Effects of La- and Pr-Substitution on the Structure and Superconductivity of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$

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Abstract: Two compositional series based on $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ and $\text{Ba}_{0.6-z}\text{Pr}_z\text{K}_{0.4}\text{BiO}_3$, with y and z being 0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, were synthesized using a molten salt method. X-ray powder diffraction data reveal that the initially undoped cubic crystal symmetry expands slightly to orthorhombic with Pr substitution but not with La substitution. A linearly reduction of the pseudo-lattice parameter following $a_p = 4.28257 - 0.02469y$ ($0.025 \leq y \leq 0.4$) can be observed in $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$. A systematic decrease of the transition temperature, T_c , is clarified by magnetic measurements and the superconductivity is finally vanished at $y, z = 0.2$ owing to the distortion of the crystal structure and the disproportions of bismuth valence.

Key words: $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$; substitution; crystal structure; molten salt method

Since superconductivity near 30 K was discovered in a copper-free phase, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO)^[1,2], this material has aroused considerable interest, although the mechanism of its superconductivity remains unclear. Further, it has been proved that it is difficult to prepare optimized superconducting BKBO owing to the volatility of the alkali, lack of reproducibility of composition and superconducting behavior, instability in air, and the variability in oxygen content^[1,3]. BKBO has been reported to have a simple cubic perovskite structure^[3] that is free of the localized magnetic moments present in cuprate superconductors. It shares some of the characteristics of conventional superconductors, including the s -wave order parameter^[4] and the superconducting gap/ T_c ratio of $2\Delta/k_B T_c = 3.5 \sim 4$ ^[5], which is indicative of a moderately strong electron-phonon coupling limit. However, for BKBO, the ratio between the superconducting carrier density and the effective mass ratio (n_s/m^*) ^[6] falls in the region characteristic of unconventional superconductors. Therefore, BKBO may provide the key to understanding the mechanism of unconventional superconductors.

Most previous work on BaBiO_3 has concentrated on the introduction of superconductivity at low T_c by substitution on the Bi site using Pb^[7]. Subsequently, superconductivity at high T_c was achieved by substitution on the Ba site using K^[1,2,8]. Consequently, there is some uncertainty concerning the relative degrees of importance of the Bi and Ba sites to the introduction of charge carriers and consequent superconductivity in the parent electrically insulating compound BaBiO_3 . Since it is well known that doping of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with rare earths on the Ba site affects the superconducting properties^[9], this observation provides the driving force for the present work, which considers that the presumed substitution of the rare earths La and Pr for Ba may alter the structure and properties.

In the present work, $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ and $\text{Ba}_{0.6-z}\text{Pr}_z\text{K}_{0.4}\text{BiO}_3$ (y and $z = 0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4$) samples were synthesized and characterized by X-ray diffraction and magnetization measurements. The effects of Pr and La doping on the crystal structure and superconductivity were assessed and compared to those of the undoped parent BKBO.

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1 Experiment

Powders of $(\text{Ba}_{0.6-y}\text{La}_y)\text{K}_{0.4}\text{BiO}_3$ and $(\text{Ba}_{0.6-z}\text{Pr}_z)\text{K}_{0.4}\text{BiO}_3$ (y and $z=0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4$) were prepared via the molten salt method^[10,11] using $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, Bi_2O_3 , $\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$, La_2O_3 , and Pr_6O_{11} (suppliers). Previous work^[10,11] showed that an optimal $\text{Bi}^{3+}/\text{Bi}^{5+}$ ratio of 1/1.1966 yielded the best homogeneity, so this ratio of 0.8357 was used. Consistent amounts of 0.06 moles (total) of mixed raw materials were dissolved in 20 g of liquid KOH in a Teflon crucible on a hot plate at 260 °C in air and maintained for 19 h, with occasional stirring. The resultant slurry exhibited partial solubility, accompanied by a color change during heating. After decantation, the solid residue was washed sequentially with distilled water and then ethanol, followed by drying in air at 75 °C for 24 h. The crystallography was examined by X-ray diffraction (Philips X'Pert MRD diffractometer, Cu K α radiation) and the superconductivity was measured over the temperature range 5~50 K using a SQUID magnetometer (Quantum Design MPMS) in a magnetic field of 796 A/m.

2 Results and Discussion

Fig.1a shows the X-ray diffraction patterns of the series of $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ samples. The slight peak splitting indicates that the structures are consistently quasi-cubic (tetragonal distortion). All diffraction peaks have been indexed although the assignment of the BaCO_3 peak is, by necessity, open to question. It can be seen that a saturated solution is obtained at $y>0.3$. Although the exsolution of Bi as Bi_2O_3 at $y=0.4$ is clear, the relatively consistent height of the BaCO_3 peak suggests that the solubility limit is not exceeded yet, and that this peak results from undissolved or recrystallized material. No exsolution of La-based compounds were observed.

Fig.1b shows that the peak positions gradually shift to higher angles with increasing of dopant level at all levels, indicating that the lattice contracts (although no internal standard was used, the patterns were obtained in continuous runs). These peaks remain relatively consistent in width, indicating no essential change in either crystallinity or crystal structure.

On the basis of the experimental results for La-doping, the following comments are made: (1) BaCO_3 and Bi_2O_3 are present as impurities in all compositions, without any trend in amounts, indicating that their presence is not associated with the doping. (2) La dissolves in the structure, as demonstrated by the alteration of the X-ray peak positions. (3) It is probable that the solid solution is substitutional since the lattice contracts. If the solid solution were interstitial, lattice expansion would be more likely. (4) Since La^{3+} is smaller than Ba^{2+} and K^{1+} but larger than Bi^{3+} and Bi^{5+} , the lattice contraction is consistent with substitution on the Ba site. (5) It can be concluded that La substitutes on the Ba site from the beginning because the addition of La is compensated by the

Fig.1 XRD patterns of the $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ ($y=0\sim0.4$) samples (a); enlarged view of (220) and (310) peaks (b) (the line is just a guide to eyes)

reduction in the amount of Ba and no significant amounts of any compounds were exsolved at any compositions up to $y=0.3$.

In contrast, the X-ray diffraction patterns of the series $(\text{Ba}_{0.6-z}\text{Pr}_z)\text{K}_{0.4}\text{BiO}_3$ samples shown in Fig.2a demonstrate that, in common with the La-doped materials, BaCO_3 and Bi_2O_3 (Bi^{3+}) are present as impurities in all compositions, without any trend in amounts, indicating that their presence is associated with the raw materials and/or processing, not doping. However, the results of Pr doping are somewhat different from those of La doping in which they show the following: Bi^{4+} and Pr^{4+} are present in the form of BiO_2 and PrO_2 , respectively, becoming detectable at $z=0.3\sim0.4$ and apparently increasing in proportion to dopant level, although the peaks are not sufficiently large to allow a definitive conclusion.

Fig.2b shows that the effects of Pr-doping on the crystal structure also are quite different from those of La-doping, as shown in Table 1. In this case, the structural effects are more significant as a function of increasing dopant level, with alteration of the quasi-cubic structure to a transient orthorhombic structure, followed by conversion to an expanded quasi-cubic structure that gradually contracts. In particular, the orthorhombic distortion is consistent with expansion in one direction (diffraction peak at lowest angle shifts significantly downwards) and contraction in the other two directions (diffraction peaks shift slightly upwards), probably resulting in a net unit cell expansion. Accordingly, it is concluded that

Fig.2 XRD patterns of the $(\text{Ba}_{0.6-z}\text{Pr}_z)\text{K}_{0.4}\text{BiO}_3$ ($z=0\sim0.4$) samples (a); enlarged view of (220) and (310) peaks (b) (the line is just a guide to eyes)

Table 1 Effect of Pr-doping on crystal structure in $(\text{Ba}_{0.6-z}\text{Pr}_z)\text{K}_{0.4}\text{BiO}_3$

Dopant level, z	Structural distortion
0	Parent quasi-cubic
0.025, 0.05, 0.1	Orthorhombic distortion
0.2, 0.3, 0.4	Expanded quasi-cubic with gradual lattice contraction

Pr dissolves in the structure and alters it, as demonstrated by the absence of reaction products or precipitates at the lowest levels of doping and the conversion from quasi-cubic to the orthorhombic distortion.

The structural distortion and the associated lattice expansion are consistent with one or both of the following solution mechanisms: substitution of the larger Pr^{3+} and/or Pr^{4+} ion on the smaller Bi^{5+} site (substitutional); solubility of the Pr^{3+} and/or Pr^{4+} ion in interstitial positions (Interstitial). Interstitial solid solubility is not likely owing to the relatively large sizes of Pr^{3+} and/or Pr^{4+} . However, the X-ray data can be explained by substitutional solid solution formation according to the following considerations: Pr^{3+} and Pr^{4+} are sufficiently small to substitute for the larger Ba^{2+} ; this would cause a lattice contraction; substitution for the larger Bi^{3+} by the smaller Pr^{3+} and Pr^{4+} would result in lattice contraction; substitution for the smaller Bi^{5+} by the slightly larger Pr^{4+} (or larger Pr^{3+}) would result in lattice expansion. Therefore, the anisotropic changes in axial dimensions and the consequent alteration of the quasi-cubic structure to the orthorhombic can be interpreted in terms of substitution for Ba and Bi by Pr

occurring simultaneously.

Oxygen content is always a very important factor to determine the physical and chemical properties of oxide and oxygen vacancies which sometimes induce carriers in the system and sometimes disturb conduction. In the present work, we use the molten salt method to prepare all the samples where seldom oxygen vacancies were detected^[10]. Therefore, it is concluded that our samples have no considerable oxygen deficiency and the contractions have been caused by the doping effect.

Fig.3 presents temperature dependence of the magnetic susceptibility. The transition temperature drops with the increase of the substitution level and vanishes when it reaches y ; $z = 0.2$ and the superconducting volume fraction both decreases with the increase of the substitution level, without consideration of a comparatively little signal of diamagnetic existing in the $y = 0.2$ and $y = 0.3$ samples for La substitution. Transition width becomes broader which suggests an in-homogeneity of the cations for La substitution. However, for Pr-substituted $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, it shows better homogeneity than the La-substituted ones, presented in Fig.3b.

Fig.4 shows the change of the pseudo-lattice parameter with the substitution level. In general, perovskite compounds have various types of distortions such as tetragonal, orthorhombic, or monoclinic cells. Strictly speaking, we must take the lattice parameters for such distorted cells with real symmetries. Therefore, we use a_p (a lattice parameter assuming cubic

Fig.3 Temperature dependence of magnetic susceptibility for $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ samples (a) and $\text{Ba}_{0.6-z}\text{Pr}_z\text{K}_{0.4}\text{BiO}_3$ samples (b) (Both are measured in an applied field of 796 A/m. Insets show enlarged view of the superconducting transition)

Fig.4 Pseudo-lattice parameter a_p dependence on substitution level of La

perovskite) as an indicator of the cell size in the present work. With the increase of La substitution, lattice parameters are reduced probably due to a decrease in the averaged ionic radius of A-site element in the perovskite-type compounds. We have fitted the drop with linear, and it is not as sharp as the doping with K content in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. It has been reported that the drop of a_p with K content is coincident with $a_p = 4.3548 - 0.1743x$ ($0.3 \leq x \leq 0.6$)^[3], but La-substituted $\text{Ba}_{1-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ just follows the equation of $a_p = 4.28257 - 0.02469y$ ($0.025 \leq y \leq 0.4$). Obviously, the effect of La substitution is not as sensitive as K doping.

It has been concluded in our previous work that the deficiency of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in the starting materials may influence superconductivity of BKBO^[10]. Fig.5 displays the reduction of T_c with increasing mass ratio of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}/\text{KOH}$ (γ_w) in the present work. The T_c of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ (30.6 K, see Fig.5 inset) and $\text{Ba}_{0.4}\text{K}_{0.6}\text{BiO}_3$ (7.2 K) in our preliminary study of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ are also presented^[10], showing comparing data with the La and Pr substitution samples. They show totally different behaviors. According to this, we can conclude that the substitution in our present work has a real effect on the transition temperature, not for the deficiency of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in the starting materials.

Fig.5 Reduction of transition temperature T_c with decreasing mass ratio of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}/\text{KOH}$ (γ_w) (the T_c of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ and $\text{Ba}_{0.4}\text{K}_{0.6}\text{BiO}_3$ were also presented to show comparison)

In the present two systems, the carrier concentration changes with the substitution at Ba-site. The replacing of every two Ba^{2+} ions by La^{3+} or Pr^{3+} ones produces two electrons, suggesting a break of hole pair in oxygen environment of bismuth. In that case, the hole-carrier density decreases and induces a suppression of T_c . Partial substitution of La and Pr for Ba or Bi induces not only a decrease of hole-carrier concentration but also a structural distortion. There have been reports on BaBiO_3 that Bi occupies two distinctive sites with different bond lengths and suggested the Bi valence disproportionation $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$ using neutron diffraction^[12]. The performed X-ray absorption spectroscopy (XAS) measurements^[13-15] proposed a charge disproportionation model in the form: $2\text{Bi}^{4+} \rightarrow \text{Bi}^{3+} + \text{Bi}^{5+}\text{L}^2$, where L^2 denotes the pair of holes in oxygen octahedral environment. These two different surroundings of the Bi ion produce two different Bi octahedrons, a stiff small octahedron and a soft large one. For $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, the addition of Bi^{3+}L^2 increases the input of the stiff small octahedron and has no tilting distortion. On the contrary, La- and Pr-substituted $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ on the Ba site as well as Pr^{4+} substitution on the Bi^{5+} site produce a decrease of the stiff small octahedron and enhance the tilting distortion.

Furthermore, the distortion is not only related to the valence of the substitution but also to the radius of the substituted element. Antipov and Kazakov^[16,17] reported the superconductivity of $\text{Sr}_{1-x}\text{K}_x\text{BiO}_3$ and $\text{Sr}_{1-x}\text{Rb}_x\text{BiO}_3$ which show that the octahedral tilt scheme influenced by the size of the A cation is also an important aspect. In our present work, the radius of La and Pr cations are all smaller than the Ba ones and enhance the octahedral distortion leading to charge disproportionation and suppression of superconductivity. Compared with La-substituted BKBO system, the simultaneous influence of Pr^{4+} substitution at the Bi^{5+} site has significantly enhanced the distortion of crystal structure and the charge disproportionation in Pr-substituted $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ system. Consequently, Pr substitution has induced a larger suppression of T_c in BKBO.

3 Conclusions

1) A series of $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ and $\text{Ba}_{0.6-z}\text{Pr}_z\text{K}_{0.4}\text{BiO}_3$ with $y, z = 0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4$ can be prepared by a molten salt method.

2) With La substitution, lattice parameters are linearly reduced for all the La contents. However, the alternation of crystal structure from quasi-cubic to orthorhombic structure can be observed in the Pr-substituted BKBO.

3) T_c is found to be suppressed at a relatively low substitution level $y, z \leq 0.1$ and vanished when $0.2 \leq y$ or $z \leq 0.4$. The distortion of the crystal structure owing to the valence of the substitution and the radius of the substituted element is recognized as the reason of the T_c suppression.

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La 和 Pr 掺杂对 $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ 结构及超导电性的影响

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摘要:利用熔盐法制备了 $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ 和 $\text{Ba}_{0.6-z}\text{Pr}_z\text{K}_{0.4}\text{BiO}_3$ 2 个系列的样品, 其中 La 和 Pr 的掺杂量 y 和 z 分别为 0, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4。X 射线粉末衍射结果显示, Pr 掺杂使得 BKBO 晶体结构由最初的立方晶系转变成为正交晶系, 但是 La 掺杂样品却没有发生此种晶体结构的变化。La 掺杂样品 $\text{Ba}_{0.6-y}\text{La}_y\text{K}_{0.4}\text{BiO}_3$ 的准晶格参数 a_p 随掺杂量的增大而线性减小, 其变化遵循 $a_p = 4.28257 - 0.02469y$ ($0.025 \leq y \leq 0.4$) 的规律。样品磁性测量结果表明, 掺杂样品的超导转变温度 T_c 均随着掺杂量的增大而系统性地减小, 并且当掺杂量达到 0.2 时, 2 个系统中的超导转变均消失。认为掺杂引起的晶体结构扭曲及铋化合价的不均衡导致了 BKBO 掺杂系统超导电性的变化。

关键词: $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$; 掺杂; 晶体结构; 熔盐法

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