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Physica C 392–396 (2003) 87–92
PHYSICA C
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Oxygen non-stoichiometry in Ru-1212 and Ru-1222 magnetosuperconductors

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Received 13 November 2002; accepted 27 January 2003

Abstract

We report here the results of thermogravimetric (TG) analysis on the oxygen non-stoichiometry of $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) and $RuSr_2(Gd_{0.75}Ce_{0.25})_2Cu_2O_{10-\delta}$ (Ru-1222) samples. With TG measurements carried out in O_2 and Ar atmospheres it is found that the oxygen content in Ru-1212 remains less affected upon various annealings, while for Ru-1222 the wider-range oxygen-content tuning is possible. When heated in H_2/Ar atmosphere the both phases release oxygen upon breaking down to mixtures of metals (Ru and Cu) and simple oxides (CeO_2, Gd_2O_3, and SrO) in two distinct steps around 300 and 450 °C. This reductive decomposition reaction carried out in a thermobalance is utilized in precise oxygen content determination for these phases. It is found that the 100-atm O_2-annealed Ru-1212 sample is nearly stoichiometric, while the similarly treated Ru-1222 sample is clearly oxygen deficient. X-ray absorption near-edge structure (XANES) spectroscopy is applied to estimate the valence of Ru in the samples. In spite of the fact that the Ru-1212 phase was shown to possess less oxygen-deficient $RuO_{2-\delta}$ layer, the valence of Ru as probed with XANES is found to be lower in Ru-1212 than in Ru-1222.

PACS: 74.25.Ha; 74.72.Jt; 75.25.+z; 75.30.Cr
Keywords: Rutheno cuprates; Oxygen stoichiometry; Thermogravimetric analysis

1. Introduction

Since the first reports on the coexistence of high-T_c superconductivity and ferromagnetism in samples of $RuSr_2[(Eu,Gd)_{0.7}Ce_{0.3}]_2Cu_2O_{10-\delta}$ (Ru-1222) [1] and $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) [2], these "magnetosuperconductor" phases have received continuous attention. Despite the intensive research made on the both phases, their basic characteristics in terms of oxygen non-stoichiometry, carrier concentration and valence state of Ru have not been clarified yet. In the present contribution we present the results of a systematic study

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doi:10.1016/S0921-4534(03)01067-0

on the oxygen non-stoichiometry in Ru-1212 and Ru-1222 samples based on thermogravimetric (TG) analyses carried out in O_2, Ar and H_2/Ar atmospheres. The TG experiments in O_2 and Ar atmospheres reveal us the degree of oxygen-content tunability in these phases. The experiments in H_2/Ar, on the other hand, enable us to determine the absolute oxygen content of the sample. Furthermore, we apply Ru L_{III}-edge X-ray absorption near-edge structure (XANES) spectroscopy to address the question on the valence state of Ru in the Ru-1212 and Ru-1222 phases. *Prior* to the present study, the very same samples have undergone thorough characterizations for structural, magnetic and superconductivity properties. The results of these studies have been reported elsewhere [3–6].

The structure of Ru-1212 is derived from that of $RBa_2Cu_3O_{7-\delta}$ or $CuBa_2RCu_2O_{7-\delta}$ (Cu-1212; R = rare earth element) with Cu in the charge reservoir replaced by Ru, such that the $CuO_{1-\delta}$ chain is replaced by a $RuO_{2-\delta}$ sheet. The Ru-1222 structure, on the other hand, results from that of Ru-1212 when inserting a (R,Ce)–O_2–(R,Ce) fluorite-type block, instead of the single oxygen-free R layer, between the two adjacent CuO_2 planes. Now the question is *whether the oxygen stoichiometry of the Ru-1212 and Ru-1222 phases can be controlled* in the same continuous manner as that well established for Cu-1212 [7,8].

2. Experimental

Samples of $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) and $RuSr_2(Gd_{0.75}Ce_{0.25})_2Cu_2O_{10-\delta}$ (Ru-1222) were synthesized through a solid-state reaction route from stoichiometric amounts of RuO_2, SrO_2, Gd_2O_3, CeO_2 and CuO. Calcinations were carried out at 1000 °C, 1020 °C and 1040 °C for 24 h at each temperature with intermediate grindings. The powder samples thus obtained were pelletized and annealed in a flow of oxygen at 1075 °C for 40 h with a slow cooling over a span of 20 h down to room temperature. A portion of these as-synthesized samples was further annealed in 100 atm O_2 atmosphere for 100 h at 420 °C and subsequently cooled slowly to room temperature in the same atmosphere. The phase purity and lattice parameters of the synthesized samples were checked by X-ray diffraction (XRD; MAC Science: MXP18VAHF[22]; CuK_α radiation). The T_c values reported for the superconductivity transition seen in the samples are from magnetization measurements carried out with a SQUID magnetometer (Quantum Design: MPMS-XL) [3–6].

The TG analyses (Perkin Elmer: TAS-7) were carried out in Ar, O_2 and 5% H_2/95% Ar atmospheres. The mass of the sample was ca. 15 mg and the heating rate was 1 °C/min. For the experiments carried out in O_2 atmosphere not only the heating curve but also the cooling curve were recorded to investigate the reversibility of the oxygen depletion/uptake process. The Ru L_{III}-edge XANES spectroscopic measurements were performed at the BL15B beamline of the Synchrotron Radiation Research Center in Hsinchu, Taiwan. Details of the experimental procedure employed were as described earlier [9–11].

3. Results and discussion

As commonly seen in the reported XRD patterns of Ru-1212 samples, a small amount of $SrRuO_3$ was detected as an impurity phase also for the present Ru-1212 samples. The Ru-1222 phase was more easily obtained in single-phase form, although a tiny trace of $SrRuO_3$ was distinguished from the XRD patterns even for the Ru-1222 samples. For the both phases, the relative amount of $SrRuO_3$ in the samples was considered to be small enough (<5 mass%) not so as to affect the results of TG and XANES analyses.

The lattice parameters for the as-synthesized Ru-1212 sample were determined in space group *P4/mmm* at: $a = b = 3.821(1)$ Å and $c = 11.476(1)$ Å. Essentially no difference was found in the lattice parameters for the Ru-1212 sample after annealed in 100 atm O_2, suggesting that the oxygen content was hardly changed upon the O_2 annealing. Also the T_c remained unchanged being at 20 K. For the Ru-1222 samples the lattice parameters were determined in space group *I4/mmm*. They are: $a = b = 3.834(1)$ Å and $c = 28.493(1)$ Å for the as-synthesized sample and

$a = b = 3.833(1)$ Å and $c = 28.393(1)$ Å for the 100-atm O_2-annealed sample. The slightly decreased c-axis parameter of the O_2-annealed sample as compared to that of the as-synthesized Ru-1222 sample indicates successful introduction of extra oxygen into the Ru-1222 structure upon the high-pressure O_2-annealing. Accordingly the value of T_c increased from 23 to 43 K.

When heating the Ru-1222 samples in a thermobalance, they exhibited definite changes in weight, apparently caused by changes in the oxygen content. A representative TG curve obtained for the 100-atm O_2-annealed Ru-1222 sample in an Ar atmosphere is shown in Fig. 1(a). The phase decomposition was found to start above 900 °C. The total amount of oxygen loss *per* formula unit by 900 °C, i.e. before the phase decomposition, was calculated at $\Delta\delta = 0.28(3)$. As heated in O_2 the Ru-1222 samples release oxygen as well. The amount of oxygen released from the 100-atm O_2-annealed sample by 900 °C upon heating in O_2 ($\Delta\delta = 0.27(3)$) was almost the same as that from the same sample heat-treated in Ar. During the slow (1 °C/min) cooling in O_2 from 900 °C down to room temperature the sample re-accommodated part of the oxygen released from it during heating. However, not all of the oxygen lost in heating was taken back to the sample during the cooling. This is due to the fact that the initial annealing of the sample had been performed in 100 atm O_2, while the TG measurement was performed in 1 atm O_2. The difference in oxygen content between the 100-atm and 1-atm O_2-annealed samples was estimated at 0.16(3) from the obtained TG curve for the heating and cooling cycles.

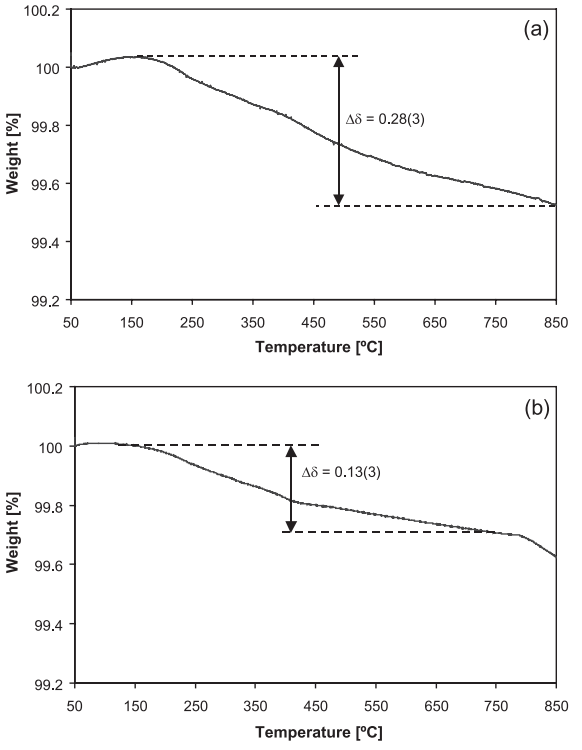

Fig. 1. TG curves recorded for (a) the 100-atm O_2-annealed Ru-1222 sample, and (b) the as-synthesized Ru-1212 sample in Ar atmosphere. The heating rate was 1 °C/min and the mass of the sample ca. 15 mg.

Experiments performed for the Ru-1212-phase samples in a thermobalance in O_2 and Ar atmospheres indicated that, as compared to the Ru-1222 phase, the oxygen in the Ru-1212 structure is relatively immovable and only small changes in the oxygen stoichiometry were seen. In Fig. 1(b), a representative TG curve for an Ar annealing of as-synthesized Ru-1212 sample is presented. The onset for a weight loss seen somewhat above 750 °C is due to the decomposition of the phase.

The absolute oxygen contents of the samples of both Ru-1212 and Ru-1222 phases were determined based on a TG heat treatment in a strongly reductive 5% H_2/95% Ar atmosphere. We present examples of such TG curves for the 100-atm O_2-annealed Ru-1222 sample and the as-synthesized Ru-1212 sample in Fig. 2(a) and (b), respectively. For both the phases the decomposition of sample occurs in two distinct steps about 200–350 and 400–500 °C. To clarify the process of the sample decomposition during the different steps of reduction, additional TG measurements were performed in the same atmosphere for the simple oxides of the constituent metals, i.e. RuO_2, CuO, Cu_2O and CeO_2. The TG curves obtained are shown in Fig. 3. It is seen that RuO_2, CuO and Cu_2O decompose into corresponding metals at low temperatures of about 100, 150 and 330 °C, respectively, while CeO_2 remains stable at least up to 750 °C. We therefore calculated the exact oxygen contents of the Ru-1212 and Ru-1222 samples from the weight losses seen in the H_2/Ar reduction

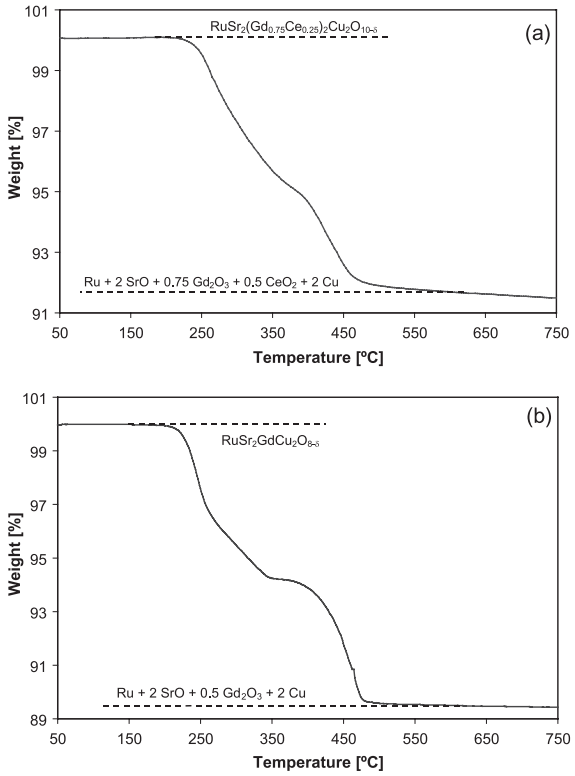

Fig. 2. TG curves recorded for (a) the 100-atm O_2-annealed Ru-1222 sample, and (b) the as-synthesized Ru-1212 sample in 95% Ar/5% H_2 atmosphere. The heating rate was 1 °C/min and the mass of the sample ca. 15 mg.

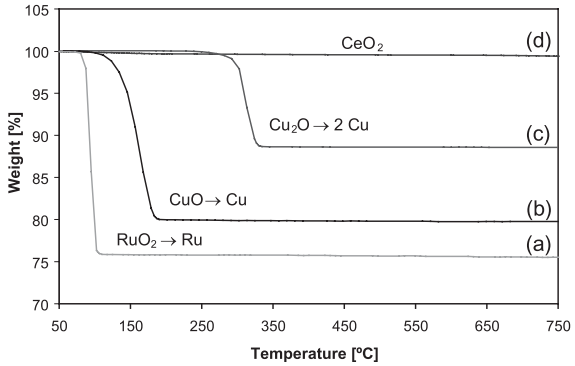

Fig. 3. TG curves recorded for (a) RuO_2, (b) CuO, (c) Cu_2O, and (d) CeO_2 in 95% Ar/5% H_2 atmosphere. The heating rate was 1 °C/min and the mass of the sample ca. 15 mg.

curves by 550 °C assuming the final decomposition product to be a mixture of oxides, SrO, Gd_2O_3 and CeO_2, and Ru and Cu metals. The results are presented in Table 1, implying that the 100-atm O_2-annealed Ru-1212 sample is stoichiometric within the error bars of the analysis, while the 100-atm O_2-annealed Ru-1222 sample is clearly oxygen deficient. Furthermore, as already assumed based on the lattice parameters and the T_c values, the difference between the 100-atm and 1-atm O_2-annealed samples is larger for the Ru-1222 phase than for the Ru-1212 phase, see also the data for relevant samples in Refs. [12,13]. In Table 1, we also show the absolute oxygen content values for the samples annealed in Ar up to the highest temperatures before the break-down of the structure, i.e. 750 °C for Ru-1212 and 900 °C for Ru-1222. These values, i.e. 7.80(5) for Ru-1212 and 9.35(5) for Ru-1222, represent the minimum oxygen contents tolerated by these phases.

The Ru L_{III}-edge XANES spectra were recorded for the as-synthesized Ru-1212 sample and the as-synthesized and 100-atm O_2-annealed Ru-1222 samples. The obtained spectra were analyzed quantitatively by fitting them to certain linear combinations of spectra for reference materials for $Ru^{IV}(Sr_2RuO_4)$ and $Ru^{V}(Sr_2GdRuO_6)$. The same fitting approach was for the first time applied in Refs. [9,10]. For the two Ru-1222 samples the spectra and fitting were shown in Ref. [11]. Here we show only the spectrum of the as-synthesized Ru-1212 sample in Fig. 4. All the three samples were found to lie between the two reference materials in terms of the ruthenium valence. Fitting the spectra revealed a valence value of +4.74(5) for Ru in the as-synthesized Ru-1222 sample and +4.81(5) in the 100-atm O_2-annealed Ru-1222 sample [11]. It seems that the valence of Ru in Ru-1222 depends on the oxygen content, thus indirectly suggesting that the changes in oxygen stoichiometry occur in the $RuO_{2-\delta}$ layer. For the as-synthesized Ru-1212 sample a valence value of +4.62(5) was obtained. This value is very close to that reported in Ref. [9] for another $RuSr_2GdCu_2O_{8-\delta}$ sample, i.e. +4.60, with the final annealing performed in O_2 at 1060 °C.

Though it would be tempting to do so, we do not calculate any precise valence values for Cu from the obtained oxygen content and Ru valence values. This is due to the fact that considering the error bars for our TG and XANES analyses, we

Table 1
The value of oxygen content as determined from the TG analysis for the variously treated Ru-1212 and Ru-1222 samples (see the text)

Synthesis/annealing conditions	$RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212)	$RuSr_2(Gd_{0.75}Ce_{0.25})_2Cu_2O_{10-\delta}$ (Ru-1222)
100-atm O_2, 420 °C	7.98(5) ($T_c = 20$ K)	9.63(5) ($T_c = 43$ K)
1-atm O_2, 1075 °C (as-synthesized)	7.93(5) ($T_c = 20$ K)	9.54(5) ($T_c = 23$ K)
1-atm Ar, 750/900 °C (Ru-1212/Ru-1222)	7.80(5)	9.35(5)

The value of T_c is given in parentheses when being measured.

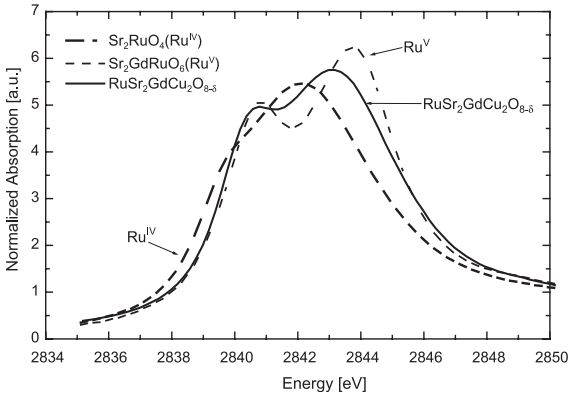

Fig. 4. Ru L_{III}-edge XANES spectrum collected for the as-synthesized Ru-1212 sample. Also shown are the spectra for reference samples Sr_2RuO_4 (Ru^{IV}) and Sr_2GdRuO_6 (Ru^{V}).

believe that such estimation would end up with not-reliable-enough Cu valence values. However, a rough assessment suggests that the valence of Cu is lower in the Ru-1222-phase samples than in the samples of the Ru-1212 phase. The considerably larger oxygen non-stoichiometry of the Ru-1222 phase, as compared to the Ru-1212 phase, might let us to believe that both the $RuO_{2-\delta}$ sheet and the $(Gd_{0.75}Ce_{0.25})$–O_2–$(Gd_{0.75}Ce_{0.25})$ fluorite block in Ru-1222 are non-stoichiometric in terms of oxygen content. However, for another *M*-1222 phase, i.e. Co-1222 at the stoichiometry of $CoSr_2(Y_{0.75}Ce_{0.25})_2Cu_2O_{9\pm\delta}$, we recently confirmed that its $(Y_{0.75}Ce_{0.25})$–O_2–$(Y_{0.75}Ce_{0.25})$ fluorite block is oxygen-stoichiometric even after the sample had been exposed to various reductive and oxygenative annealings [14].

4. Conclusion

In the present study we have shown that the Ru-1212 phase is easily obtained as oxygen stoichiometric, while the Ru-1222 phase was clearly oxygen-deficient even after 100-atm O_2-annealing. Also shown was that the oxygen content in the Ru-1212 phase remains less affected by various annealings, while for the Ru-1222 sample a wider-range oxygen-content tuning is possible. We also derived the conditions for the TG H_2/Ar reduction to determine the absolute oxygen contents in samples of Ru-1212 and Ru-1222.

Acknowledgements

The present work has been supported by a Grant-in-Aid for Scientific Research (grant no. 11305002) from the Ministry of Education, Science and Culture of Japan and by the Academy of Finland (decision no. 46039). M. Matvejeff acknowledges Finnish Cultural Foundation, Sasakawa Foundation and the Komppa Foundation for grants for Ph.D. studies.

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