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Effect of Ca substitution on crystal structure and superconducting properties of ferromagnetic superconductor $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$

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ABSTRACT

We have investigated the effect of Ca substitution for Sr site on structural, magnetic and superconducting properties of $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system. In this system, the magnetic coupling of RuO_2 and CuO_2 plays an important role in magnetic and superconducting states. X-ray diffraction analysis shows that all samples are single phase and the lattice parameters decrease continuously by increasing Ca content. The onset superconducting transition temperature is found to decrease with Ca substitution. As Ca content increases, rotation of the RuO_6 octahedron increases and Ru–O(1)–Ru angle decreases. These variations strengthen the magnetic moments in the RuO_2 planes. The enhancement of weak ferromagnetic component and hole trapping by Ru magnetic moments in RuO_2 planes reduces the electrical conduction, and destroys the superconducting state in the system. Analysis of the resistivity data (ρ) based on the hoping conduction mechanism, indicates a variation of the hoping exponent (p) across the magnetic transition at T_m. The hoping exponent p is not affected sharply by Ca concentration.

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1. Introduction

The coexistence of superconductivity (SC) and ferromagnetism (FM) at microscopic level in the ruthenocuprate family $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (Ru-1222) is still a controversial subject, and has attracted intense research interest due to the antagonistic nature of SC and FM. The Ru-1222 compound exhibits a weak FM order at relatively high temperature, $T_M = 180$ K, and becomes superconductive at $T_c = 42$ K, within the ferromagnetic order state [1–4]. The weak ferromagnetic component is due to the slight deviations of the magnetic moments of Ru ions whose magnetic order is predominately antiferromagnetic, from the direction of the *c*-axis caused by antisymmetric Dzyaloshinsky–Moriya (DM) exchange interaction between the neighboring Ru ions [1,5]. The crystal structure of Ru-1222 is similar to that of $REBa_2Cu_3O_{7-\delta}$ (RE-123), where Ba and Cu (chain atom) are replaced by Sr and Ru, respectively and a three layer fluorite-type block $Gd(Ce)O_2$ instead of a single oxygen free rare earth element layer is inserted between the two CuO_2 planes of the RE-123 structure [6,7]. The fluorite-type layer supports variable oxygen occupancy, which is denoted with the parameter δ in the formula. The superconductivity is associated with the CuO_2 layers, as in the RE-123 superconductors, while the ferromagnetism arises in the RuO_2 layers.

There have been many publications in the field of competition between superconductivity and magnetism in the Ru-1222 compound. Studies in this area can be categorized into two basic approaches. The first one measures the physical properties of a standard sample using different techniques, which should supply complementary information sufficient to support or discard a specific model. Significant results have been obtained in this way, although sometimes there have been contradictions in results between different groups [8–12]. A second approach is the investigation of chemically altered compounds, where by proper chemical substitutions one can control relevant parameters that affect the sample's properties and, in this way, get a better understanding of the mechanisms involved in it [13–20]. This second approach is particularly interesting for exploring the possible microscopic coexistence of superconductivity and magnetic order in the ruthenocuprate family.

One strategy to explore the coexistence of SC and FM in Ru-1222 compound is the study of relationship between crystal structure and physical properties of these ferromagnetic superconductors by careful chemical substitutions. Heterovalent substitutions by Sb [18], Pb [19], Sn [20], Mo [13] or Co [14] into Ru site have been used to investigate both magnetic order and superconductivity via the alternations in carrier density in the CuO_2 planes and the magnetic coupling between the Ru ions. However, these heterovalent substitutions have several interconnected effects like valence change, magnetic impurity ion scattering, charge localization, and increase of structural distortions and

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disorder at the same time; it is not useful to investigate the bare relationship between the crystal structure and superconducting properties. From computational point of view, we have recently investigated this relationship between the crystal dimension and electronic properties, in Ru-1212 by applying hydrostatic pressure [21]. The control of crystal structure and physical properties by Ca substitution for Sr, in particular, is very attractive since in this case both ions have similar valence but different ionic radii, with Ca smaller than Sr. This causes no change in the carrier density but due to the different ionic radii, it leads to the compression of lattice along the *c* direction. By this way, we can tune the separation between the layers in which superconductivity and magnetism occur, retaining the formal oxidation state of the ions. Therefore, it is expected that changes in the superconducting behavior will be mostly due to the possible coupling of magnetism and superconductivity in this system.

In this paper, we have investigated the Ca substitution in $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ ruthenocuprates, with $x=0$, 0.1, 0.2, 0.3. The smaller size of the Ca ion with respect to the Sr ion, enables the possibility to change the interlayer separation in which SC and FM occurs, retaining the formal oxidation state of the ions, and to examine the relationship between crystal dimensions and physical properties such as interaction between magnetism and superconductivity in these ferromagnetic superconductors.

2. Experiments

The compounds with nominal compositions of $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ with $x=0$, 0.1, 0.2, 0.3 were prepared by the solid state reaction method from starting powders RuO_2, $SrCO_3$, $CaCO_3$, Gd_2O_3, CeO_2 and CuO with 99.9% purity. The powders were ground, die-pressed into pellets and calcined for 24 h at 950 °C in air. The calcination was repeated several times with intermediate grinding to reach a homogeneous powder. The samples were reground, re-pelleted and sintered for 72 h in oxygen atmosphere at 1070 °C and then slowly cooled down to ambient temperature. The phase purity and the lattice parameters examined by a Philips Xpert powder diffractometer with CuK α radiation. The magnetization measurements performed using SQUID magnetometer. Zero field cooled (ZFC) and field cooled (FC) measurements performed at 50 Oe field in the range 2–200 K. An ac four-probe method with $f=33$ Hz used for the resistivity measurements of the samples from 10 to 300 K. The measuring current for the resistivity was 10 mA. A Lake Shore-330 temperature controller with a Pt-100 resistor used to indicate and control the temperature.

3. Results and discussion

3.1. XRD and structural analysis

Fig. 1 shows the X-ray diffraction (XRD) patterns in the range from 20° to 100° for $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ samples with $x=0$, 0.1, 0.2, 0.3, respectively. Structural analysis was carried out using general structure analysis system GSAS for Rietveld refinement of X-ray diffraction spectra [22]. X-ray diffraction analysis shows that all samples are single phase with no trace of impurity phases. The diffraction peaks were successfully indexed on the basis of a tetragonal unit cell with the I4/MMM (No. 139) space group (Table 1), as denoted in Fig. 1.

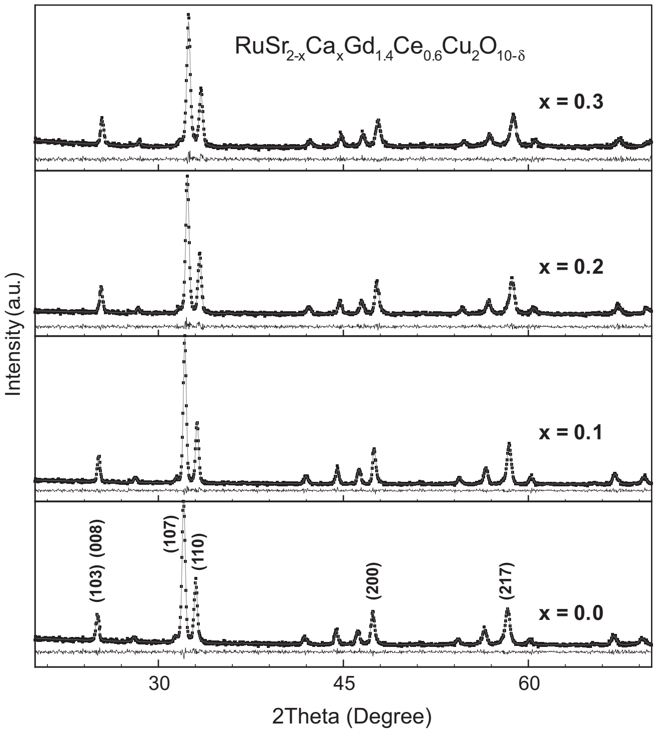

Fig. 1. Powder XRD patterns of the Ca substituted $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$.

Table 1
Results of refined atomic parameters for $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ solid solutions using GSAS program. The structure model with the I4/MMM (No. 139) space group yields the best fit for all samples. Atom positions are Ru 2a (0, 0, 0), Sr/Ca 4e (0, 0, *z*), Gd/Ce 4e (0, 0, *z*), Cu 4e (0, 0, *z*), O(1) 8j ($\frac{1}{2}$, *y*, 0), O(2) 4e (0, 0, *z*), O(3) 8g (0, $\frac{1}{2}$, *z*), O(4) 4d (0, $\frac{1}{2}$, $\frac{1}{4}$).

Atom	Parameter	$x=0$	$x=0.1$	$x=0.2$	$x=0.3$
	a (Å)	3.8431(3)	3.8402(2)	3.8371(3)	3.8359(4)
	c (Å)	28.587(2)	28.582(2)	28.573(2)	28.569(2)
Ru	U_{iso} (Å)^2	0.009(2)	0.011(2)	0.008(3)	0.010(2)
Sr/Ca	*z*	0.4219(3)	0.4216(2)	0.4211(2)	0.4209(3)
	U_{iso} (Å)^2	0.019(2)	0.021(3)	0.019(3)	0.022(2)
Gd/Ce	*z*	0.2945(2)	0.2943(2)	0.2939(3)	0.2935(2)
	U_{iso} (Å)^2	0.012(1)	0.011(1)	0.011(1)	0.010(1)
Cu	*z*	0.1411(3)	0.1403(2)	0.1396(3)	0.1391(3)
	U_{iso} (Å)^2	0.021(1)	0.021(2)	0.020(2)	0.019(2)
O(1)	*y*	0.1184(5)	0.1315(4)	0.1422(4)	0.1508(5)
	U_{iso} (Å)^2	0.021(2)	0.022(2)	0.022(1)	0.020(2)
O(2)	*z*	0.0672(3)	0.0643(2)	0.0617(3)	0.0597(3)
	U_{iso} (Å)^2	0.035(3)	0.036(3)	0.035(3)	0.038(3)
O(3)	*z*	0.1492(2)	0.1464(2)	0.1431(3)	0.1424(3)
	U_{iso} (Å)^2	0.038(3)	0.036(3)	0.039(3)	0.039(3)
O(4)	U_{iso} (Å)^2	0.037(3)	0.039(3)	0.037(3)	0.038(3)

Upon Ca substitution, the overall Bragg reflections shift toward the high-angle sides. From Rietveld refinement analysis, the unit cell volume is found to slightly decrease on Ca substitution. The lattice parameters *a* and *c* for the samples as a function of Ca content are presented in Fig. 2. This result shows that both lattice parameters tend to decrease by increasing the Ca-doping concentration in the single-phase region of $0.0 \le x \le 0.3$, indicating that Ca entered the lattice, which is in good agreement with the smaller ionic size of $Ca^{2+}=1.48$ Å with respect to $Sr^{2+}=1.58$ Å with 12-fold coordination number. A mismatch between the in-plane Ru–O and Cu–O bonds leads to the rotations of the RuO_6 octahedra around the *c*-axis. From the refined crystal structure, we have extracted the bond lengths and the rotation angles for the RuO_6 octahedra and the buckling angle in the Cu–O planes. The reduction in the *a* cell parameter, on going from $x=0.0$ to 0.3 in $RuSr_{2-x}Ca_xGd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ increases the rotations of the RuO_6 octahedra, quantified by the Ru–O(1)–Ru angle in Table 2.

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