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Hydrothermal synthesis of superconductors $Ba_{1-x}K_xBiO_3$ and double perovskites $Ba_{1-x}K_xBi_{1-y}Na_yO_3$

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ABSTRACT

Superconductors $Ba_{1-x}K_xBiO_3$ and body-centered double perovskites $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ have been selectively synthesized by a facile hydrothermal route. The appropriate ratio and adding sequence of initial reagents, alkalinity, reaction temperature and time are the critical factors that influence the crystal growth of the compounds. The purity and homogeneity of the crystals were detected by the ICP, SEM, EDX and TEM studies. Magnetic measurements show that the superconducting transition temperatures T_C of $Ba_{1-x}K_xBiO_3$ decrease from 22 K (for $x = 0.35$) to 8 K (for $x = 0.55$) with increasing the K doping level.

1. Introduction

The superconductivity remains one of the most attractive and challenging forefronts of materials science research. In recent years, many efforts have been devoted to explore new superconducting materials and improving the preparation methods of existent superconductors [1–4]. As the first copper-free oxide superconductor with the transition temperature as high as 30 K, the $Ba_{1-x}K_xBiO_3$ system has triggered extensive research in recent decades [5–10]. However, the synthesis routes of these oxides are not so convenient due to their poor thermal stability. The conventional solid state reactions for this system were commonly carried out in special apparatus with various protective atmospheres [5–7]. Because of the high reaction temperature and the volatility of K, the inhomogeneous chemical composition and the multiphase of the sample usually cannot be avoided. Subsequently, electrochemical deposition method was also adopted to prepare the $Ba_{1-x}K_xBiO_3$ system [11,12], especially for the growth of its large single crystals [13]. Nevertheless, the chemical composition and the superconducting properties are limited by many factors due to the complex reaction mechanism. Moreover, some non-superconductor phases, such as layered bismuthate ($(Ba,K)_3Bi_2O_7$) [14] and the body-centered double cubic perovskite ($Ba_{1-x}K_xBi_{1-y}Na_yO_3$) [15], could also be formed during the electrolysis. Although the molten salt process seems somewhat straightforward, the multiphase usually occurs and the crystal morphologies of $Ba_{1-x}K_xBiO_3$ are comparatively poor [16–18]. Thus, a facile and mild synthesis method is worthwhile to prepare $Ba_{1-x}K_xBiO_3$ system and even to exploit new superconducting materials.

For the advantages of the mild reaction conditions, convenient operation process, easy to handle and simple apparatus, hydrothermal synthesis has been utilized to prepare numerous oxides of high purity, narrow particle size distribution, high phase homogeneity, controlled particle morphology and a high degree of crystallinity [19–21]. Actually, it is also available for the preparation of several superconductors, such as La_2CuO_{4+y} [22] and $BaPd_{1-x}Bi_xO_3$ [23]. However, to the best of our knowledge, the hydrothermal synthesis of the superconducting $Ba_{1-x}K_xBiO_3$ has never been reported so far. Moreover, it is still a challenge to selectively synthesize the $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$, which usually coexist in the electrolysis and molten salt process. In this paper, we present a selective synthesis of superconductors $Ba_{1-x}K_xBiO_3$ and body-centered double perovskites $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ by a convenient hydrothermal route.

2. Experimental

For a typical synthesis of $Ba_{0.65}K_{0.35}BiO_3$, 0.325 mmol $Bi(NO_3)_3$, 0.65 mmol $Ba(NO_3)_3$, 0.675 mmol $NaBiO_3$ and 1 mol KOH were dissolved in 65 ml distilled water. After stirring for an hour, the reaction mixture was then transferred into an 80 mL Teflon-lined stainless steel autoclave with a filling capacity of 70% and heated at 180 °C for 1–5 days. After the autoclave was cooled and depressurized, the products were washed with distilled water and sonicated. And then, single-phase $Ba_{0.65}K_{0.35}BiO_3$ was obtained as a fine deep blue-black crystal product at the bottom of the beaker. $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ crystals were obtained via the same procedure as $Ba_{0.65}K_{0.35}BiO_3$ by just not adding the reagent $Bi(NO_3)_3$. The detailed reaction conditions for other compounds are given in Table 1.

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Table 1
The optimal synthesis conditions for $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$.

Compounds	g[a]	KOH/M	T/°C	T_C/K
$Ba_{1-x}K_xBiO_3$				
$x = 0.06$	1.0:0.5:0.5	10	180	–[b]
$x = 0.35$	0.600:0.325:0.675	10	180	22
$x = 0.5$	0.50:0.25:0.75	12	180	14
$x = 0.55$	0.450:0.225:0.775	15	180	8
$Ba_{1-x}K_xBi_{1-y}Na_yO_3$				
$x = 0$; $y = 0.25$	1.00:0.75:0	10	180	–
$x = 0.15$; $y = 0.17$	1:1:0	10	160	–

[a] g for the mole ratio of initial reagents: $n[Ba(NO_3)_2]$:$n[NaBiO_3]$:$n[Bi(NO_3)_3]$.
[b] Non-superconductor phase.

The crystallinity and purity of the products were examined by powder X-ray diffraction data of the studied samples collected on a Rigaku D/Max-2000 diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å) at 40 kV, 100 mA and a graphite monochromator at the secondary beam. The morphology and microstructure of the samples were investigated by scanning electron microscopy (SEM, performed on a FEI Quanta 200F microscope operating at 3 kV) and transmission electron microscopy (TEM, carried out on a JEM2100F with an accelerating voltage of 200 kV). The chemical compositions were confirmed by energy dispersive spectroscopy (EDS) and inductively couple plasma (ICP) analysis carried out on a PROFILE SPEC ICP instrument. The superconducting transition temperatures were determined from the magnetic studies using a quantum design physical properties measurement system (PPMS). The DC susceptibility measurements were performed in a 100 Oe magnetic field for temperatures ranging from 2 to 100 K.

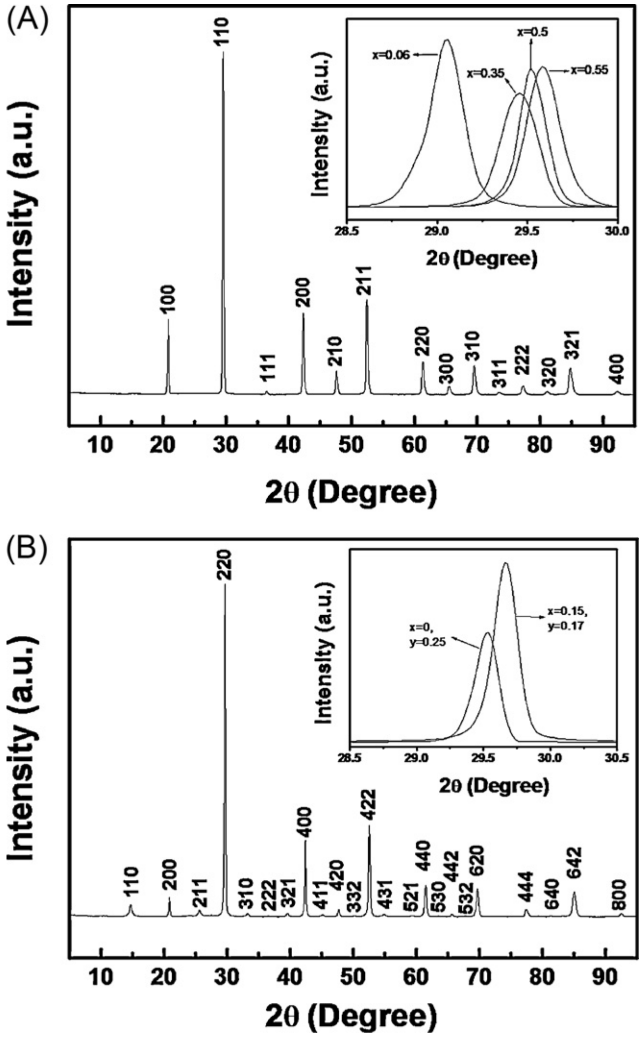

Fig. 1. Powder XRD patterns for $Ba_{1-x}K_xBiO_3$ (A) and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ (B). The insets show the peak shifts for various compositions of $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$, respectively.

3. Results and discussion

The room-temperature powder XRD patterns for $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ are shown in Fig. 1. All Bragg peaks of $Ba_{1-x}K_xBiO_3$ can be perfectly indexed to a cubic phase with space group $Pm\overline{3}m$ (No. 221) for $0.35 < x < 0.55$ and a monoclinic phase with space group $I2/m$ (No. 12) for $x = 0.06$ respectively. These results are consistent with the one reported in pioneering work [24,25]. It can be found that the XRD peaks shift towards the low d-spacing (shown as the insert of Fig. 1(A)), which indicated a slight decrease in the unit cell volume with the increase of the K doping level. For $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ system, the peaks can be indexed to a body-centered cubic perovskite phase with space group $Im\overline{3}m$ (No. 229) as previously reported [15,26]. There is also a slight decrease

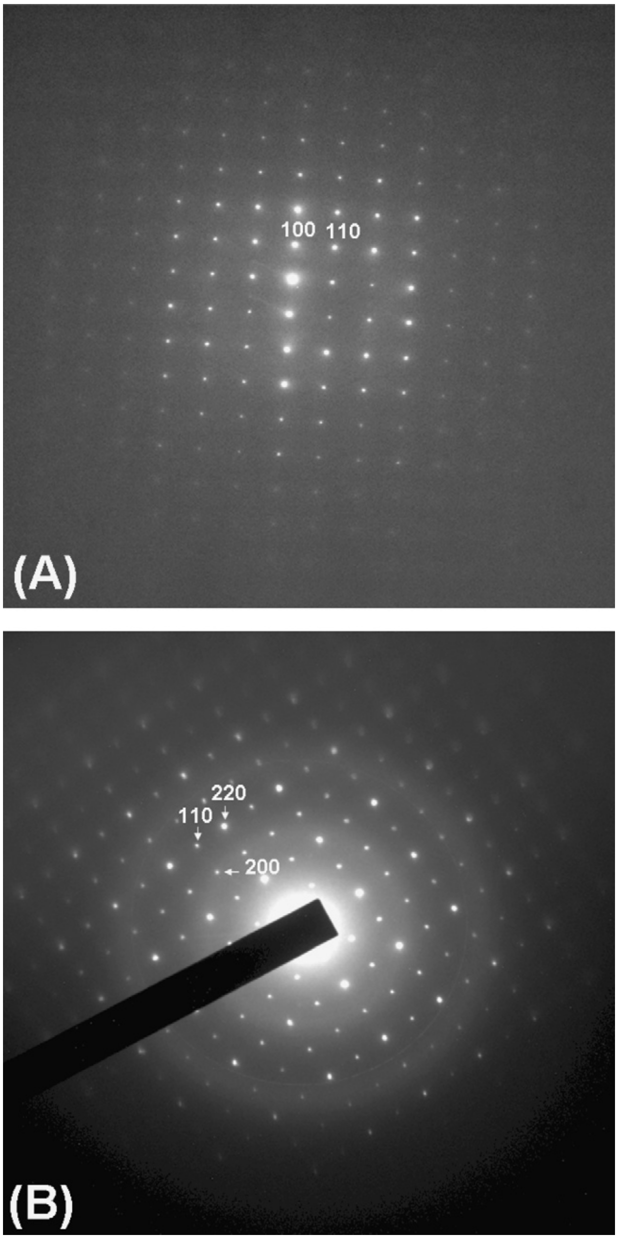

Fig. 2. Electron diffraction patterns of two representative crystalline samples: (A) for simple cubic $Ba_{0.65}K_{0.35}BiO_3$ along [001] zone axis; (B) for body-centered cubic $BaBi_{0.75}Na_{0.25}O_3$ along [001] zone axis.

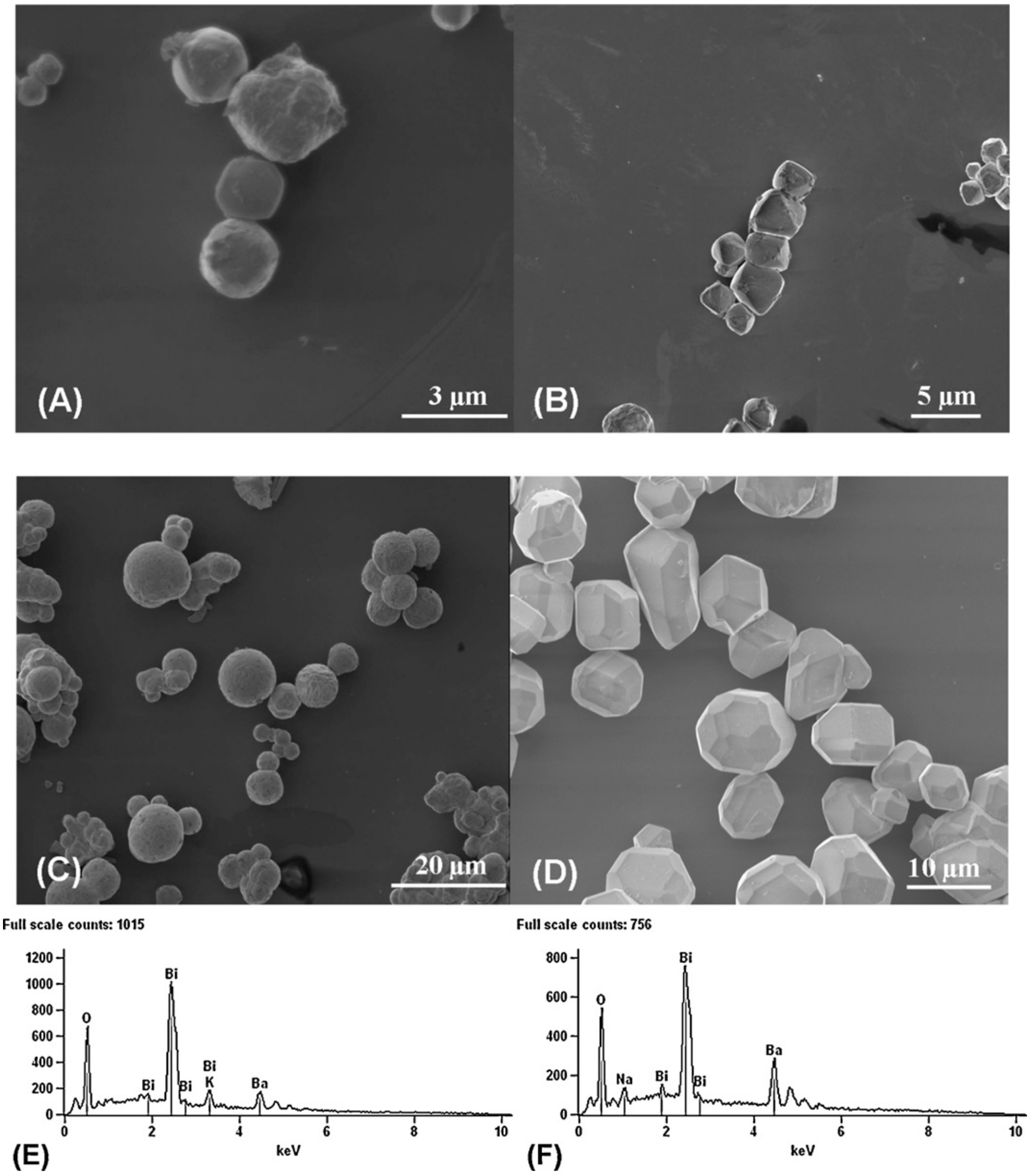

Fig. 3. SEM images of crystalline samples (A) for $Ba_{0.65}K_{0.35}BiO_3$ obtained by adding KOH solid directly, (B) for $Ba_{0.65}K_{0.35}BiO_3$ obtained by dissolving KOH in distilled water first, (C) for $Ba_{0.85}K_{0.15}Bi_{0.83}Na_{0.17}O_3$ and (D) for $BaBi_{0.75}Na_{0.25}O_3$ and the EDX analysis for $Ba_{0.65}K_{0.35}BiO_3$ (E) and $BaBi_{0.75}Na_{0.25}O_3$ (F).

in the unit cell volume with increasing the K doping level (shown as the insert of Fig. 1(B)).

The structures of the samples are also confirmed by TEM studies. Fig. 2 shows the electron diffraction patterns of two representative specimens: $Ba_{0.65}K_{0.35}BiO_3$ (Fig. 2(A)) and $BaBi_{0.75}Na_{0.25}O_3$ (Fig. 2(B)). It clearly revealed a simple cubic perovskite cell for $Ba_{0.65}K_{0.35}BiO_3$ and a double supercell along both zone axial directions for $BaBi_{0.75}Na_{0.25}O_3$, which corresponded well with the structure models obtained from the XRD data. The excellent crystallinity of the products obtained by hydrothermal synthesis was confirmed by SEM images shown in Fig. 3, which show clearly the materials to be made up from unique small crystallites, around 3–10 μm in a narrow particle size distribution. EDX analysis of selected regions for the sample showed the presence of all elements in area analyzed with a constant ratio, indicating the crystals are uniform in their composition (shown in Fig. 3). The superconducting transition temperatures T_C were determined by magnetic studies of the samples. Fig. 4 shows the DC magnetization curves of superconducting $Ba_{1-x}K_xBiO_3$ samples, which reveals that the T_C values decrease with increasing the K doping level. The highest T_C

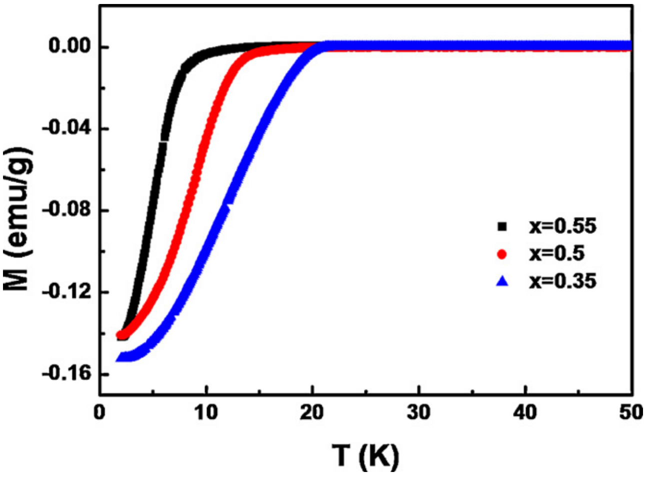

Fig. 4. The temperature-dependent magnetization curves of superconducting $Ba_{1-x}K_xBiO_3$ samples cooled in an applied field of 100 Oe.

is about 22 K observed in $Ba_{0.65}K_{0.35}BiO_3$, which is somewhat lower than the maximal values previously reported in $Ba_{1-x}K_xBiO_3$ system [6,7,16] presumably due to the different synthesis conditions. As known for non-superconductor phase, the magnetic studies of $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ system revealed the nonmagnetic nature.

It has been known that preparative methods may affect the final structures, morphologies and physical properties of products, such as in the cases of solid state reactions and hydrothermal reactions where the mechanisms for the crystal growth may be totally different between the two. In our study on hydrothermal chemistry, we understand that possible reactions may play an important role in the formation of final products. We here applied the co-precipitation reaction to prepare the title compounds. The proposed chemical reactions can be written as:

$$(1-x)Ba^{2+} + xK^+ + \frac{(1-x)}{2Bi^{3+}} + \frac{(1+x)}{2BiO_3} + (3-3x)OH$$
$$\rightarrow Ba_{1-x}K_xBiO_3 + \frac{(3-3x)}{2H_2O};$$

$$(1-x)Ba^{2+} + xK^+ + yNa^+ + (1-y)BiO_3 + 6yOH$$
$$\rightarrow Ba_{1-x}K_xBi_{1-y}Na_yO_3 + 3yH_2O$$

In present hydrothermal process, there are many influencing factors for the crystal growth of the title compounds, including appropriate ratio and adding sequence of initial reagents, alkalinity, reaction temperature and time.

For the synthesis of $Ba_{1-x}K_xBiO_3$ system, the K doping level can be adjusted by the relative amount of Ba^{2+} ions to the total Bi ions. We have noted that the actual reactions lie on not only the stoichiometric ratio but also the thermodynamic stability of the final products. Except the compositions with $0.35 \le x \le 0.55$ and $x \sim 0.06$, other compositions failed to be obtained in this work. This result is similar with the one reported in previous molten salt process by Liu and Fu [18], which is associated with the thermodynamic instability of other compositions. The adding sequence of initial reagents also plays an important role for the crystal growth of $Ba_{1-x}K_xBiO_3$. Taking the preparation of $Ba_{0.65}K_{0.35}BiO_3$ for example: if we added the KOH solid directly into the mixture (containing $Ba(NO_3)_3$, $Bi(NO)_3$ and $NaBiO_3$), a black product was formed immediately due to the exothermic reaction between KOH solid and water. With prolonging the reaction time, the crystallization degree of the sample was increased, but the impurity ($Ba_{1-x}K_xBi_{1-y}Na_yO_3$) was hard to be avoided and the crystal morphology was irregular (Fig. 3(A)). These phenomena can be also observed in molten salt process, which probably indicated the similar growth mechanism with each other. However, if we first dissolved the KOH solid in distilled water and cooled it to room temperature, there was no obvious change when we transferred the KOH solution into the mixture (containing $Ba(NO_3)_3$, $Bi(NO)_3$ and $NaBiO_3$). After heating the mixture at 180 °C for 3 days, a blue-black product with regular octahedral crystal morphology was obtained (Fig. 3(B)). The difference between the two processes can be attributed to spontaneous growth mechanism and homogeneous reaction in the latter process.

On the other hand, the synthesis of $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ system is more facile and controllable. The pure products can be synthesized by controlling the appropriate ratio of $Ba(NO_3)_2$ to $NaBiO_3$. In present work, we obtained only two compositions with unique crystal morphology, viz. the polyhedral $BaBi_{0.75}Na_{0.25}O_3$ (Fig. 3(C)) and the spherical $Ba_{0.85}K_{0.15}Bi_{0.83}Na_{0.17}O_3$ (Fig. 3(D)). Up to now, the researches concerning this system are limited in two specimens: $BaBi_{0.75}Na_{0.25}O_3$ (prepared by a thermal decomposition method under high oxygen pressure [26]) and $Ba_{3.04}K_{0.96}Bi_{3.37}Na_{0.63}O_{12}$ (prepared by an electrodeposition method [15]). Compared with the two methods, the present synthesis route has obvious advantages of convenient operation process and mild reaction condition.

It is worth noting that the crystal growths of $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ are also sensitive to the reaction temperature. The reactions can occur under a wide temperature range from 120 °C to 220 °C. With increasing the temperature, the purity and crystallization degree of the samples are improved. However, if the reaction temperature is higher than 200 °C, the products began to dissolve in the KOH solution. When the reaction temperature is higher than 240 °C, we cannot obtain any solid but a clear solution from the hot autoclaves. This result probable suggests the amphoteric nature of these compounds. Moreover, the alkalinity of the reaction system also considerably influences the crystallization of title compounds. In the present work, KOH not only maintained the alkalinity but also acted as a mineral reagent. If the alkalinity is less than 8 M, we cannot obtain the products but a powder mixture of Bi_2O_3, $KBiO_3$ and $BaCO_3$. With increasing the amount of alkalinity, the purity of the products was improved and the crystallization degree was increased. Furthermore, the crystal sizes of both $Ba_{1-x}K_xBiO_3$ and $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ are markedly increased with prolonging the reaction time.

4. Conclusions

In summary, the superconductor $Ba_{1-x}K_xBiO_3$ and body-centered double perovskite $Ba_{1-x}K_xBi_{1-y}Na_yO_3$ have been selectively synthesized by a hydrothermal route with advantages of relatively mild conditions, one-step synthesis procedure and easy handling. The influence factors in the hydrothermal process were discussed in detail. The ICP, SEM, EDX and TEM studies confirmed the purity and homogeneity of the crystals. The superconducting transition temperatures were determined by magnetic studies. The present work done by us can be a possible route to fabricate other superconducting system and even to exploit new superconductors.

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