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Thermal stability of $RuSr_2GdCu_2O_8$, $Ru_{1-x}Sr_2GdCu_2O_{8-y}$, RuO_2

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Abstract

Thermal stability of $RuSr_2GdCu_2O_8$, $Ru_{0.9}Sr_2GdCu_2O_{8-y}$, and RuO_2 powders in oxygen has been studied by thermogravimetry. Decomposition of $RuSr_2GdCu_2O_8$ and $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ samples in 0.85 bar of oxygen appears as a solid phase process at ~1050 °C. This is followed by peritectic decomposition with onset starting at ~1110 °C for the stoichiometric sample and at ~1090 °C for the Ru deficient one. We observed that sublimation of ruthenium oxide in 0.85 bar of oxygen starts at ~850 °C and sample's humidity significantly increases a sublimation rate. Enhanced sublimation above 1060 °C was observed for powder mixtures ($RuO_2 + xCuO$), $x = 0.1$, 0.2, 0.5. Analysis of the sublimation process of these mixtures suggests existence of an unknown compound in Ru–Cu–O system with approximate composition $Ru_{1-x}Cu_xO_{2-y}$, $x \leqslant 0.1$. Various aspects of a synthetic route of rutenates and, in particular $RuSr_2GdCu_2O_8$ phase, eliminating Ru off-stoichiometry and phase separation, are discussed.

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1. Introduction

A report on coexistence of superconductivity (SC) and ferromagnetism (FM) in $RuSr_2GdCu_2O_8$ (Ru-1212) phase [1] has stimulated investigations of this and related compounds. Though homogeneity of Ru-1212 samples was confirmed by synchrotron X-ray [2] and neutron powder [3] diffractions methods, the question of phase purity is not yet resolved to a satisfactory level [4,5]. Neutron diffraction experiments cannot detect Ru/Cu substitutions due to very close scattering cross-sections of Ru and Cu for thermal neutron [5,6]. X-ray diffraction method is also not informative to determine low-level substitutions of Cu for Ru, because of identical values of ionic radii of Ru^{+4}(VI) and Cu^{+2}(IV) ions of 0.62 Å [7]. (Cu is

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expected to be in a square coordination like in $YBa_2Cu_3O_7$ if it replaces Ru.) There are reports [8–11] that solid solutions $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-z}$ [(Ru,Cu)-1212] possesses superconductivity for $0 < x \leqslant 0.75$, implying that the substitutions might be responsible for superconductivity in Ru-1212 samples, whereas the stoichiometric Ru-1212 phase bears ferromagnetic properties. The possibility of phase separation into SC and FM phases of Ru-1212 phase [4,5,12] and related $RuSr_2LnCu_2O_8$ (Ln = Y, Dy, Ho, Er) compounds [13] has been demonstrated.

Usually superconductivity in Ru-1212 samples is achieved after synthesis at or above 1060 °C. Specific structural transformations observed in Ru-1212 samples after long annealing at 1060 °C were proposed to be essential for establishing superconductivity [3]. On the other hand, decomposition of the Ru-1212 phase, which was observed by thermogravimetry (TG) at ~1050 °C [14], suggests an origin of SC and FM based on phase separation. In our previous work [15,16] we observed decomposition of Ru-1212 phase at ~1060 °C and have brought evidence for cation redistribution. It was proposed [15] that decomposition of the Ru-1212 phase occurs via formation of Ru-deficient $Ru_{1-x}Sr_2GdCu_2O_{8-y}$ [Ru-$(1-x)$212] phase due to sublimation of ruthenium oxide, producing Cu-substituted $(Ru_{1-x}Cu_x)Sr_2GdCu_2O_{8-z}$ phase.

Therefore, to elucidate the decomposition process of Ru-1212 phase we study here the thermal stability of $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ one and in addition RuO_2 by TG. Formation of Cu-substituted (Ru,Cu)-1212 phase as a by-product of decomposition of Ru-$(1-x)$212 phase is concluded from comparative analysis of decomposition of the stoichiometric and Ru-deficient samples.

Furthermore, the thermal stability of Ru-1212 phase and $SrRuO_3$ in argon has been investigated, since $SrRuO_3$ often appears as impurity in Ru-1212 samples. To eliminate this impurity it was proposed [1] to decompose Ru-1212 samples in oxygen-poor atmosphere at 1010 °C before their final sintering in oxygen. This route was then widely employed [2,3,17–20]. We show that decomposition of the Ru-1212 sample followed by re-oxidation could result in Ru-deficiency and thereby lead to formation of Cu-substituted (Ru,Cu)-1212 phase whilst retaining $SrRuO_3$ phase unchanged.

Suggestions for synthetic route of Ru-1212 samples preventing Ru-deficiency are given.

2. Experimental

$RuSr_2GdCu_2O_8$, $Ru_{1-x}Sr_2GdCu_2O_{8-y}$ and $SrRuO_3$ samples were prepared by a conventional solid state reaction. Powders of CuO (99.99%), RuO_2 (99.9%), $SrCO_3$ (99.9%) were dried at 700 °C, and Gd_2O_3 (99.99%) at 1000 °C for 3 h in air before use. The crucibles with RuO_2 and Gd_2O_3 powders were taken from a furnace at ~400 °C upon cooling and placed in a dry box to cool down to room temperature to avoid them to moisten because they are highly hygroscopic materials. The mixtures of components were grounded in acetone in an agate mortar accordingly to the nominal compositions. The mixtures were calcined two times at 800 °C in air for 10 h with intermediate regrinding in acetone. After that the powders were pressed in pellets, sintered in oxygen at 1040 °C for 48 h, and cooled down to room temperature at a cooling rate of 2°/min.

The thermal stability was investigated by thermogravimetry. Small amounts of powders (30–50 mg) were heated in the DTA–TG apparatus (NETZSCH STA-449C) in Al_2O_3 crucibles with a heating rate of 5°/min in argon (99.999%) or O_2/Ar gas-mixture flow with the highest available oxygen content of 85%. Total gas flow rate was 10–60 ml/min. X-ray diffraction data were taken on powdered samples using Philips PW 3710 apparatus equipped with a curved C-monochromator on a diffracted beam with CuKα radiation. SEM analysis was done by a JEOL JSM-6400 scanning electron microscope.

3. Results and discussion

Powder X-ray diffraction patterns of samples with nominal compositions $RuSr_2GdCu_2O_8$ and $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ are shown in Fig. 1. The samples have nearly equal cell dimensions. The

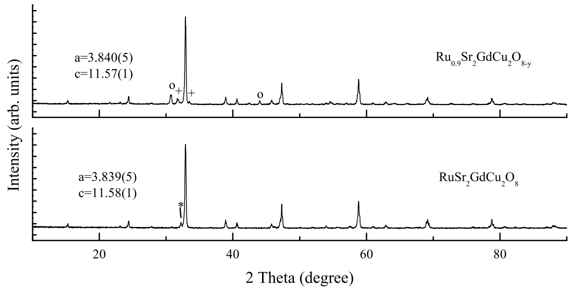

Fig. 1. X-ray diffraction patterns of $RuSr_2GdCu_2O_8$ and $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ samples. Labels correspond to following impurity phases: "o"—Sr_2GdRuO_6, "+"—Sr_2CuO_3, "*"—$SrRuO_3$ or Gd_2CuO_4.

stoichiometric Ru-1212 sample has a small amount of $SrRuO_3$ as impurity. The Ru-deficient one contains Sr_2GdRuO_6 and Sr_2CuO_3 as impurities. The amount of Sr_2GdRuO_6 (2116) was estimated to be ~10 wt% from comparison of X-ray peak intensities obtained for a powder mixture (Ru-1212 + 10 wt% 2116). The fraction of impurities could not be reduced after two additional heat treatments at 1040 °C in oxygen for 10 h each.

Thermogravimetry of $RuSr_2GdCu_2O_8$ phase in oxygen has been carried out and analyzed in details in our previous work [15]. It was observed that decomposition occurs in three stages: (i) subsolidus decomposition in a temperature range of ~1060–1115 °C; (ii) peritectic decomposition in a temperature range of ~1115–1135 °C; (iii) liquid phase decomposition above 1135 °C. The TG curve is reproduced in Fig. 2. From X-ray phase analysis of decomposition products the first stage decomposition was proposed as following [15]:

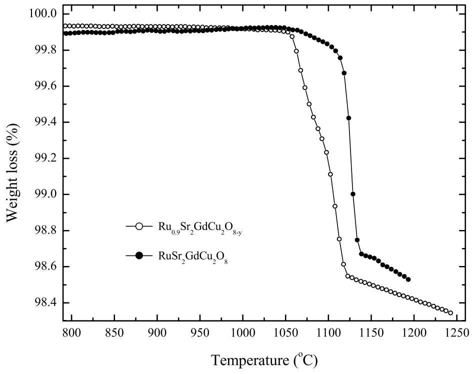

Fig. 2. TG curves of $RuSr_2GdCu_2O_8$ and $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ samples in 0.85 bar of oxygen.

(i) decomposition of the stoichiometric Ru-1212 phase into Ru-deficient Ru-$(1-x)$212 phase and ruthenium oxide sublimating from the sample:

$$RuSr_2GdCu_2O_8 \rightarrow Ru_{1-x}Sr_2GdCu_2O_{8-y} + xRuO_2(\text{sublimation}) \qquad (1)$$

(ii) decomposition of Ru-deficient phase:

$$Ru_{1-x}Sr_2GdCu_2O_{8-y} \rightarrow (1-x)Sr_2GdRuO_6 + \text{liquid(CuO-rich)} + zCu_2O + \delta O_2 \qquad (2)$$

(iii) incorporation of copper appeared on the second stage into Ru-vacancies formed on the first stage and formation of copper substituted (Ru,Cu)-1212 phase:

$$Ru_{1-x}Sr_2GdCu_2O_{8-y} + xCuO \rightarrow (Ru_{1-x}Cu_x)Sr_2GdCu_2O_{8-z} \qquad (3)$$

This scenario implies that the first stage of decomposition of the stoichiometric Ru-1212 phase occurs through formation and decomposition of Ru-deficient phase, hence one expects that decomposition of Ru depleted sample should be more pronounced.

The TG curve of the sample with a nominal composition $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ is shown in Fig. 2. It is seen that decomposition is also observed in three stages similar to the stoichiometric sample but the first stage is indeed much more pronounced. Albeit some impurities (Sr_2RuGdO_6 and Sr_2CuO_3) exist in the sample, this pronouncement should be associated with Ru-deficient phase as the impurity phases are stable in this temperature range. (In accordance with our TG data (not shown here) Sr_2RuGdO_6 is stable in oxygen till ~1200 °C and a stability limit of Sr_2CuO_3 in oxygen is around 1220 °C [21].)

To clarify reactions occurred on the first stage a piece of the Ru-deficient sample was annealed in oxygen at 1075 °C for 1 h. SEM analysis showed very little amount of a melt appeared on grain boundaries indicating subsolidus decomposition. X-ray analysis of the sample showed slight increase of Sr_2RuGdO_6 and formation of Gd_2CuO_4

phase. Therefore, the first stage of decomposition of Ru-deficient phase was associated with subsolidus process described by formula (2). Gd_2CuO_4 is apparently crystallized from CuO-rich liquid based on Sr–Gd–Cu–O eutectic, which appears in a small quantity as a side product of subsolidus decomposition.

The second stage of decomposition of the Ru-deficient sample occurred above ~1090 °C is a peritectic process as a melt was observed by SEM after annealing of the sample in oxygen at 1110 °C for 1 h. X-ray analysis has shown a lot of Sr_2RuGdO_6 and Gd_2CuO_4 phases alone with a (1212)-compound and with some additional minor phases. As it was mentioned above Gd_2CuO_4 forms upon cooling by crystallization from the liquid and hence cannot originate this stage. Sr_2RuGdO_6 is stable at these temperatures and does not decompose but instead forms on this stage as it is seen from its increasing amount in comparison with the first stage. Thereby, this stage is associated with a (1212)-compound appeared as a product of the first (subsolidus) stage. In accordance with the formula (3) this (1212)-compound is Cu-substituted (Ru,Cu)-1212 phase, which forms by incorporation of CuO, appeared from partial decomposition of Ru-deficient Ru-$(1-x)$212 phase, into Ru-vacancies. Besides Cu-substituted (Ru,Cu)-1212 phase another (1212) compound with mutual substitutions between Sr and Gd, can also form [22]. However, its formation involves more complex cation replacements leading to lower yield of this phase in comparison with the Cu-substituted one. Therefore, we associate the second stage of the Ru-deficient sample decomposition with peritectic decomposition of (Ru,Cu)-1212 phase starting at ~1090 °C. Thus, analysis of decomposition process of the deficient Ru-$(1-x)$212 sample supports the scenario for decomposition of Ru-1212 phase but that should be accomplished by a stage: peritectic decomposition of Cu-substituted (Ru,Cu)-1212 phase above ~1090 °C.

The peritectic temperature for the Cu-substituted phase appears to be much lower than that for the stoichiometric Ru-1212 phase indicating less stability of the substituted phase in comparison with the stoichiometric one.

Decomposition of both the stoichiometric and the Ru-deficient phases leads to formation of the Cu-substituted (Ru,Cu)-1212 phase. Whilst decomposition of the former phase observes at ~1060 °C the decomposition of the latter one occurs already at ~1050 °C (see Fig. 2). Therefore, to prevent formation of the Cu-substituted (Ru,Cu)-1212 phase synthesis temperature should not exceed 1050 °C and precautions should be taken to avoid Ru off-stoichiometry. Ru-deficiency may appear on a stage of pre-sintering because of a trivial mistake in a nominal composition, as RuO_2 is highly hygroscopic material or due to sublimation of ruthenium oxide if calcination temperature exceeds 850 °C [15]. Here we investigated a thermal stability of a fresh dried RuO_2 powder and the same powder after a couple of weeks holding in a tightly closed vessel outside of a desiccator ("old dried" sample). TG curves of these RuO_2 samples are shown in Fig. 3. Weight of the fresh dried sample slightly increases from ~100 till ~850 °C indicating slight increase of oxygen content in RuO_2 apparently due to pre-oxidation of ruthenium oxide as it sublimates as higher oxides RuO_3 or RuO_4 [23]. Weight decrease corresponding to sublimation of ruthenium oxide starts with onset at ~850 °C. Weight of the "old dried" sample smoothly decreases till ~700 °C indicating release of water; from 700 till 1000 °C the weight recovers due to pre-oxidation. This process is much more pronounced in comparison with that of the dried sample. Above ~1000 °C weight decreases show-

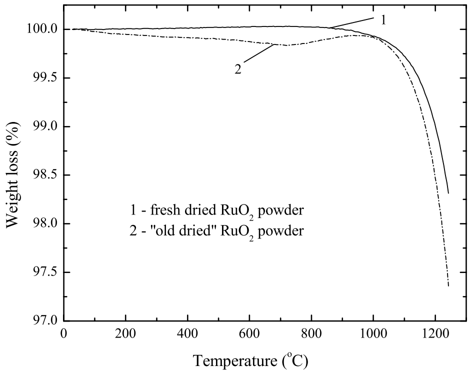

Fig. 3. TG curves of fresh dried and "old dried" RuO_2 samples in 0.85 bar of oxygen.

ing sublimation. The decrease has a higher rate than that of the dried sample indicating faster sublimation. This hints on lower sublimation temperature of the humid (“old dried”) sample in comparison with the dried one, however, it cannot be seen because pre-oxidation process (oxygen absorption) prevails and screens sublimation process.

Thus, these data illustrate that RuO_2 can easily absorb water and water promotes its sublimation. Hence following recommendations could be given for synthesis of ruthenates to obviate ruthenium off-stoichiometry: (i) RuO_2 powder should be dried at ~700 °C just before weighing; (ii) pre-sintering process should include a step of a few hours holding at ~700 °C for drying the sample; (iii) calcination temperature should not exceed 850 °C to avoid sublimation of ruthenium oxide before formation of stable ruthenates. These recommendations are essential for synthesis of any ruthenates, for example Sr_2RuGdO_6, which is used as a precursor for synthesis of Ru-1212 phase.

Sublimation of ruthenium oxide from Ru-1212 samples in oxygen at 1060 °C was confirmed by condensation of ruthenium oxide from oxygen flowing through a furnace during synthesis [16]. Oxygen was bubbled through water and a little of black powder was obtained there after synthesis of a number of samples. The compositional analysis of the powder by atomic emission spectroscopy gave an approximate atomic content of 93–95% Ru and 5–7% Cu. X-ray pattern of the powder could not be assigned neither to simple oxides RuO_2, CuO nor to dihydrate $RuO_2{\cdot}2H_2O$, which has X-ray pattern not that of RuO_2 [24,25] and could be formed at those synthetic conditions. Observed co-evaporation of ruthenium and cooper oxides has encouraged us to investigate a thermal stability of Ru–Cu–O system in oxygen. Powders of CuO and RuO_2, and powder mixtures of RuO_2 and CuO of nominal compositions $(0.9RuO_2 + 0.1CuO)$, $(0.8RuO_2 + 0.2CuO)$, $(0.5RuO_2 + 0.5CuO)$ were thoroughly grounded and then dried in air at 700 °C for 3 h just before the measurements. TG curves of these powders are shown in Fig. 4. (TG curve of the RuO_2 sample is that represented in Fig. 3.) TG curves of the mixtures deviate from the curve of RuO_2 above 1060 °C indicating enhanced sublimation, which could be attributed to promote oxidation of RuO_2 by CuO. However, for a solid phase process one expects a maximum of activation at ~30–50 mol.% of promoter, what is not observed here as TG curves of all three mixtures have nearly identical shape up to starting point of CuO decomposition at ~1095 °C. Therefore, we associate the enhanced sublimation with formation and evaporation of $Ru_{1-x}Cu_xO_{2-y}$, $(x \leqslant 0.1)$ compound, in support of the suggestion that in Ru–Cu–O system there is unknown phase with low Cu content [16]. It

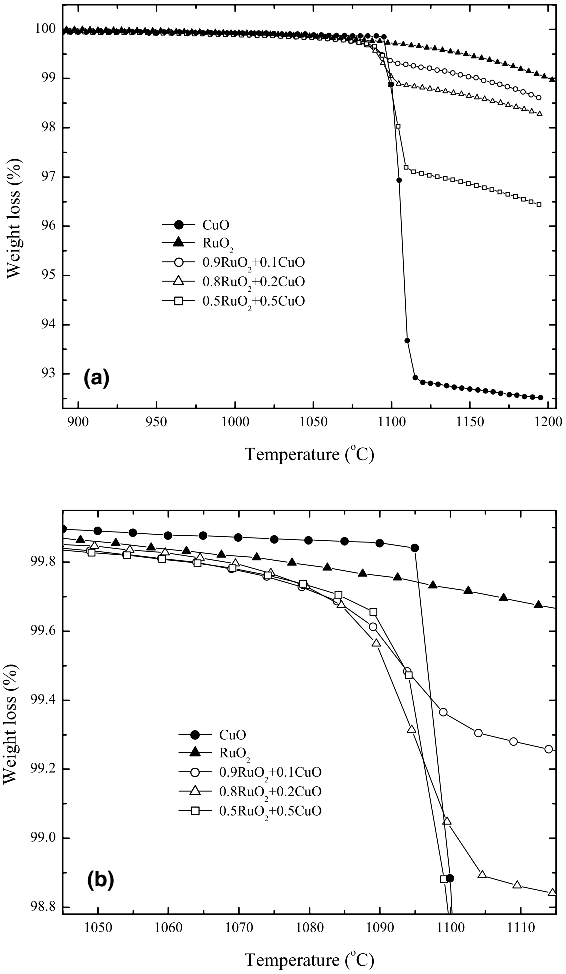

Fig. 4. TG curves of CuO, RuO_2, and powder mixtures of RuO_2 and CuO with nominal compositions $(0.9RuO_2 + 0.1CuO)$, $(0.8RuO_2 + 0.2CuO)$, $(0.5RuO_2 + 0.5CuO)$ obtained in 0.85 bar of oxygen.

should be mentioned that our attempts to synthesize this phase by solid phase reaction from oxides were unsuccessful and we did not observe any additional phases beyond RuO_2 and CuO. From a vapor transport synthesis we obtained well-shaped (mostly tetragonal) single crystals alone with conglomerates of needle-like crystals. EDX composition analysis of the former crystals gave RuO_2 with 0.2–0.5 at.% of Cu, whereas the latter ones included at least up to 3 at.% of Cu. HRTEM and ED analysis are in progress to find out a crystal structure of the needle-like crystals, whether they are a solid solution of Cu in RuO_2 structure or a distinct phase (to be published elsewhere).

Ru-1212 samples often include $SrRuO_3$ as impurity. It was proposed [1] to decompose Ru-1212 samples in nitrogen at 1010 °C prior to sintering in oxygen with an aim towards minimizing the formation of $SrRuO_3$ formed during calcination; this route was then repeated in [2,3,17–19] and in [20] for argon atmosphere. Therefore, we investigated a thermal stability of Ru-1212 and $SrRuO_3$ in argon (oxygen content ~0.001%). TG curves of these powders are shown in Fig. 5. Weight loss of Ru-1212 sample appears in two stages: a strong decrease in a range of ~900–1020 °C followed by a slow decrease above 1020 °C. In the first step (900–1020 °C) the weight loss is ~2.1–2.2%. Assuming the reduction of entire copper from Cu^{+2} to Cu^{+1} a calculated weight loss is 2.3%. A good agreement between the observed and calculated values indicates that the first stage of decomposition in argon corresponds to a transition of the whole amount of copper from (+2) to (+1) oxidation state. To determine the decomposition products the Ru-1212 sample was annealed in argon flow at 900 °C for 12 h and then quenched to room temperature also in argon flow. The product was a friable powder without any sign for a liquid. X-ray analysis indicated a mixture of Sr_2RuGdO_6, Ru-1212, and Cu_2O. Thus, the first stage of decomposition in the temperature range of ~900–1020 °C is subsolidus decomposition expressed by the following equation:

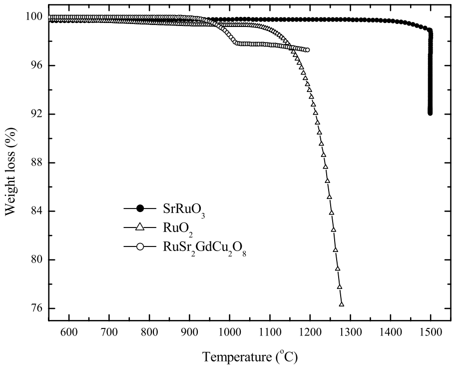

Fig. 5. TG curves of $RuSr_2GdCu_2O_8$, $SrRuO_3$, and RuO_2 in argon.

$$RuSr_2GdCu_2O_8 \rightarrow Sr_2RuGdO_6 + Cu_2O + 0.5O_2 \tag{4}$$

X-ray analysis of the sample annealed in Ar at 1200 °C for 3 h showed a mixture of $Sr_3Ru_2O_7$, Gd_2O_3, and Cu_2O. Therefore, the second stage of the weight loss in the temperature range of ~1020–1200 °C is due to reduction of Ru^{+5} to Ru^{+4} because of decomposition of the 2116 phase. It is worth noting that after the heating till 1200 °C the sample was partially melted, therefore, reduction of copper in a liquid above ~1080 °C also takes place giving some contribution to the weight loss.

Thermal stability of $SrRuO_3$ in argon was measured up to 1500 °C (the highest safely reached temperature in our TG device). Weight decrease indicating decomposition is seen at ~1400 °C (Fig. 5). (In fact, a very slow weight decrease starts above ~1200 °C, but this is not visible in scales of Fig. 5.) At 1500 °C the sample was kept for 3 h to ensure a complete reaction. The final weight loss of $SrRuO_3$ after 3 h holding at 1500 °C was ~7% what is very near to loss of one oxygen atom per $SrRuO_3$ molecular. X-ray analysis of the decomposition product gave a mixture of Sr_2RuO_4 and metal Ru, indicating decomposition process described by formulas:

$$2SrRuO_3 \rightarrow Sr_2RuO_4 + RuO_2 \tag{5}$$

$$RuO_2 \rightarrow Ru + O_2 \tag{6}$$

Formula (6) expresses decomposition of RuO_2 in Ar, which observes as a slow process from ~900 °C followed by rapid decomposition above 1050 °C. The corresponding TG curve is shown in Fig. 5.

Thus, in contrast to Ru-1212 phase $SrRuO_3$ appears to be a stable at least till 1200 °C, what renders the elimination of $SrRuO_3$ by argon or nitrogen annealing of Ru-1212 samples at 1010 °C as meaningless. (Observed sample's purification [1] means that the impurity was not $SrRuO_3$ but probably Gd_2CuO_4, which have very close main X-ray peaks and hence could be mixed [26].) Moreover, decomposition of Ru-1212 samples and their re-sintering in oxygen may lead to Ru-deficiency because metallic Ru appeared due to decomposition in accordance with the formula (6) oxidizes to sublimating trioxide (RuO_3) or tetroxide (RuO_4) even easily than dioxide [27].

4. Conclusions

Thermal stability of $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ sample in oxygen has been studied by thermogravimetry. It appears that Ru-deficient $Ru_{1-x}Sr_2GdCu_2O_{8-y}$ phase is less stable than stoichiometric $RuSr_2GdCu_2O_8$ phase. Subsolidus decomposition of the Ru-deficient phase observes at 1050 °C followed by incongruent melting above ~1090 °C. Cu-substituted $(Ru_{1-x}Cu_x)Sr_2GdCu_2O_{8-z}$ phase was recognized to form as a product of subsolidus decomposition of Ru-deficient phase, which then decomposes peritecticaly above ~1090 °C. Thus, decomposition process of $Ru_{0.9}Sr_2GdCu_2O_{8-y}$ sample supports the scenario of $RuSr_2GdCu_2O_8$ phase decomposition proposed in [15], which involves sublimation of ruthenium oxide causing cation replacements and formation of Cu-substituted (Ru,Cu)-1212 phase.

Sublimation of RuO_2 powder in oxygen observes at ~850 °C and sample's humidity significantly increases a sublimation rate and apparently lowers the sublimation onset temperature.

Enhanced sublimation above 1060 °C was observed for powder mixtures ($RuO_2 + xCuO$), $x = 0.1, 0.2, 0.5$. Analysis of a sublimation process of these mixtures suggests existence of unknown compound in Ru–Cu–O system with approximate composition $Ru_{1-x}Cu_xO_{2-y}$, $x \leqslant 0.1$ in agreement with the previous report [16].

Decomposition of Ru-1212 samples at 1010 °C in nitrogen or argon cannot minimize $SrRuO_3$ phase, as it is stable at least up to 1200 °C. Decomposition of Ru-1212 samples by reduction in oxygen-poor atmosphere (N_2, Ar) and their re-sintering in oxygen may lead to Ru-deficiency because of sublimation of ruthenium oxide during oxidation of metallic Ru.

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