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High efficiency preparation of $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconducting thin films by an acetate based Sol-Gel process

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HIGHLIGHTS

- A high-efficiency and environmentally friendly acetate based sol-gel method for Bi-2212 films is proposed.
- The whole heat treatment process only needed 4 h, which is good for environment protection and energy conservation.
- The prepared Bi-2212 superconducting films exhibit good growth textures and excellent superconductivity.

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ABSTRACT

$Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) superconducting thin films with *c*-axis epitaxial orientation were prepared on $LaAlO_3$ (LAO) single crystal substrates via a Sol-Gel technique using metallic acetates as starting materials. The influence of the growth temperature and oxygen partial pressure (pO_2) on the phase purity and superconducting properties of Bi-2212 was discussed. The results show that Bi-2212 films prepared at 820 °C with the pO_2 of 1.4 KPa exhibit good in-plane and out-of-plane growth textures and excellent superconducting properties with high critical transition temperature (T_c) of 88 K and narrow transition width (ΔT_c) of 4.8 K.

1. Introduction

Since the discovery of $Bi_2Sr_2Ca_nCu_{n+1}O_\delta$ (BSCCO), it has been researched extensively, due to its good properties, for improving its superconductivity and structure property. Therefore, BSCCO is found to be a potential candidate for superconducting wires [1], superconducting tapes [2] and microelectronic devices [3]. In addition, BSCCO superconducting thin films have been expected to realize the application of THz technology due to its intrinsic Josephson effect [4]. In Bi-based superconductor system: Bi-2201 phase with Tc of ~24 K, Bi-2212 phase with Tc between 80 K and 96 K and Bi-2223 phase with Tc of ~110 K. Besides a good superconductivity, Bi-2212 is much more thermodynamically stable over a wide temperature than Bi-2223 phase [5]. As a consequence, Bi-2212 has attracted considerable attention for a long time. So far, Bi-2212 thin films have been prepared on single crystal substrates, Ag substrates, or MgO substrates by Pulsed Laser Deposition [6], Mechanical Exfoliation [7], Microwave Techniques [8] or Molecular Beam Epitaxy [9]. In some cases, Bi-2212 superconducting films can be produced directly from Bi-2212 powders in pure oxygen or vacuum condition [10–12]. Pb-doped Bi-2212 phase can not only lower the heat-treatment temperature but also shorten the heat-treatment time, however, it is toxic and unfriendly to environment [13,14].

Therefore, a simple and eco-friendly method for preparing Bi-2212 thin films is urgently needed. Compared with other techniques, Sol-Gel technique has many advantages such as low cost, high efficiency, easy handling, molecular level homogeneity, environment protection and energy conservation [15-18]. So far, there are only a few reports about BSCCO superconductors prepared by Sol-Gel technique. And most of the researchers chose alkoxides or nitrates as starting materials [19–21]. As we known, alkoxides are expensive, and nitrates usually release NH_3 and NO_2 that destroy the surface quality of Bi-2212 films during the heat treatment process [22].

To avoid these problems mentioned above, *c*-axis epitaxial Bi-2212 films were prepared on $LaAlO_3$ (LAO) substrates by Sol-Gel method using Bi-acetate, Sr-acetate, Ca-acetate and Cu-acetate as starting materials. LAO (3.8 Å) and Bi-2212 (5.4 Å) has a small lattice mismatch of 0.49% in 45-degree rotated lattice matching relation in a-b plane, it is good for improving film growth and film quality. The effects of heat-treatment temperature and oxygen partial pressure on the quality of Bi-2212 films were investigated in detail to improve their phase purity and

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superconductivity. After optimizing heat treatment parameters, the whole heat-treatment time was shortened to 4 h.

2. Experimental procedure

2.1. Preparation of Bi-2212 films

Analytical reagent $Bi(CH_3COO)_3$((Bi)Ac3), $Sr(CH_3COO)_2{\cdot}1/2H_2O$(Sr(Ac)2), $Ca(CH_3COO)_2{\cdot}H_2O$($Ca(Ac)_2$) and $Cu(CH_3COO)_2{\cdot}H_2O$($Cu(Ac)_2$), acrylic acid (AA) and methanol (MeOH) were used as starting material, chemical modifier and solvent to synthesize Bi-2212 solution. Fig. 1 shows the process for the preparation of Bi-2212 solution. $(Bi)Ac_3$, $Sr(Ac)_2$, $Ca(Ac)_2$ and $Cu(Ac)_2$ were dissolved into AA and MeOH respectively in a stoichiometric quantity of $(Bi)Ac_3$:AA:MeOH = 1:10:20, $Sr(Ac)_2$:AA:MeOH = 1:12:20, $Ca(Ac)_2$:AA:MeOH = 1:12:20 and $Cu(Ac)_2$:AA:MeOH = 1:3:60 at room temperature to prepare Bi-solution, Sr-solution, Ca-solution and Cu-solution, respectively. Then the four solutions were mixed in the controlled stoichiometry of Bi:Sr:Ca:Cu = 2:2:1:2, stirred and aged for 48 h to form the stable Bi-2212 solution.

In order to investigate the effect of heat treatment temperature on phase purity of Bi-2212, four groups of Bi-2212 gel films were prepared on LAO substrates by dip-coating method and heat treated at 780 °C, 800 °C, 820 °C and 840 °C, respectively. Fig. 2 shows the heat treatment profile of Bi-2212 films. During the heat-treatment process, Bi-2212 gel films were firstly heated up to 420 °C from room temperature in humid N_2, it is aim to exhaust air and avoid film toughing and drying. Subsequently, Bi-2212 films were heated up to 600 °C in dry O_2, and the content of O_2 should be enough to form the intermediate phase completely at this stage. Then the Bi-2212 films were heated up to 780 °C, 800 °C, 820 °C or 840 °C and crystallized for 40 min in humid N_2 mixed with small amounts of O_2. Oxygen content has an important effect on the phase formation of Bi-2212 during high-temperature phase formation process, and it will be discussed in detail in 3.2. Finally the Bi-2212 films were dwelled at 550 °C for 50 min in dry O_2 to fill oxygen vacancies [23]. The whole heat treatment process only needed 4 h and the high-temperature phase formation process only needed 40 min.

2.2. Characterization

A SmartLab X-ray diffractometerin θ-2θ, ω and φ scan modes (XRD) is used to determine the phases, the out-of-plane texture, and the in-plane texture, respectively. Scanning electron microscopy (SEM) experiments are conducted on a JEM-6700F and energy dispersive spectrometry (EDS) was adopted to detect the composition of the films. Curves depicting the resistance–temperature (R–T) characteristics of the films were measured by A VersaLab multi-function vibrating sample magnetometer (VSM).

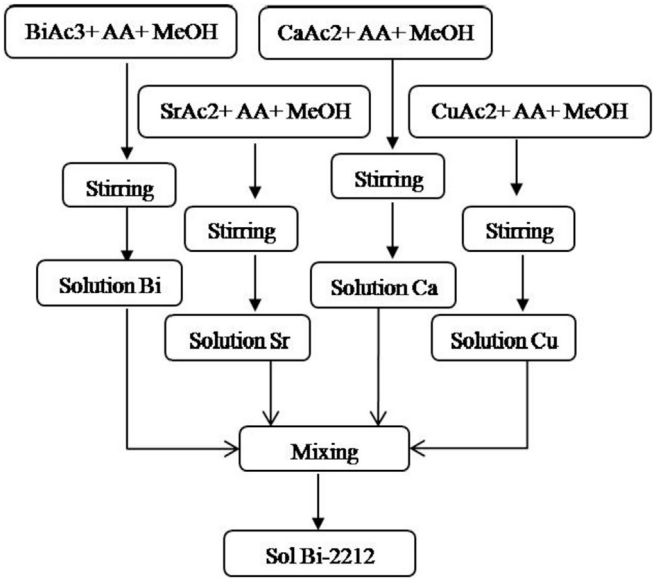

Fig. 1. Flowchart for the preparation of Bi-2212 Solution.

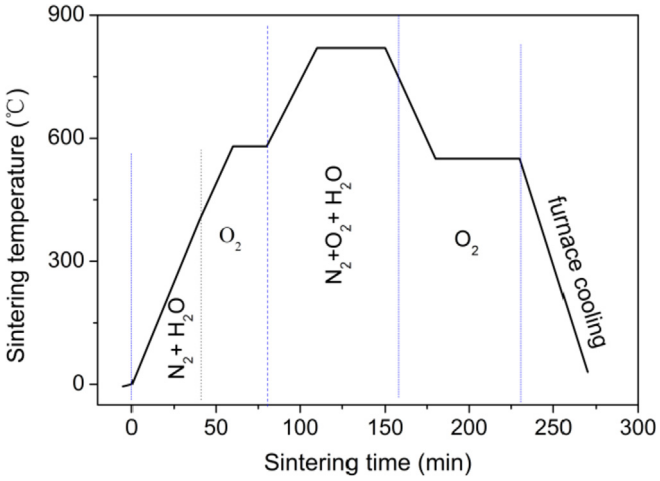

Fig. 2. Profile for the heat treatment of Bi-2212 thin films.

3. Results and discussion

3.1. The effect of heat treatment temperature on phase purity of Bi-2212

Fig. 3 shows XRD patterns of the Bi-2212 films heat-treated at 600 °C. As seen, Bi_2O_3, SrO, CaO, CuO, $CaSrCuO_3$ and $Bi_2Sr_3Cu_2O_8$ were detected, indicating that the acetates have been decomposed to form the above oxides and then the oxides interreacted with each other to yield some other intermediate products at 600 °C. The related chemical reactions are represented in equations (1)–(6).

$$2Bi\ (CH_3COO)_3 + 12O_2 \rightarrow Bi_2O_3 + 12CO_2\uparrow + 9H_2O \quad (1)$$

$$Sr(CH_3COO)_2 + 4O_2 \rightarrow SrO + 4CO_2\uparrow + 3H_2O \quad (2)$$

$$Ca(CH_3COO)_2 + 4O_2 \rightarrow CaO + 4CO_2\uparrow + 3H_2O \quad (3)$$

$$Cu(CH_3COO)_2 + 4O_2 \rightarrow CuO + 4CO_2\uparrow + 3H_2O \quad (4)$$

$$SrO + CaO + CuO \rightarrow CaSrCuO_3 \quad (5)$$

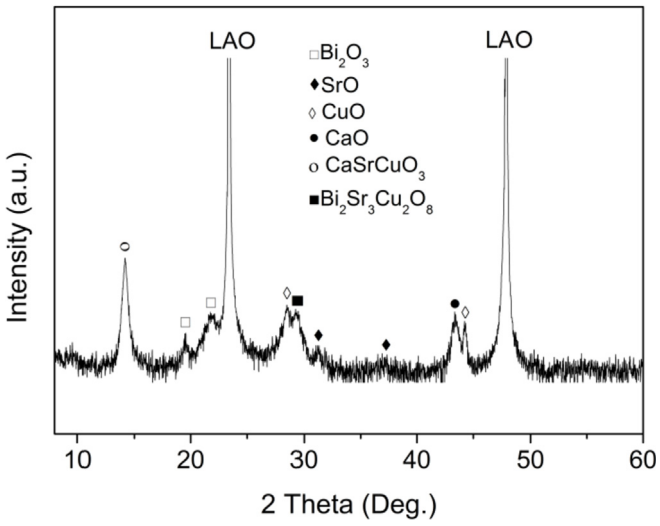

Fig. 3. XRD patterns of Bi-2212films heat-treated at 600 °C.

$$Bi_2O_3 + 3SrO + 2CuO \rightarrow Bi_2Sr_3Cu_2O_8 \quad (6)$$

Four groups of Bi-2212 films were respectively prepared at 780 °C, 800 °C, 820 °C and 840 °C with pO_2 of 1.5 KPa for studying the phase evolution at different temperature. Fig. 4 shows the XRD patterns of the four groups of Bi-2212 films. For the Bi-2212 films heat-treated at 780 °C, it is clear that main phases in films are $CaCuO_2$ (JCPD-ICDD 48–0197), $CaCu_2O_3$ (JCPD-ICDD 34–0284) [24,25], Bi_4SrO_7 (JCPD-ICDD 46–0752) [5] and Sr_2CuO_3 (JCPD-ICDD 48–1495) [26], which were generated through the reactions between the oxides of Bi_2O_3, SrO, CaO and CuO formed at 600 °C. The related chemical reactions are represented in equations (7)-(10).

$$CaO + CuO \rightarrow CaCuO_2 \quad (7)$$

$$CaO + 2CuO \rightarrow CaCu_2O_3 \quad (8)$$

$$2Bi_2O_3 + SrO \rightarrow Bi_4SrO_7 \quad (9)$$

$$2SrO + CuO \rightarrow Sr_2CuO_3 \quad (10)$$

For the Bi-2212 films heat-treated at 800 °C, Bi-2201 and Bi-2212 are the main phase with a little Bi_4SrO_7 and Sr_2CuO_3. XRD pattern shows obvious Bi-2201 (JCPD-ICDD 39–0283) (002), (006) peaks and Bi-2212 (JCPD-ICDD 41–0317) (0010), (0020), (2010) peaks, indicating that the oxidation products formed at 600 °C can be inter-reacted with each other to form Bi-2201 and Bi-2212 (reactions (11)–(12)) [27–29]. If we want to get the pure Bi-2212, the heat treatment temperature should be raised.

$$Bi_2O_3 + 2SrO + CuO + O_2 \rightarrow Bi_2Sr_2CuO_{6+\delta} \quad (11)$$

$$Bi_2O_3 + 2SrO + CaO + 2CuO + O_2 \rightarrow Bi_2Sr_2Ca\,Cu_2O_{8+\delta} \quad (12)$$

For the Bi-2212 films heat-treated at 820 °C, (002), (006), (008), (0010), (0012), (0016), (0020) peaks of Bi-2212 were observed. The single Bi-2212 phase was obtained and its growth orientation was c-axis. It indicates that the pure Bi-2212 phase can not only be formed by reacting Bi_2O_3, SrO, CaO and CuO with O_2 (reaction (12)) but also be formed by reacting Bi-2201 with CaO, CuO or $CaCuO_2$ (reactions (13)–(14)) [24,25].

$$Bi_2Sr_2CuO_{6+\delta} + CaO + CuO \rightarrow Bi_2Sr_2Ca\,Cu_2O_{8+\delta} \quad (13)$$

$$Bi_2Sr_2CuO_{6+\delta} + CaCuO_2 \rightarrow Bi_2Sr_2Ca\,Cu_2O_{8+\delta} \quad (14)$$

For the Bi-2212 films heat-treated at 840 °C, Bi-2201, $CaCuO_2$, (2010) and (210) peaks of Bi-2212 appear again. The results indicate that higher temperature is not helpful for the formation of Bi-2212 phase, and even results in the formation of non-epitaxial Bi-2212 films. The related chemical reactions are represented in equations (7), (11) and (12).

The XRD analysis reveals that the heat treatment temperature has an important effect on the phase purity of Bi-2212 films. When the Bi-2212 films were heat-treated at the lower temperature, the intermediate phases may be transformed to Bi-2212 phase incompletely. However, under the higher temperature condition, the stability of Bi-2212 may be degraded. Therefore the c-axis epitaxial Bi-2212 films can be prepared at temperature of 820 °C–840 °C.

3.2. The effect of oxygen partial pressure on superconductivity of Bi-2212

With the phase formation temperature being constant, the oxygen partial pressure has an important effect on the superconducting properties of Bi-2212. The generation of superconductivity of Bi-based superconductors depends on the Bi-O current carrier layer provides enough charges to Cu-O_2 conductive layer. The distortion degree of Cu-O_2 layer (c-axis length) depends on the oxygen content that exists between the two Bi-O layers. As a consequence, the oxygen partial pressure strongly affects T_c values of Bi-2212 films [30].

Fig. 5 shows the *R-T* characteristics curves of the Bi-2212 films prepared at 820 °C with different oxygen partial pressure of 0–2.4 KPa. It can be seen that the resistance of Bi-2212 films prepared at the pO_2 of 0 KPa did not go to zero when the temperature drops down to 50 K, the trend is directly related to residual resistivity value. Other Bi-2212 films grown at the pO_2 of 0.7–2.4 KPa realize the superconducting transition, and their T_c values range from 79.8 K to 88 K and ΔT_c values range from 4.8 K to 7K.

Fig. 6 shows the relationship of pO_2–T_c and pO_2–ΔT_c. It is found that T_c values of Bi-2212 films increased with the pO_2 up to 1.4 KPa and decreased with further increase of pO_2, while ΔT_c changes in the opposite trend. The reason for the change of T_c and ΔT_c is that a high level of oxygen content increases the current carrier content in the whole Bi-2212 phase. Mean while the current carrier content of every Cu-O_2 increases, which leads to the decrease of T_c value [31,32]. Bi-2212 films grown under the pO_2 of 1.4 KPa exhibit the highest T_c value of 88 K and lowest ΔT_c of 4.8 K that is smaller than that of the Bi-2212 films prepared by other methods [22,33,34].

Fig. 7 shows the SEM micrograph of the Bi-2212 film prepared at 820 °C with the pO_2 of 1.4 kPa for 40 mins. It can be seen that the films contain the stacked terrace-like grain structures and are layered mainly *c*-axis oriented [35]. The surface morphology of films exhibits that the

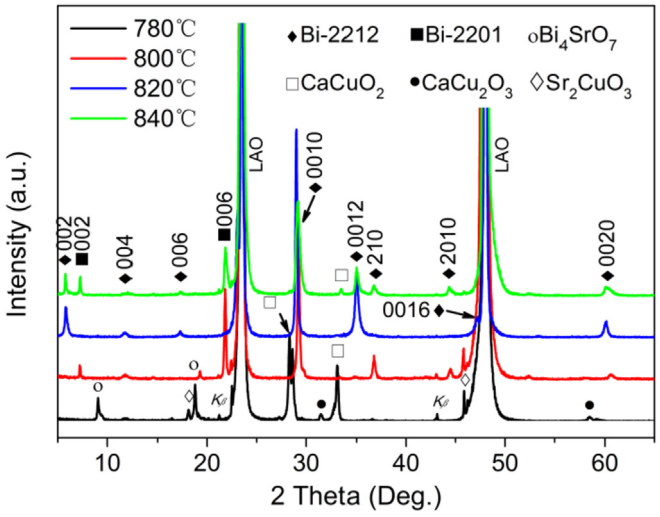

Fig. 4. XRD patterns of Bi-2212 films prepared at the different heat treatment temperature with pO_2 of 1.5 KPa.

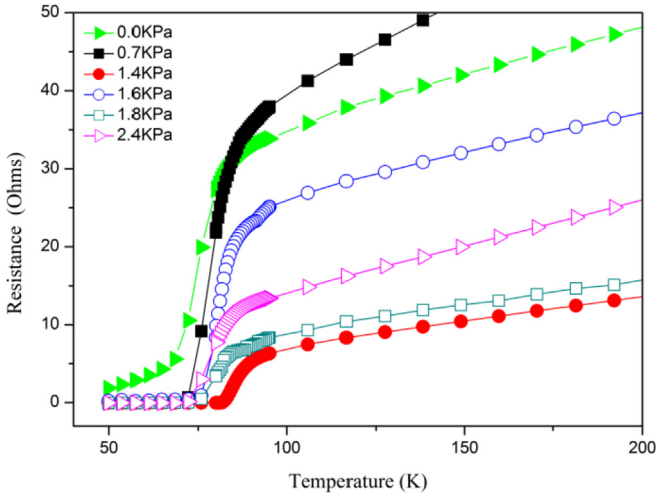

Fig. 5. *R–T* curves for Bi-2212 films prepared at 820°Cwith different oxygen partial pressure.

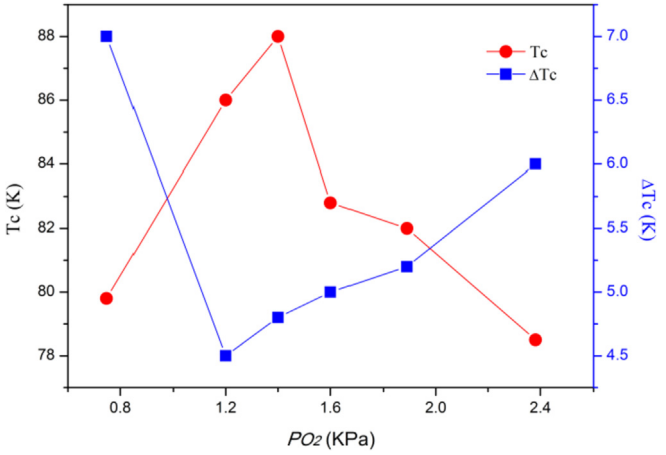

Fig. 6. Variation of T_c and ΔT_c of Bi-2212 films at 820°Cwith different oxygen partial pressure.

a-b plane of large grains of the Bi-2212 films mostly grew along *c*-axis orientation on *a-b* plane of LAO single crystal substrate. The Bi-2212 film was subjected to cross-sectional scanning electron microscopy (SEM) experiments, as shown in Fig. 8. The Bi-2212 film has approximately 222 nm thickness. EDS measurement shows the atomic ratio of Bi, Sr, Ca, Cu is close to 2:2:1:2, which indicates the existence of Bi-2212 phase.

Fig. 9 shows the φ scanning and ω scanning of the Bi-2212 film. It can be learned that there are fourfold symmetry diffraction peaks with similar intensities from the φ scanning curves for Bi-2212, the average full-width at half-maximum (FWHM) of (115) plane was about 1.00°. The FWHM of the Bi-2212 (0010) diffraction peaks from the ω scanning curves is about 0.41°. The results indicate that the grains in Bi-2212 films have a good in-plane texture and out-of-plane texture.

4. Conclusions

Bi-acetate, Sr-acetate, Ca-acetate, Cu-acetate were used as starting materials to fabricate c-axis epitaxial Bi-2212 films on LAO substrate by Sol-Gel method. The microstructure, superconductivity, and crystal orientation of Bi-2212 films were investigated, and the main conclusions can be drawn as follows:

(1) Bi-2212 films were prepared by acetate based Sol-Gel method and heat-treated at 820 °C for 40min, the whole treatment process needed 4 h and the high-temperature phase formation process only needed 40 min. This method not only shortened the heat treatment time and greatly improved the preparation efficiency but also conserved energy and protected environment.

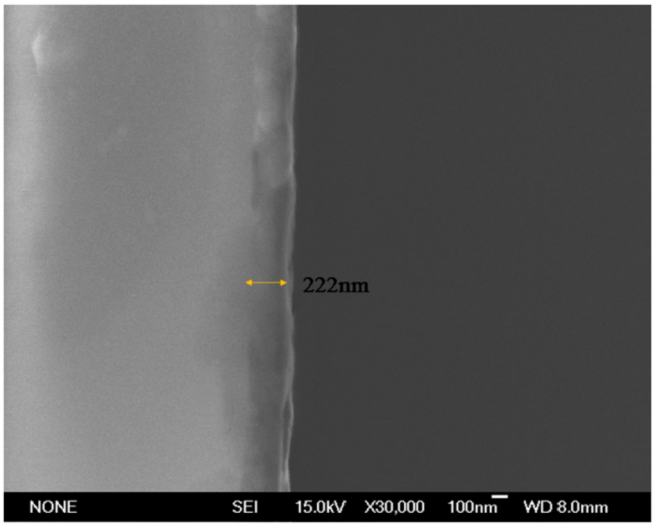

Fig. 8. SEM micrograph of cross sectional Bi-2212 film prepared at 820 °C.

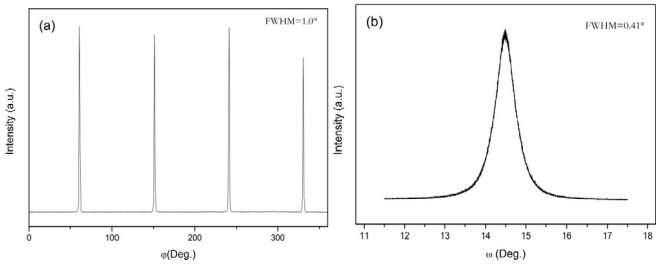

Fig. 9. Texture analysis of Bi-2212 film prepared at 820 °C with the pO_2 of 1.4 kPa. (a) XRD φ scanning of (115) plane and (b)ω scanning of (0010) plane.

(2) Heat treatment temperature and oxygen partial pressure have an important effect on the phase purity and superconductivity of Bi-2212 films. The results indicate that Bi-2212 films prepared at 820 °C with the pO_2 of 1.4 kPa in $N_2 + O_2$ atmosphere have a high purity and a high T_c of 88 K and a small ΔT_c of 4.8 K.

Acknowledgments

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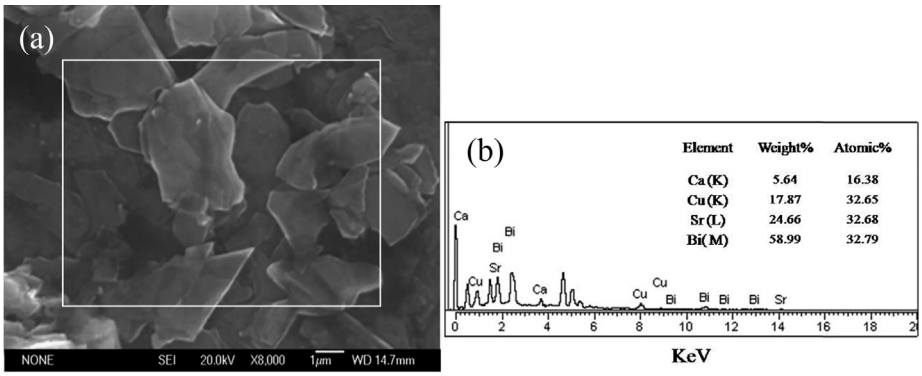

Fig. 7. Analysis of surface morphology and chemical composition of Bi-2212 films prepared at 820 °C with the pO_2 of 1.4 kPa. (a) SEM micrographs and (b) relative content of elements from the rectangular region in (a) with EDS.

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