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Structural and superconducting properties of co-doped $YBa_{2-x}La_xCu_{3-x}M_xO_z$ and La-free $YBa_2Cu_{3-x}M_xO_z$ (M = Al, Zn) high-T_C superconductors

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ABSTRACT

Two co-doped high-T_c superconducting systems, $YBa_{2-x}La_xCu_{3-x}Al_xO_z$ and $YBa_{2-x}La_xCu_{3-x}Zn_xO_z$ ($0 \leqslant x \leqslant 0.3$), both of which have not been reported up to the present, were synthesized. The structural and superconducting properties have been investigated by X-ray diffraction (XRD) and DC magnetization measurement. Comparing the properties of these co-doped systems with single-doped systems $YBa_2Cu_{3-x}Al_xO_z$ and $YBa_2Cu_{3-x}Zn_xO_z$, it shows that in the Al-single-doped YBCO system, the depression of the critical temperature (T_c) with doping is stronger than that in (La, Al)-co-doped system, however, in the Zn-single-doped system, the T_c descends slower than that in (La, Zn)-co-doped system. This is possibly due to the opposite change of the distance between the Ba site and the CuO_2 plane induced by the La doping. Besides, the La doping has another effect of improving the solid solubility compared with the Al- or Zn-single-doped system.

1. Introduction

As is known, copper oxide high-T_c superconductors are quite complicated physical systems that the intrinsic mechanism of the superconductivity has been still under exploration up to the present. A key factor of its complicacy is the complex crystalline structure of the cuprates. Unlike the conventional BCS superconductors, the cuprates are quasi-two-dimensional, with the key superconducting subunit located in the CuO_2 planes. Besides, their unit cells can be divided into two structural blocks, referred as perovskite block and rock-salt block, respectively, without any exception [1,2]. Hence, with a view to the special structures of the cuprates and their importance to the high-T_c superconductivity (HTSC), research on the correlation between the crystalline structure and the superconducting property will be necessary and crucial for the revelation of the origin of HTSC.

In order to explore the mechanism of this new type of superconductor, cation substitution is one of the most effective and widely used methods. For $YBa_2Cu_3O_7$ system, numerous element-doping cases have been reported. In the Al-doped Y-123, Al^{3+} is believed to occupy Cu(1) site [3,4]. Due to the shorter bond length of Al–O along the c-axis direction compared with that of Cu–O, the lattice constant c decreases with the substitution of Al atoms [5,6]. Besides, Al^{3+} impurity will increase the oxygen content and induce the oxygen atoms to reorder in the unit cell, leading to the orthorhombic–tetragonal (O–T) transition around the doping level $x = 0.1 – 0.2$ [7,8]. In contrast, in the Zn-doped Y-123, Zn^{2+} resides at Cu(2) site [9,10]. Since the atom radius of Zn^{2+} (0.74 Å) and Cu^{2+} (0.72 Å) are almost the same, the lattice parameters a, b and c change slightly with the doping of Zn [7,11]. In addition, the oxygen content is independent of Zn doping [7,12–14], and all the $YBa_2Cu_{3-x}Zn_xO_z$ samples reported are orthorhombic.

In this paper we study two co-doped systems, $YBa_{2-x}La_xCu_{3-x}Al_xO_z$ and $YBa_{2-x}La_xCu_{3-x}Zn_xO_z$, both of which are synthesized and investigated for the first time. The structural and superconducting properties are reported, with a comparative study on the La-free single-doped systems of $YBa_2Cu_{3-x}Al_xO_z$ and $YBa_2Cu_{3-x}Zn_xO_z$. Some interesting variations of the crystalline structure induced by La substitution are observed, which has a direct influence on HTSC.

2. Experimental

Samples were prepared using the conventional solid-state reaction method. Pure Y_2O_3, $BaCO_3$, La_2O_3, CuO, Al_2O_3 and ZnO were weighted and mixed according to the corresponding chemical formulas of $YBa_{2-x}La_xCu_{3-x}Al_xO_z$ and $YBa_{2-x}La_xCu_{3-x}Zn_xO_z$ with $x = 0$, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3, respectively. Each mixture was ground thoroughly for 3 h and calcined at 930 °C for 18 h in air. The resultant powders were reground and pressed into pellets, and sintered at 940 °C for 24 h, followed by an annealing at 400 °C for 24 h in flowing O_2.

The crystalline structures of these samples were characterized by XRD on a Philips X'pert MRD diffractometer with Cu Kα radiation. Detailed structural parameters were obtained by Rietveld

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refinements. The goodness of fits (GOFs) of all the refinements are less than 2, demonstrating all the fittings are reliable.

The T_cs of the samples were determined by the DC magnetization measurements at a magnetic field of 20 Oe, using the Quantum Design MPMS system.

3. Results and discussion

Fig. 1a–d shows the doping dependence of the lattice constants in the two co-doped Y-123 systems and the corresponding two single-doped systems from [7]. Comparison of Fig. 1a and b indicates that the evolution of the lattice constants in the Al-doped YBCO and in the (La, Al)-co-doped YBCO have the same trend with doping. The detailed differences between the two systems can be summarized as two aspects. Firstly, the O–T transition occurred around the doping level between $x = 0.1$ and $x = 0.2$ in the Al-doped case, however, in the (La, Al)-co-doped case, all the samples ($0 \leqslant x \leqslant 0.3$) investigated here are orthorhombic, although the curves of a and b show an abrupt approach at $x = 0.1$, as if the onset of O–T transition. Secondly, c contracts faster in the Al-doped case than in the (La, Al)-co-doped case. These differences are caused by the effect of La doping. The cation of Ba^{2+} substituting by La^{3+} introduces positive charges (holes) into the unit cell. Accordingly the oxygen content increases so as to balance the extra holes [15–18]. Hence, the importation and reordering of the oxygen in the unit cell induced by La interferes the process of the O–T transition, so the samples of $YBa_{2-x}La_xCu_{3-x}Al_xO_z$ hold the orthorhombic symmetry with x up to 0.3. In addition, the radius of La^{3+} (1.27 Å) is smaller than that of Ba^{2+} (1.52 Å), resulting in faster contraction of c in the (La, Al)-co-doped samples than in the Al-doped ones. The same effect also exists in the (La, Zn)-co-doped system when compared with Zn-doped system (see Fig. 1c and d).

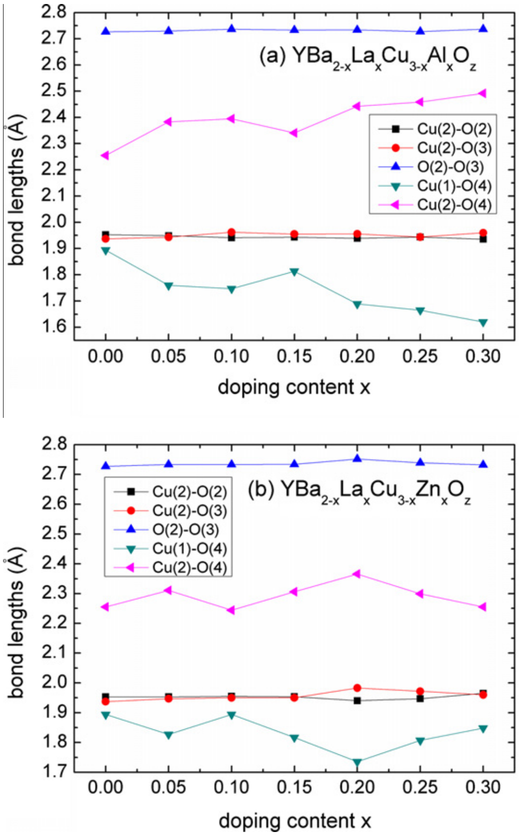

Fig. 2. (a and b) Changes of some bond lengths with doping.

In order to get more detailed information about the crystalline structures, all the bond lengths in the unit cell are calculated according to the results of the refinements. Some bond lengths related to Cu and O atoms are illustrated in Fig. 2a and b. It is evident that the bond lengths of Cu(2)–O(2), Cu(2)–O(3) and O(2)–O(3) have little fluctuation with the change of the doping level, implying that the adjacent atoms in the CuO_2 planes, Cu(2), O(2) and O(3), form a steady "fixed triangle", whose shape and size are both nearly invariable, independent of doping. On the other hand, in a unit cell of a cuprate crystal, the CuO_2 plane can be viewed as the combination of four O(2)–Cu(2)–O(3) triangles. Hence, the stability of the O(2)–Cu(2)–O(3) triangle represents a stable CuO_2

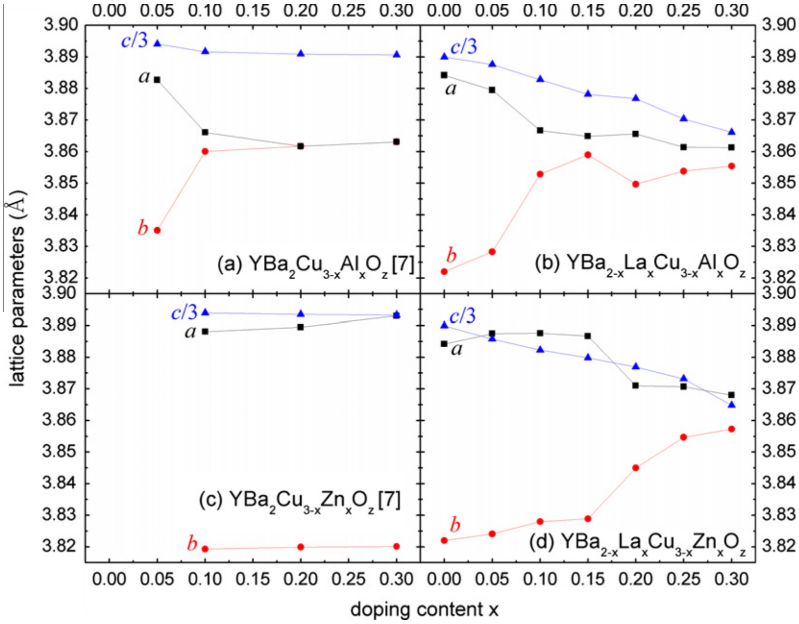

Fig. 1. (a–d) Lattice constants a, b and $c/3$ versus doping concentration x in the systems of $YBa_2Cu_{3-x}Al_xOz$, $YBa_{2-x}La_xCu_{3-x}Al_xO_z$, $YBa_2Cu_{3-x}Zn_xO_z$ and $YBa_{2-x}La_xCu_{3-x}Zn_xO_z$. The black, red, and blue symbols represent a, b and $c/3$, respectively. The data of the $YBa_2Cu_{3-x}Al_xO_z$ and the $YBa_2Cu_{3-x}Zn_xO_z$ systems are from Ref. [7]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)