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2009 J. Phys.: Condens. Matter 21 254210

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Effect of chemical composition on superconductivity and magnetism in layered ruthenocuprates

E Casini, M Kempf, J Krämer and H F Braun

Physics Department, University of Bayreuth, 95440 Bayreuth, Germany

E-mail: Hans.braun@uni-bayreuth.de

Received 22 March 2009

Published 29 May 2009

Online at stacks.iop.org/JPhysCM/21/254210

Abstract

The ruthenium-based layered cuprates $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (RuGd1212) can be considered naturally occurring magnetic and superconducting multilayer systems. We have concentrated on the preparation of RuGd1212-type compounds with nominally stoichiometric composition under ambient pressure conditions. For small rare earth ions $R = \text{Gd}, \text{Eu}$ (and Sm), single phase compounds are obtained with the typical ordered layered structure and no significant changes of physical properties. With large rare earth ions ($R = \text{Nd}, \text{Pr}$), multiphase samples are obtained. In these cases, no ordered layered structure was observed. The effect of substituting Sr^{2+} with the smaller Ca^{2+} and larger Ba^{2+} is examined. A different number and different types of phases in equilibrium are found with different alkaline earths ($A = \text{Ca}, \text{Sr}, \text{Ba}$) at the nominal $\text{RuA}_2\text{NdCu}_2\text{O}_8$ composition. The variation in the mismatch of the A/Nd size does not lead to the formation of an ordered layered $\text{RuA}_2\text{NdCu}_2\text{O}_8$ compound. Chemical transport in an open system was used to vary the Ru content in the RuGd1212 samples during the annealing step. With an increase of the Ru mass transport to the sample, the composition can be driven beyond the limit of the homogeneity range. Systematic changes in the phase composition of the resulting sample were observed. The magnetic and superconducting transition temperatures vary in a systematic way and are attributed to a variation of the Ru content in the RuR1212 phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The ruthenocuprates $\text{RuSr}_2(\text{Gd}, \text{Ce})_2\text{Cu}_2\text{O}_{10}$ (RuR1222) and $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (RuR1212) are layered cuprates whose structure is similar to that of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y-123), where Y and Ba are replaced by Gd or one of a range of rare earth elements (R) and Sr, respectively. The Cu–O chains in the charge reservoir block are replaced by RuO_2 layers which together with the apical oxygen of the CuO_2 double layer form a sheet of corner-sharing RuO_6 octahedra [1, 2], see figure 1. These ruthenocuprates appear today to provide the first example of superconductivity [3] developing at temperatures far below the transition into a weakly ferromagnetic state, with coexistence of both ordering phenomena [4–7]. The weak ferromagnetism (WFM) is associated with the ordered antiferromagnetic (AF) state of the Ru moments which appears at a Néel temperature (T_N)

of about 138 K in RuR1212, while the Gd moments order antiferromagnetically below 3 K [8–10]. Superconductivity is carried by the CuO_2 double layers at critical temperatures (T_c) of about 40 K. While superconductivity was readily observed in RuR1222, RuR1212 has been a more problematic case, with strong effects of the details of sample preparation [11–13] on its superconducting properties. In the following, we will focus on the RuR1212-type phase.

Despite extensive research, the magnetic as well as the superconducting properties of RuR1212 are far from being understood. The ferromagnetic transition of RuR1212 is clearly established in dc magnetization measurements [6, 11, 14]. Muon-spin relaxation [6] and Gd^{3+} EPR measurements [15] indicate a spatially homogeneous FM ordered state which remains unchanged below the superconducting transition. Neutron diffraction reveals antiferromagnetic order of the Ru moments with a Néel

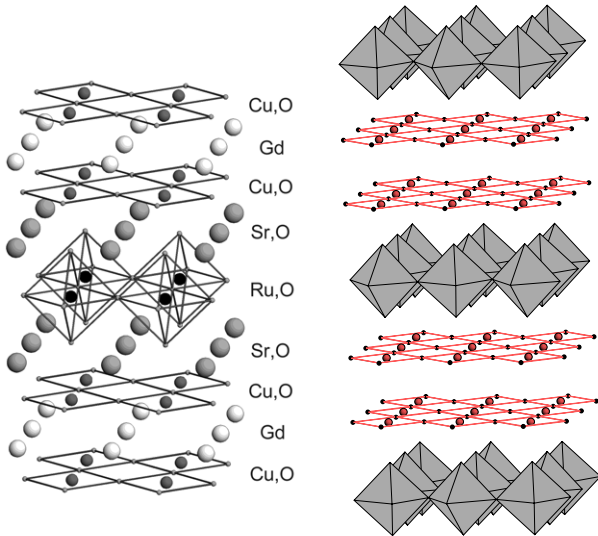


Figure 1. The average structure of RuR1212 (left) and possible ordered RuO₆ rotations in a $\sqrt{2}a \times \sqrt{2}a \times 2c$ cell, spacegroup $I4/mcm$ (right, R and Sr omitted).

temperature coincident with the previously reported onset of ferromagnetism, a Ru moment of $1.18 \mu_B$ along the c axis and an upper limit of $0.1 \mu_B$ to any zero-field ordered moment [9]. There is no evidence for a ferromagnetic component perpendicular to the c -axis with an upper limit of about $0.3 \mu_B$ [8]. However, ferromagnetism along the c axis, itinerant ferromagnetism or a canted antiferromagnetism could not be excluded [8].

In the first study of RuR1212 [1], as-sintered samples were semiconducting. Resistive transitions to superconductivity were reported in samples that were slowly cooled or annealed under oxygen pressure (figure 2 of [1]). Absence of superconductivity in RuSr₂GdCu₂O₈ was also reported [16–18], while the magnetic transition observed at ≈ 138 K could have been due to trace amounts of the perovskite-type SrRuO₃, a known ferromagnet.

The appearance of perovskite impurities could be minimized by a two-step synthesis procedure involving a mixture of Sr₂GdRuO₆ and CuO as precursors [3, 11, 19]. This procedure has been widely used (see, e.g. [6, 7, 20–28]) to obtain superconducting RuR1212, including the observation of a bulk Meissner effect [29] and a jump of the heat capacity at T_c [30], with evidence for microscopically uniform superconductivity and magnetism [5, 6]. On the other hand, Chu *et al* suggest non-uniform, non-bulk superconductivity [31–34] with evidence for phase separation into superconducting and magnetic regions [35–39].

The existence of such phase separations appears to result from the particular crystal structure of the ruthenocuprates. In fact, the ‘T1212 type’, originally observed with the transition metals T = Nb, Ta [40, 41], later in solid solutions (Nb, Ru) [42], with a variety of rare earth and alkaline earth elements replacing the Y and Ba of Y-123, has been described in spacegroup $P4/mmm$ [9, 20, 40, 42] (with $a \approx 0.384$ nm, $c \approx 1.155$ nm for RuSr₂GdCu₂O₈ [1, 11]) leading to straight T–O–T bonds in the octahedron layer.

However, this description might correspond to an average structure from which subtle deviations can occur. From crystal-chemical considerations it is expected that the mismatch between Cu–O and Ru–O distances [8, 11, 20] induces ordered rotations of the RuO₆ octahedra (figure 1). Such ordered rotations are manifest in high-resolution electron transmission microscopy or electron diffraction. While from synchrotron x-ray diffraction it is concluded that the average crystal structure is tetragonal at 10 and 295 K, subdomains of typical size 5–20 nm are observed, separated by sharp antiphase boundaries that may arise from coherent rotations of the RuO₆ octahedra [20]. The structures with rotated octahedra have been described with a superstructure cell $\sqrt{2}a \times \sqrt{2}a \times c$ [20] in tetragonal spacegroup $P4/mbm$ [8] or, doubling c , with $I4/mcm$ [43, 44] or orthorhombic $Pbam$ [45, 46]. The occurrence of such superstructures and lattice deformations depends on details of sample preparation [47] and may be related to strain [45] or variations of phase composition.

Since weak ferromagnetism may have its origin in the rotation of the RuO₆ octahedra and a canting of the Ru moments [4, 10] through the Dzyaloshinsky–Moriya mechanism [48, 49], the hypothesis of a phase separation into magnetic and superconducting domains due to a defect structure with rotated RuO₆ octahedra appears plausible. On the other hand, it has been proposed that WFM could arise from a double-exchange interaction, promoted in these cuprates by the mixed valence state of the Ru ions [50–52]. In RuR1212, the (average) Ru valence derived from NMR and x-ray absorption studies is between four and five, with 40–50% Ru⁴⁺ and 60–50% Ru⁵⁺ [50, 52, 53], whereas in doped (Ru_{1-x}M_x)Sr₂GdCu₂O₈ (M = Sn, Nb) the average Ru valence is 4.8 [54] independent of x . This opens the possibility of charge segregation in the RuO₆ layer [50, 53]. A change of the average Ru valence gives rise to a doping of the CuO₂ layers according to $\text{Ru}^{5+} + \text{Cu}_2^{2+} \rightarrow \text{Ru}^{(5-\epsilon)+} + \text{Cu}_2^{(2+\epsilon/2)+}$. In a similar way, the loss of ruthenium at fixed oxygen content would contribute to doping according to $\text{Ru}^{5+} + \text{Cu}_2^{2+} \rightarrow \text{Ru}_{1-\delta}^{5+} + \text{Cu}_2^{(2+5\delta/2)+}$. A recent magnetization study [55] in a pulsed field up to 47 T and at 4.2 K confirmed the hypothesis of a mixed Ru⁴⁺/Ru⁵⁺ valence state with a proposed 87%/13% ratio on the basis of the higher Ru moment ($1.8 \mu_B$) estimated from data collected up to 47 K, assuming the same values for the magnetic moment of the Ru⁴⁺ and Ru⁵⁺ ions as reported in the NMR study and a hole concentration $p \approx 0.065$. The authors therefore proposed that the magnetic sublattice of the Ru moment is predominantly antiferromagnetic involving Ru⁵⁺ ions, interrupted by ferromagnetic stripes which are characterized by charge transfer between Ru⁴⁺ and Ru⁵⁺ ions.

In order to obtain a better understanding of the magnetic and superconducting properties of the layered RuR1212 ruthenocuprates, it would be important to affect the structural peculiarities discussed above in a controlled way. We have studied the effect of atomic substitution on the structure, superconducting and magnetic properties of RuR1212 and present a report on the stability of this phase if prepared under ambient pressure against replacements on the rare earth and alkaline earth site as well as the effect of a variation of the Ru content.

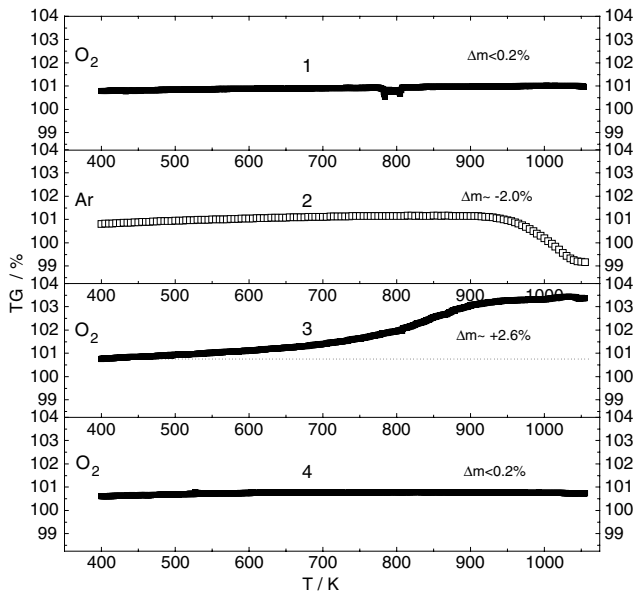


Figure 2. Thermogravimetric analysis up to 1060 °C during (1) synthesis of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ from precursors, (2) decomposition into $\text{Sr}_2\text{GdRuO}_6$ and Cu_2O in Ar, (3) re-synthesis in O_2 , and (4) post-treatment of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ in O_2 , from [11].

2. Effect of chemical substitutions on phase stability and physical properties

2.1. Experimental details

Samples of nominal composition $\text{RuA}_2\text{RCu}_2\text{O}_8$ with $A = \text{Ca}, \text{Sr}, \text{Ba}$ and $R = \text{Pr}, \text{Nd}, \text{Gd}, \text{Eu}$ were prepared by conventional solid state reaction from dried powders. Whenever possible, the precursor route was followed as described elsewhere [3, 56], involving the preparation of A_2RRuO_6 in an intermediate step [12, 13] which is then reacted with CuO . Since Sr_2RRuO_6 did not form with Pr and Nd, these $\text{RuA}_2\text{RCu}_2\text{O}_8$ samples were synthesized in a single step from oxides. Phase formation was monitored by simultaneous differential thermal (DTA) and thermogravimetric analysis (TG) and the reaction products were analysed by x-ray powder diffraction (XRD) and electron microprobe (EDX) analysis.

2.2. Rare earth substitutions

A puzzling picture appears when RuR1212 is prepared with different rare earth elements ($R = \text{Pr}, \text{Nd}, \text{Tb-Er}$). Bauernfeind *et al* [1] reported that the size of the rare earth ions affects the formation of the RuR1212 phase, such that under standard preparation conditions, under equilibrium at ambient pressure, a disordered perovskite compound is obtained with R^{3+} ions larger than Sm whereas the formation of a single phase compound at ‘1212’ composition is not favoured with the small rare earth elements.

RuPr1212 has been reported in an essentially single phase form [57, 58]. It appeared to be isostructural to the layered RuGd1212 and a magnetic ordering transition at temperature below 150 K is detected [57]. A compound of RuNd1212 composition was reported with a disordered cubic structure

due to the trend of the Nd^{3+} ions to substitute on the alkaline earth ion site [59, 60]. Neither a superconducting transition nor magnetic ordering were detected [59]. On the other hand, Kuzmicheva *et al* [61] report the synthesis of a multiphase product where the amount of a layered RuNd1212 phase is $\approx 35\%$.

Substitution on the Gd site with smaller R^{3+} ions can be achieved by using high pressure conditions. The synthesis of single phase RuR1212 ($R = \text{Tb-Er}$) has been carried out following a two-step procedure under high pressure conditions [62].

In early reports, the RuGd1212 was prepared with a final sintering step at 1060 °C in 1 bar flowing oxygen. This was based on TG which did not show any significant mass loss up to this temperature, see figure 2. In fact, RuGd1212 decomposes in reducing atmosphere into $\text{Sr}_2\text{GdRuO}_6$ and Cu_2O under loss of oxygen and forms again under oxygen uptake when heated in 1 bar flowing oxygen. Later, it was found that 1060 °C is at the very limit of decomposition [63, 64] of the RuGd1212 phase. In order to avoid the possible partial decomposition, we have repeated the synthesis of RuR1212 with $R = \text{Gd}$ and Eu as described in section 2.1 with a final sintering step at 1055 °C in 1 bar flowing oxygen. In both cases, the RuR1212 -type structure was obtained. While samples with $R = \text{Gd}$ were single phase, in samples with $R = \text{Eu}$, traces of a disordered double perovskite $(\text{Sr}_{1-x}\text{Eu}_x)(\text{Ru}_{1-y}\text{Cu}_y)\text{O}_{3\pm\delta}$ were present. As shown in figures 3(a), (b) and 4, magnetic and superconducting transitions are observed at $T_M \approx 132$ K and $T_c \approx 43$ K for RuGd1212 and at $T_M \approx 133$ K and $T_c \approx 27.5$ K for RuEu1212 , where T_M is taken from the peak position of the zero field cooled (ZFC) susceptibility and T_c is identified with the intragranular transition (T_{intra}).

The XRD patterns of nominally stoichiometric RuR1212 with $R = \text{Nd}, \text{Pr}$ prepared as described in section 2.1 with final sintering in 1 bar flowing oxygen between 1010 °C and up to 1095 °C or 1060 °C, respectively, were remarkably similar but distinctly different from those of the samples with Gd and Eu. They could not be indexed assuming a single phase compound nor could the phases present be identified from the tabulated patterns reported in the ICDD Powder Diffraction database. Scanning electron microscopy (SEM) analysis of these samples after long annealing (100 h or longer in oxygen flow at 1095 °C and 1060 °C, respectively) showed a coarse microstructure suitable for chemical analysis by EDX measurements. In both samples three distinct phases were identified. The majority phase has a composition related to a disordered perovskite $(\text{Sr}_{2-x}\text{R}_x)(\text{Ru}_{2-y}\text{Cu}_y)\text{O}_{6-\delta}$ ($R = \text{Nd}, \text{Pr}$), while the other two phases appear in smaller amounts and can be described by the chemical formulae $\text{Sr}_2\text{RRuCuO}_7$ ($R = \text{Nd}, \text{Pr}$) and $\text{Sr}_{14-x}\text{R}_x\text{Cu}_{24}\text{O}_{41}$ ($R = \text{Nd}, \text{Pr}$). A layered RuR1212 -type ruthenocuprate was not formed under these conditions.

2.3. Alkaline earth substitution

The successful synthesis of nominally stoichiometric $\text{RuCa}_2\text{NdCu}_2\text{O}_8$ has been reported, with a proposed crystal structure described as a distorted orthorhombic variant of the

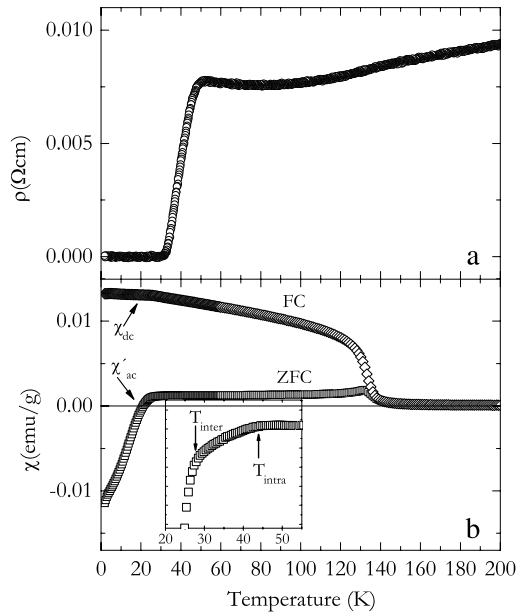


Figure 3. Temperature dependence of the resistivity (a) and of the magnetic susceptibility (b) for the RuGd1212 sample. In the χ versus T plot the real part of the ac susceptibility (χ'_{ac}) measured in ZFC mode with a stimulus $H = 3.9$ Oe at a frequency $f = 22$ Hz and the dc susceptibility (χ_{dc}) measured in FC mode at a field $H = 1$ Oe are displayed with squares and rhombi, respectively. Inset: low temperature ZFC χ'_{ac} versus T data showing the intragrain (T_{intra}) and the intergrain (T_{inter}) transitions.

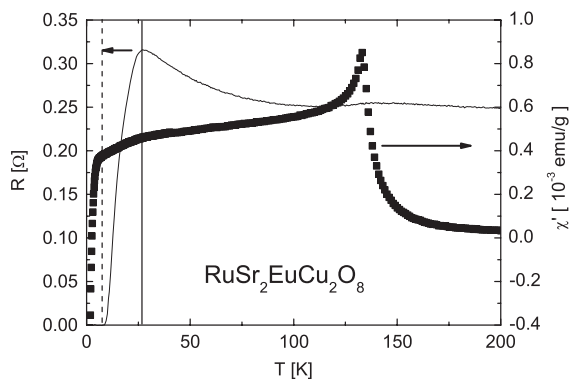


Figure 4. Temperature dependence of the resistance and of the real part of the ac susceptibility χ'_{ac} for the RuEu1212 sample. The real part of the ac susceptibility is measured in ZFC mode with a stimulus $H = 3.9$ Oe at a frequency $f = 22$ Hz.

layered RuGd1212-type structure [65]. The as-prepared sample, where unidentified impurities were present, showed diamagnetic behaviour with T_c onset at 36 K developing into a WFM ordered state with $T_M \approx 49$ K.

Since A_2RuNdO_6 ($A = Ca, Ba$) compounds have been reported [66, 67], we followed the precursor route as described in section 2.1 in the preparation of $RuA_2NdCu_2O_8$ ($A = Ca, Ba$). The reaction path of the mixture $Ca_2RuNdO_6 + 2CuO$ has been monitored by XRD after heat treatment for 24 h each in flowing oxygen at 980, 1012, and 1047 °C. The sample treated at 1047 °C appeared to be partially melted, in agreement with DTA results. In figure 5, a comparison of

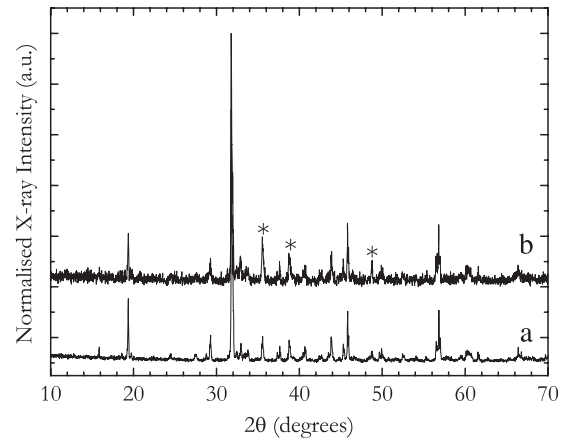


Figure 5. XRD patterns of a sample with nominal $RuCa_2NdCu_2O_8$ composition after treatment at (a) 1012 °C and (b) 1047 °C. The marked (*) reflections belong to CuO.

the XRD patterns collected after the treatments at 1012 and 1047 °C is displayed. The collected patterns are very similar to the one reported for the isostructural Pr-substituted compound which had been ascribed to a distorted orthorhombic layered $RuR1212$ phase [65]. Nevertheless, after an investigation of our samples by XRD and EDX analysis, we found several phases in equilibrium at the nominal $RuCa_2NdCu_2O_8$ composition.

While CuO is readily identified in the mixture, for the other phases we could just propose some ideal compositions from EDX results, most likely corresponding to a disordered double perovskite and a $n = 2$ Ruddlesden Popper phase, that require further confirmation. Neither resistivity nor temperature dependent magnetization studies performed on our samples reveal traces of superconductivity. Two magnetic transitions are observed at ≈ 33 K and ≈ 2.5 K, possibly related to magnetic ordering of the Ru ions and the Nd ions, respectively. In a study of the magnetic properties of Ca_2RuREO_6 ($R = Y, La-Lu$), Sakai *et al* [68] observed for the Ca_2RuNdO_6 compound an antiferromagnetic transition of the Ru^{5+} ions at 11.5 K and at lower temperature (≈ 2.1 K) another small anomaly that could be related to the magnetic ordering of the Nd^{3+} ions.

Ba-substitution at the nominal $RuA_2NdCu_2O_8$ composition is also investigated following the precursor route ($Ba_2RuNdO_6 + 2CuO$). The XRD study of the mixture after the treatment at 1070 °C (24 h) in oxygen flow reveals traces of $Nd(Ba_{1-x}Nd_x)_2Cu_3O_{7\pm\delta}$ together with the reflections of unreacted Ba_2RuNdO_6 and CuO. An increase of the temperature results in the melting of CuO which will seep from the pellet, thus strongly affecting the composition. We conclude therefore that neither with Ba nor with Ca is the formation of a layered $RuNd1212$ achieved at the nominal $RuA_2NdCu_2O_8$ composition.

2.4. Ru content

The possible volatility of RuO_x plays a role in the final Ru/Cu composition reached in $RuR1212$ compounds and

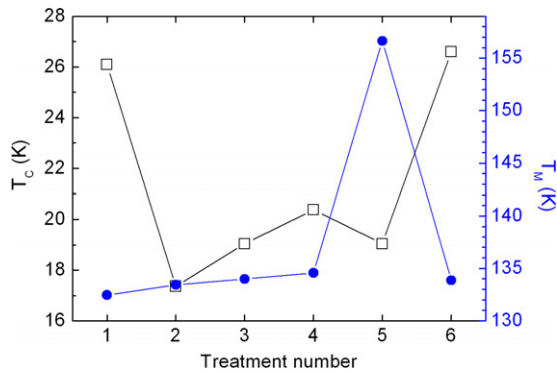


Figure 6. T_c (open squares) and T_N (closed circles) of RuGd1212 successively treated with higher RuO_x exposure. (1) Pure oxygen, (2) RuO₂ kept at 525 °C, (3) 656 °C, (4) 740 °C, (5) 800 °C, (6) pure oxygen.

thus may have an effect on their physical properties (see e.g. [13]). The sublimation of pure RuO₂ in Ar/O₂ atmosphere becomes discernible above about 850 °C at a heating rate of 5 K min⁻¹ [69]. While appreciable amounts of SrRuO₃ are formed at temperatures as low as 600 °C when the RuR1212 phase is synthesized from the binary oxides in air or oxygen, non-negligible formation of RuR1212 was observed only at temperatures approaching 1000 °C. Since Sr₂GdRuO₆ does not appear to be susceptible to loss of volatile RuO_x under these preparation conditions, the danger of Ru loss in the precursor route appears much smaller than the experiments with pure RuO₂ [69] would suggest.

In order to study the effect of Ru loss or Ru uptake during sintering on the superconducting and magnetic properties of RuGd1212, we have exposed samples to an oxygen atmosphere containing a controlled partial pressure of Ru-oxide [70]. The RuGd1212 samples prepared via the two-step precursor route were kept at 1050 °C for 20 h while being exposed to a flow of dried oxygen gas that had passed over a heated RuO₂ pellet. The temperature of the pellet (490–900 °C) was used to control the RuO_x partial pressure in the flow [70]. In the following, the pellet temperature is used to indicate the preparation conditions.

One sample that initially had $T_c = 26$ K was treated successively several times keeping the RuO₂ pellet at a different temperature. With increasing RuO_x exposure, the T_c dropped to 17 K, while the magnetic ordering temperature increased from $T_N = 133$ to 157 K (figure 6). Both T_c and T_N were restored to their original values after a final treatment in pure oxygen atmosphere (step 6 in figure 6). The non-monotonic variation of T_c and T_N in steps 2–5 is attributed to the slow diffusion of Ru into the sample and the resulting sample inhomogeneity.

This was investigated in a second series of four samples. While one sample was treated in a pure oxygen flow the others were exposed to RuO_x with the RuO₂ pellet kept at different temperatures. Pieces taken from the surface and the core of the samples were subjected to XRD and EDX analysis and T_c measurements (figure 7). Near the surface of the sample treated in pure oxygen, Ru-free and Ru-poor impurity phases were identified. The surface and core piece

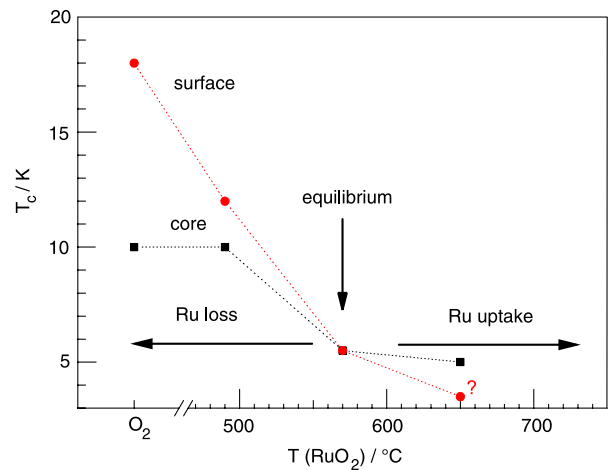


Figure 7. T_c of pieces taken from the surface or the core of RuGd1212 samples plotted versus the temperature of the RuO₂ pellet.

of this sample and of that with the RuO₂ pellet at 490 °C have higher T_c due to Ru loss (figure 7). The equilibrium between Ru uptake (or loss) and diffusion into/from the bulk when the RuO₂ pellet is kept at 650 °C leads to equal T_c of core and surface piece. For this sample, EDX did not reveal any impurity phases. For samples with higher Ru exposure, Ru-rich impurity phases were detected in the surface pieces whereas the core piece remained single phase. While the effect of Ru loss or Ru uptake is evident, the heat treatment time of 20 h obviously was not sufficient to establish equilibrium in the volume of these samples. Pulsed-field magnetization measurements reveal a higher Ru moment for a sample treated in O₂/RuO_x flow, indicative of a higher fraction of Ru⁵⁺ in this sample as compared to a sample treated only in oxygen atmosphere [55, 71, 72].

3. Conclusions

The layered ruthenocuprate of RuA₂RCu₂O₈ type prepared at standard conditions, under equilibrium at ambient pressure, is stable with A = Sr and a limited range of rare earth elements R = Sm, Gd and Eu. With the larger rare earth elements Pr and Nd, no layered RuSr₂RCu₂O₈ type was found under these conditions. The layered structure could not be stabilized for R = Nd through a complete substitution of the alkaline earth Sr by Ba or Ca.

The Ru content of RuSr₂GdCu₂O₈ could be varied by preparing samples in an oxygen/RuO_x atmosphere. With increasing Ru content, T_c decreases and T_N increases. This effect can be reversed when the samples are treated in pure oxygen due to the resulting Ru loss from the sample. The Ru concentration affects the average Ru valence. It remains to be examined whether the defect structure related to RuO₆ octahedra rotations can be affected by the variation of the Ru content. It would be interesting to see whether intrinsic self-organized modifications of the layered ruthenocuprate such as the formation of subdomain islands, octahedra rotations or stripes with different Ru valence could be affected by the preparation conditions.

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