

## Systematic X-Ray Diffraction Study of $Ba_{1-x}K_xBiO_3$ <sup>†</sup>

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Single crystals of  $Ba_{1-x}K_xO_3$  (BKBO), grown by an anodic electro-crystallization process with measured bulk  $T_c = 15$  K, 20 K and 25 K, were studied by X-ray single crystal method and X-ray powder Rietveld analysis. Good single crystals, selected from each batch of samples were used in single crystal structure determination, whereas powdered samples from the same batches were studied by Rietveld analysis for comparison. Furthermore, the same samples used in the single crystal structural determination were used again in the measurement of their  $T_c$ , employing the Superconducting Quantum Interference Devices (SQUID). These measurements showed that the BKBO prepared by the anodic electrocrystallization are capable of producing perfect single crystals of size  $(0.1 \times 0.1 \times 0.1 \text{ mm}^3)$ . However there exists an inhomogeneity in the bulk samples, as evidenced by the inconsistencies in the results of the lattice constants  $a$  and the potassium solubility  $x$  between single crystals and powder analyses. The  $T_c$  values measured using SQUID for the single crystals are lower than those measured for bulk samples. The potassium solubilities,  $x$  values, also exceed the limit in the phase diagram of BKBO [6]. The electron density maps from the results of the single crystal structure determinations also indicate the nonlocalization of the oxygen electrons.

### I. INTRODUCTION

K and Pb substituted  $BaBiO_3$  compounds,  $Ba_{1-x}K_xBiO_3$  and  $BaPb_{1-x}Bi_xO_3$  respectively, are well known for their superconductivity without 2-dimensional copper oxide layers with  $T_c$  about 30 K [1-3] and 12 K [4] respectively. In the early stage of high-T,

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era,  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  compound partially inspired the discovery of La-Ba-Cu-O system [5]. Further studies resulted in the discovery of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ , which is superconducting at  $T_c = 30$  K with  $x = 0.4$ .

The basic structure of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  is perovskite type ( $\text{ABO}_3$ ), with Ba atom and K atom randomly distributing in A-site, Bi atom in B-site. Previous studies revealed that at room temperature in the region  $0 < x < 0.37$ ,  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  belongs to orthorhombic system, semiconducting and in the region  $0.37 < x < 0.5$ , it belongs to cubic, space group  $\text{Pm}\bar{3}\text{m}$ , superconducting with  $T_c = 30$  K at  $x = 0.37$  [2,3,6]. Both the structure phase transition and the incommensurate modulation have been extensively studied [2,3,6,7].

In this article, systematic studies on various  $x$  of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  compounds are presented. The structures, composition  $x$  and their relationship with  $T_c$  for both single crystals and polycrystalline state bulk samples as well as the electron density maps are reported.

## II. EXPERIMENT

The growth of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  crystals was carried out in a special KOH molten flux cell described elsewhere [8]. The exact growth mechanism of the low temperature anodic electrochemical technique in the bismuthate system is not quite clear. The temperature, applied potential, deposition time and flux composition are correlated with product properties. To obtain crystals with different  $x$  values, the molten flux in 100 ml Teflon cell typically consists of 1.6 g  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and 7.11 g  $\text{Bi}_2\text{O}_3$  dissolved in 60 g KOH. The temperature of the cell is controlled at 260 °C. Reduced  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  concentration or increased applied potential can drive the dopant profile to higher K contents with increasing time.

Black grain-like crystals of size about  $(0.1 \times 0.1 \times 0.1 \text{ mm}^3)$  were selected from each batch of samples by precession photography and used for single crystal structure determinations. The data were collected by using Siemens R3m/V four-circle diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation. More than 130 independent reflections were collected. Powder samples from the same batch were used for Rietveld analysis. The data were collected with the Rigaku Rotaflex RTP 500RC power diffractometer,  $\text{CuK}\alpha$  Radiation,  $2\theta$  range from  $10^\circ$  to  $140^\circ$ . More than 30 reflections were collected.

## III. RESULTS AND DISCUSSION

The final results of the crystallographical parameters, determined from the Rietveld analysis, of single crystals are listed in Table IA and IB. Fig. 1 shows the scheme of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  crystal structure. Bi atom occupies the special position  $(1/2, 1/2, 1/2)$ , Ba/K  $(0, 0, 0)$  and O  $(0, 1/2, 1/2)$  for all the samples. The very good R-values and good of fitness

TABLE IA. Refined results for  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  crystals by single crystal structure determination

Sample	$T_c^*$	$R$	$wR$	$x$	G.O.F.	a(A)
BKBOA	14 K	1.2 %	1.5 %	0.592	0.50	4.2707(6)
BKBOB	**	1.2 %	1.4 %	0.600	0.46	4.2613(3)
BKBOC	***	2.3 %	2.7 %	0.679	1.08	4.2459(4)
BKBOD	15 K	1.5 %	1.6 %	0.446	0.54	4.2817(5)
Reference [11]					0.128	4.3223(5)

\* Measured by SQUID.

\*\* Sample dropped off during the SQUID measurement.

\*\*\* Measured but found to be nonsuperconducting.

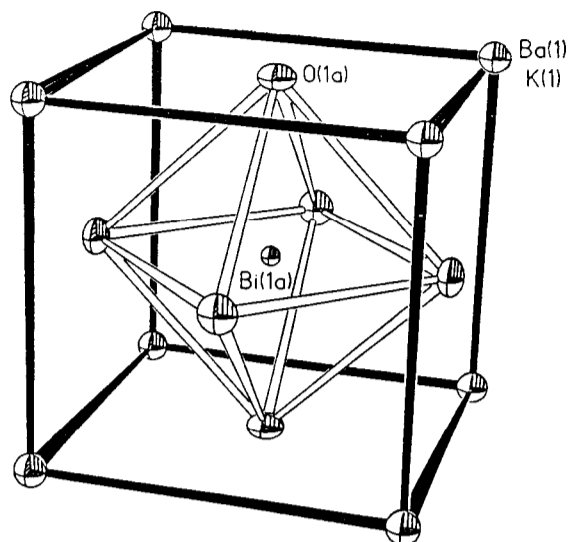
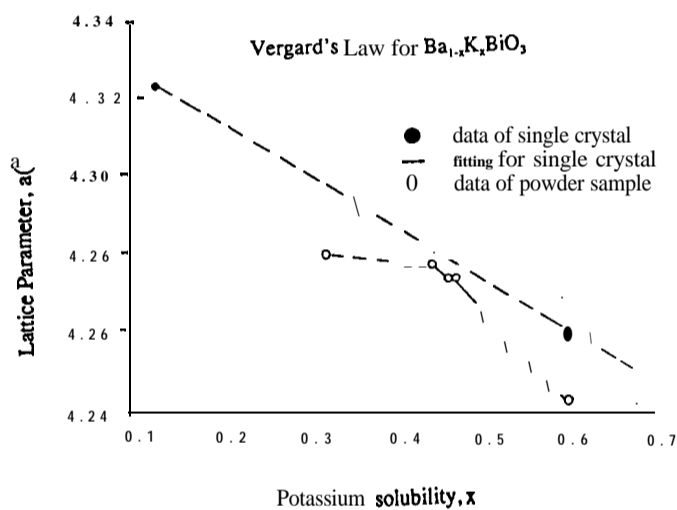
TABLE IB. Refined results for  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  crystals by Rietveld analysis [10]

Sample	$T_c$	$Rb$	$Rwp$	$x$	G.O.F.	a(A)
BKBOA	20 K	3.30 %	7.26 %	0.315	1.91	4.2804
BKBOB#	20 K	3.53 %	7.71 %	0.458	1.86	4.2746
BKBOB1#	20 K	2.86 %	6.90 %	0.466	1.81	4.2747
BKBOC	15 K	3.14 %	7.49 %	0.599	1.99	4.2434
BKBOD	25 K	3.14 %	7.42 %	0.439	1.99	4.2783

# BKBOB and BKBOB1 are samples from the same batch to test the repeatability of Rietveld analysis.

[10] in Table IA show that we can get quite perfect crystals grown from the low temperature anodic electrochemical technique.

The lattice parameters  $a$  and  $x$  values in Table IA from single crystal determination obey the Vegard's law very well as shown in Fig. 2, whereas those in Table IB from Rietveld analysis are far from the law. The  $r$ -values from single crystal determination and Rietveld analysis for the same batch of sample preparation are also different. These results strongly reveal that inhomogeneity exists in the growth of crystals by the low temperature anodic electro-chemical technique resulting in the mismatch values of  $x$  from the results of single crystal and powder analyses. The results from Rietveld analysis is only an average value over the entire batch of the sample.

FIG. 1. The structure scheme of  $Ba_{1-x}K_xBiO_3$ .FIG. 2. Lattice parameter  $a$  vs. Potassium solubility  $x$ .

The  $T_c$  values for single crystals were measured by SQUID [9]. The  $T_c$  values were also measured from the pressed bulks for powder samples. The  $T_c$  values of BKBOA and BKBOD, 14 K and 15 K respectively as shown in Table IA for single crystals, are lower than those of the bulk measurement in the previous study [3,6]. All  $T_c$  values for bulk

measurements in our study are also lower than corresponding values from the previous study [3,6], as shown in Table IB.  $T_c = 20$  K was observed for bulk sample BKBOA ( $x=0.311$ ), which contradicts the conclusion that  $T_c < 10$  K for  $x < 0.35$  [3,6]. Furthermore our potassium solubilities, for both single crystal BKBOC ( $x = 0.679$ ) and powder sample BKBOC ( $x = 0.599$ ), are beyond the solubility limit of the BKBO phase diagram [6]. Moreover powder sample BKBOA should not even be cubic according to the previous study [6].

Electron density maps show much differences between superconducting and nonsuperconducting single crystals. Fig. 3 shows the (001) section of electron densities with  $z = 0.5$  (refer to Fig. 1). The black dots represent the relevant atoms. For nonsuperconducting sample BKBOC (Fig. 3a), there is a nearly spherical distribution of the density for Bi atoms, whereas there is quite spherical distributions as shown in Fig. 3b. The density distribution is perfectly spherical for Bi atoms, But it is worthy to notice that residual peaks occur between the neighboring O atoms, whose heights are as high as O atoms and the positions about  $(1/4, 1/4, 1/2)$  and  $(0, 0, 1/2)$ .

From the occurrence of the residual peaks it can be reasonably concluded that the electrons of oxygen hop between O atoms and between Ba atoms. This conclusion may help to get the understanding of the mechanism of superconductivities.

The anisotropic thermal displacement factors for all  $Ba_{1-x}K_xBiO_3$  samples are of reasonable values and are similar either from single crystal or Rietveld analysis.

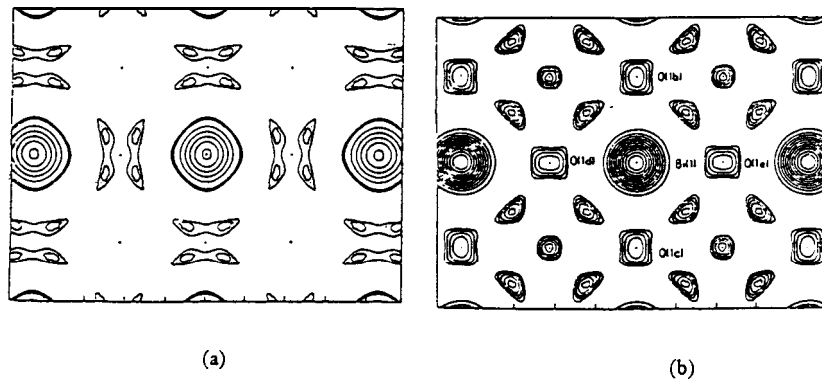


FIG. 3. Electron density map, (001) section,  $z = 1/2$ . (a) for nonsuperconducting sample BKBOC. The density distributions for both Bi and O atoms are localized. (b) For all the superconducting samples. There are residual peaks between neighboring O atoms, the position about  $(1/4, 1/4, 1/2)$  and another residual one is between neighboring Ba atoms, position about  $(0, 0, 1/2)$ .

#### IV. SUMMARY

Some of our results have been shown to be different from the previous studies in our present systematic structure study on the series of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  samples [3,6]. There do exist some inhomogeneities on the bulk samples grown from the low temperature anodic electrochemical technique. The values of  $T_c$  and solubility  $x$  differ significantly from the former measurements as well as the former phase diagram [6]. The electron density maps show the correlations between the electrons along certain orbits, which may offer the way to understand the high-T, superconductivities. Further studies on this system are in progress.

#### ACKNOWLEDGMENT

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#### REFERENCES

- [ 1 ] L. F. Mattheiss, E. M. Gyorgy, D. W. Johnson, Jr, Phys. Rev. B37, 3745 (1988).
- [ 2 ] R. J. Cava, B. Batlogg, J. J. Krajewski, R. Farrow, L. W. Rupp Jr, A. E. White, K. Short, W. F. Peck, and T. Komentani, Nature 332, 814 (1988).
- [ 3 ] D. G. Hinks, B. Dabrowski, J. D. Jorgenson, A. W. Michell, D. R. Richards, S. Pei, and D. Shi, Nature 332, 836 (1988).
- [ 4 ] A. W. Slight, J. L. Gillson, and P. E. Bierstedt, Solid State Commun. **17**, 27 (1975).
- [ 5 ] J. G. Bednorz and K. A. Müller, Z. Phys. B64, 189 (1986).
- [ 6 ] S. Pei, J. D. Jorgenson, B. Dabrowski, D. G. Hinks, D. R. Richards, A. W. Mitchell, J. M. Newsam, S. K. Sinha, D. Vaknin, and A. J. Jacobson, Phys. Rev. B41, 4126 (1990).
- [ 7 ] M. Verwerft, G. Van Tendeloo, D. G. Hinks, B. Dabrowski, D. R. Richards, A. W. Mitchell, D. T. Marx, S. Pei, and J. D. Jorgenson, Phys. Rev. **B44**, 9547 (1991).
- [ 8 ] M. L. Norton and H. Y. Tang, Chem. Mater. 3, 1431 (1991).
- [ 9 ] Charles P. Poole, Jr. Timir Datta, and Horacio A. Farach, Copper Oxide Superconductors, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, 1988, p. 9.
- [10] Fundamentals of Crystallography. Edited by C. Giacovazzo, International Union of Crystallography, Oxford University Press (1992).
- [11] J. P. Wignacourt, J. S. Swinnea, H. Steinfink, and J. B. Goodenough, Appl. Phys. Lett. 53, 1753 (1988).