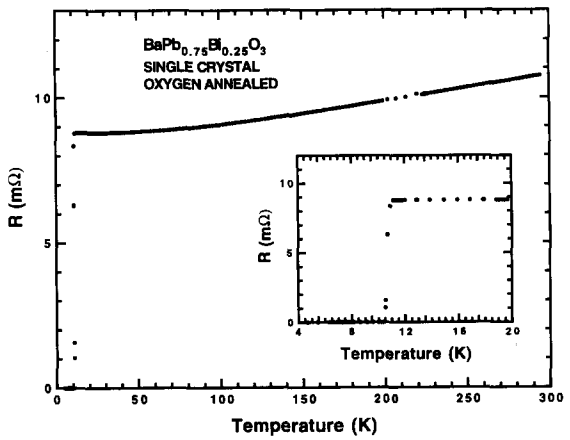

Fig. 3. Resistance measurement along the "*ab*"-axis of a single crystal of $BaPb_{0.75}Bi_{0.25}O_3$, oxygen annealed, showing a sharp superconducting transition.

Table 1
Electron-microscope analysis of the Pb:Bi ratio in the crystals of $BaPb_{0.75}Bi_{0.25}O_3$ grown starting from melts with excess of PbO

Excess PbO in melt	Analysed Pb:Bi ratio
2.5%	3.8:1
5.0%	3.6:1
7.5%	3.2:1

4. Melt processing of $Ba_{1-x}K_xBiO_3$

The preparation of polycrystalline $Ba_{1-x}K_xBiO_3$ requires special conditions due to the reactive nature of one of the starting materials, KO_2. We have synthesized high-density $Ba_{1-x}K_xBiO_3$ (~ 100 % density) by a new melt-processing technique using an IR furnace and obtained good-quality superconducting material. The starting material was first synthesized by mixing together $BaBiO_3$, KO_2 and Bi_2O_3 in the stoichiometric ratios. This had to be done inside a glove bag filled with N_2 gas as KO_2 is highly reactive in air. After grinding the mixture well, the powder was compressed into rods. The starting composition was nominally $x=0.4$ with a 5% excess of KO_2 to compensate for losses while melting. The rods were then mounted inside the IR furnace. The rods were melted, fused together and a fast molten zone passed up the feed rod. The melting was carried out in one atmosphere of N_2 gas pressure inside the furnace, in spite of which there appeared to be a slight loss of

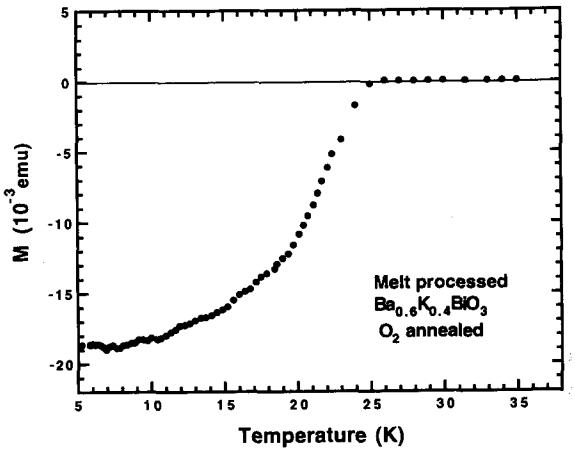

Fig. 4. Superconducting transition of the melt-processed $Ba_{0.6}K_{0.4}BiO_3$, oxygen annealed, measured using a VSM, $H=10$ G, zero-field cooled.

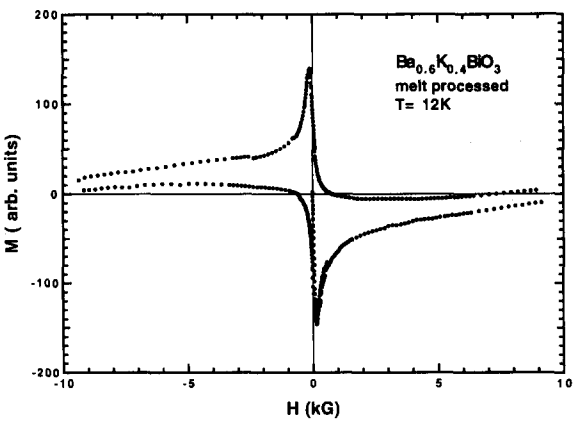

Fig. 5. The M vs. H loop measured on the melt-processed $Ba_{0.6}K_{0.4}BiO_3$, at 12 K.

KO_2. The melt-processed rod was bluish black in colour indicating that the phase had been formed, but was not superconducting at this stage. To make the material superconducting, it was necessary to anneal the processed rod in O_2 gas for 1 h at $T=425$°C [10].

Pieces of the annealed rod were tested for superconductivity; superconducting transitions with onsets around 25 K were observed in all portions of the annealed rod, thus showing that the bulk of the melt-processed material is a superconductor. Fig. 4 shows the superconducting transition measured on a piece of annealed $Ba_{0.6}K_{0.4}BiO_3$ by DC magnetization. The M versus H loop measured on this sample at 12 K

using a vibrating sample magnetometer is shown in Fig. 5.

5. Conclusions

Single crystals of both the parent compound $BaBiO_3$ and $BaPb_{1-x}Bi_xO_3$ have been grown. Whilst $BaBiO_3$ single crystals were grown by both conventional cooling from the melt as well by the floating zone method using the IR furnace, crystals of the superconducting compound $BaPb_{1-x}Bi_xO_3$ were grown by fast cooling from the melt using excess of PbO. The crystals produced are of good quality and sharp superconducting transitions have been observed in oxygen-annealed $BaPb_{1-x}Bi_xO_3$ crystals, the compositions with $x \sim 0.3$ showing the highest T_c's. High-density $Ba_{0.6}K_{0.4}BiO_3$ has been synthesized by a new one-step melt-processing method using the IR furnace. The melt-processed material is superconducting on oxygen annealing with T_{conset} at around 25 K.

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