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Cation-stoichiometry of functional oxides modified by oxygen vacancy through growth kinetics control

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ABSTRACT

Among all functional perovskite oxides, LRE-Ba-Cu-O (LREBCO, LRE123, LRE: light rare earth = Sm, Nd, et al.) superconductors possess outstanding properties of higher critical transition temperature (T_c) and higher critical current density (J_c) than YBCO superconductors. However, cation off-stoichiometry caused by the substitution of LRE elements for Ba sites could deteriorate superconducting properties. Here, we develop a new approach for fabricating high performance superconductors crystal of nearly ideal stoichiometric $Sm_{1+x}Ba_{2-x}Cu_3O_y$ (i.e. low x value) in air through oxygen vacancy control. In the peritectic reaction of Sm211 (solid) + Ba–Cu–O (liquid) + O_2 (gas) → $Sm_{1+x}Ba_{2-x}Cu_3O_y$ (solid), the higher growth rate (achieved via the high cooling rate during growth) leads to the less absorbed-oxygen in $Sm_{1+x}Ba_{2-x}Cu_3O_y$ (i. e. low y value), which could balance the whole valence of cations to gain a low x value, equivalent to a low substitution level of Sm^{3+}/Ba^{2+}. As a result, by using the normal precursor (Sm123 + Sm211), SmBCO bulks with the high performance (T_c^{mid} over 94 K with the sharp transition) are successfully grown in air. Thus this path effectively realizes the control of cation stoichiometry for SmBCO by oxygen vacancy modification, which could be applicable in synthesizing other functional oxides with desirable performance.

1. Introduction

Multi-component functional oxides attract enormous attention from scientists due to their attractive physical properties. It is important to control cation stoichiometry in the crystal growth, because cation off-stoichiometry may cause negative effects on the functional properties. Among numerous amount of functional perovskite materials, $(LRE)_{1+x}Ba_{2-x}Cu_3O_y$ (LRE123, LREBCO, LRE = Sm, Nd, etc.) superconductors exhibit remarkable superconducting performance of high critical transition temperature (T_c) and high critical current density (J_c), which have great potential applications in advanced devices, such as flying wheel, motors and maglev transportation [1–4]. However, cation non-stoichiometry caused by the substitution of LRE elements for Ba sites, especially prepared in air, leads to the deterioration of superconducting capabilities, such as a decrease of T_c [5–8]. Therefore, LREBCO with low substitution level are highly required to realize their full potential application.

Unlike oxygen non-stoichiometry, which could be easily removed by post-oxygenation process, cation non-stoichiometry is difficult to recover because of its poor mobility in closed packed perovskite-type structures [9]. In order to prepare superconductors with desirable cation stoichiometry and excellent physical properties, many studies have been performed to suppress the substitution of LRE^{3+} for Ba^{2+} site. The oxygen-controlled melt-growth (OCMG) method has been proved to be a reliable approach to obtaining superconductors with nearly ideal stoichiometry, which requires a low pO2 (oxygen partial pressure) atmosphere during growth process [10–13]. In the growth of LREBCO superconductors, the substitution of Sm^{3+} on Ba^{2+} results in increasing the valence of

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cations. In the view of thermodynamic, the concentration of oxygen in $LRE_{1+x}Ba_{2-x}Cu_3O_y$ (i. e. y value) can be reduced with a decrease of pO_2, leading to the reduction of the whole valence of the cations in $LRE123_{ss}$ (ss = solid solution), which is in favor of suppressing the substitution level of LRE^{3+}/Ba^{2+}. As a cost-saving and convenient method, composition-controlled melt-growth (CCMG) featuring the exploitation of Ba-rich precursors is also an effective way to suppress the substitution of LRE^{3+}/Ba^{2+}, by which air-processed Sm123 with high T_c of 94 K was fabricated [14,15]. Same as OCMG, the principle of the CCMG method could be interpreted on the basis of thermodynamics too.

On the other hand, both Z. P. Li et al. and D. A. Muller et al. reported that the oxygen vacancy during growth served as a dominant role in tuning the cation stoichiometry, which helped to obtain functional oxides with optimal functional properties [16,17]. The above-mentioned reports indicate that oxygen vacancy may also play an effective role in preparing LRBCO crystals with nearly ideal cation stoichiometry close to 1:2:3 (LRE:Ba:Cu). In the peritectic reaction of LREBCO system, the formation of LREBCO crystals involves in an oxygen-absorption phenomenon. Therefore, it can be deduced that the high growth rate leads to an intake of less oxygen in $LRE_{1+x}Ba_{2-x}Cu_3O_y$ (i. e. low y value or high oxygen vacany), which is supposed to have a positive effect on suppressing the substitution effect of LRE^{3+}/Ba^{2+}.

In this work, by tuning oxygen vacancy, using normal starting materials of Sm123 + 30 mol% Sm211+1wt.% CeO_2, a new method is applied to prepare high T_c Sm123 samples under air atmosphere in the view of growth kinetics. A series of Sm123 multi-grains by spontaneous nucleation and growth were prepared under various cooling rates (CRs, CR: cooling rate) in air. Through oxygen vacancy control, optimal cation stoichiometry $Sm_{1+x}Ba_{2-x}Cu_3O_y$ samples with high T_c were obtained. Following this result, by seed-induced melt-growth, the large Sm123 single-domain grain with both high T_c and sharp transition value was also gained under the optimized growth procedure.

2. Experimental procedure

Sm123, Sm211 were independently calcined by solid state reaction. The original powders (Sm_2O_3, $BaCO_3$ and CuO) were well mixed in a stoichiometric ratio in air and the mixture was synthesized at 900 °C for 48 h by three times with intermediate grindings to obtain pure powder. The powders were then mixed according to a nominal composition of Sm123 + 30mol%Sm211 with an excess of 1wt% CeO_2, which can refine LRE211 particle and reduce the leakage loss of Ba–Cu–O liquid.

Sm123 multi-grains grown by spontaneous nucleation and growth without seeds and Sm123 single grain grown by seed-induced melt-growth were prepared in the experiment.

1) For spontaneous nucleation and growth, the mixed precursor powders were uniaxially pressed into pellets with 20 mm in diameter and 8 mm in thickness. Fig. 1 shows a typical growth procedure for the growth of Sm123 multi-grains. CR ranges from 0.15 to 1.0 °C/h. The superconducting performance of SmBCO multi-grains prepared under CR of 0.3, 0.5, 0.8 K/h were measured twice. After growth, samples with a size of approximately 2.0 × 2.0 × 1.0 mm^3 were cut from crystals by spontaneous nucleation and growth, and they were annealed in oxygen atmosphere, holding at 350 °C for 200 h.
2) In seed-induced melt-growth, the mixtures were pressed into a pellet with 20 mm in diameter and 8 mm in thickness and a mini-pellet with 5 mm in diameter. And the small one was placed on the top surface of the big one. Furthermore, seed materials with remarkable superheating properties is necessary due to high peritectic temperature (T_p) in LREBCO (LRE = Sm, Nd, etc.) systems [18,19]. A c-axis oriented NdBCO/YBCO/MgO thin film was placed on the mini-pellet as a seed, which possesses outstanding superheating capability [18]. After growth, samples with a size of approximately 2.0 × 2.0 × 1.0 mm^3 were cut from as-grown crystals by seed-induced melt-growth, which were then annealed in oxygen atmosphere, holding at 350 °C for 200 h. For as-grown Sm123 bulks (16 mm in diameter and 6 mm in thickness), a post-annealing procedure, holding at 850 °C for 48 h in N_2 atmosphere, was also applied before oxygenation process [20].

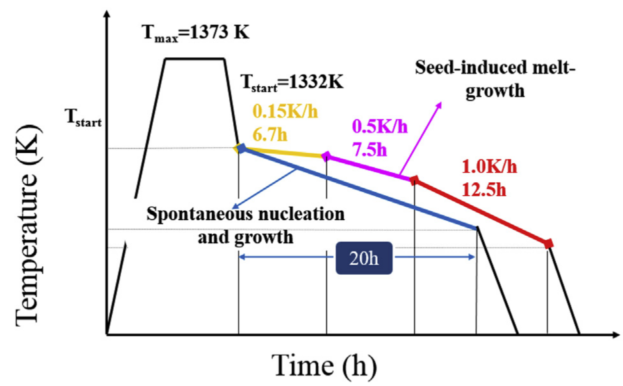

Fig. 1. The typical growth procedures for fabricating Sm123 bulks in air by both spontaneous nucleation & growth and seed-induced melt-growth.

Critical transition temperature of those specimens were measured by the Physical Property Measurement System (PPMS-9T, EC-II). In this paper, T_c^{mid}, the temperature where 50% of the transition was observed, is chosen as characterizing superconducting properties. Transition width is also an important indicator for evaluating superconducting performance. High T_c with broad transition width does not present the good superconducting performance. (transition width: the difference in temperature between 10% and 90% of the maximum diamagnetic momentum).

The levitation forces of Sm123 samples are measured at 77 K under a zero-field-cooling state by applying a NdFeB magnet of 30 mm in diameter, 30 mm in thickness and a surface magnetic field of 0.5 T.

The measurements of trapped magnetic field were carried out by magnetizing the bulk samples in a 10 T superconducting magnet. The bulk samples were cooled to the liquid nitrogen temperature in a magnetic field of 1.5 T applied parallel to the c-axis and kept there for 15 min. After switching off the external field, the profile of the trapped magnetic flux density was measured by scanning a Hall probe sensor. The total gap between the top surface of the sample and the active area of the Hall sensor was 1.2 mm, including the sensor mold thickness of 0.7 mm. After mapping the field distribution, the Hall sensor was moved to the peak position of the profile and was lowered to make a contact with the sample to measure the axial component of the trapped magnetic flux density (B_z^{max}) at the height of the active area of the Hall sensor.

3. Results and discussion

3.1. Spontaneous nucleation and growth

Sm123 samples by spontaneous nucleation and growth were prepared in air. After the melting process Sm123 multi-grains were naturally obtained due to spontaneous nucleation. In order to investigate the relationship between T_c^{mid} and CR, a series of