

Thermal characterization of $\text{GdSr}_2\text{RuCu}_2\text{O}_y$ -based mixtures in the $\text{GdSr}_2\text{RuO}_6$ - CuO pseudobinary system

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Fundamental to investigating the coexistence of superconductivity and magnetic ordering in $\text{GdSr}_2\text{RuCu}_2\text{O}_y$ (Gd1212) is the fabrication of macroscopic crystallographically oriented samples. To achieve this, we need to identify the conditions in which Gd1212 incongruent melting reaction, producing solid $\text{GdSr}_2\text{RuO}_6$ (Gd1210) in Cu-rich liquid, dominates over decomposition due to RuO_2 sublimation. Only in these conditions is it possible, indeed, to grow oriented samples by any melting and resolidifying technique. Moreover, the optimal mixture of Gd1212 and its melting products has to be identified to perform melt-textured or flux-flow growth. By means of thermogravimetric and differential thermal analysis (TG-DTA) we analyzed, up to 1200 °C in air, several mixtures of Gd1212 with Gd1210 or CuO, performing a scan of the entire CuO-Gd1212-Gd1210 coexistence line of the Gd-Sr-Ru-Cu-O phase diagram. Gd1212 melting temperatures have shown a certain dependence on composition, decreasing about 30 °C for high Gd1210 content samples and about 20 °C for high CuO content samples with respect to pure Gd1212. A huge undercooling was observed for resolidification processes that were revealed to start at temperatures around 990 °C. Measurements proved that in this range of temperatures in air, no mass is lost at the end of each melting process, so that they are not affected by RuO_2 sublimation. A strong dependence on the atmosphere has also been observed for pure Gd1212, melting temperature decreasing by more than 80 °C from 100% O_2 atmosphere to He atmosphere (less than 10⁻²% O_2). Measurements revealed that high O_2 partial pressures favor RuO_2 sublimation, whereas low oxygen atmospheres prevent resolidification.

I. INTRODUCTION

A wide interest has recently spread over the ruthenocuprate compound $\text{GdSr}_2\text{RuCu}_2\text{O}_y$ (Gd1212),¹ because it shows the coexistence of superconductivity and highly anisotropic magnetic ordering.^{2,3} The two behaviors are generally considered mutually excluding. The superconductivity seems to be correlated to Cu planes (analogously to $\text{Y123} = \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$), and the magnetic ordering to Ru planes. The coexistence of these phases can be explained by hypothesizing a magnetic ordering due to canted antiferromagnetism,⁴ but its real nature is still debated.³⁻⁸ To clarify these properties it could be very helpful to grow large oriented superconducting samples, but fabrication difficulties appear to be still huge. In particular, the unavailability of single crystals makes rel-

evant the fabrication of oriented samples by melt-textured growth (MTG) techniques.

A good knowledge of melting processes and of high-temperature reactions and decomposition processes of the compound is needed to fabricate oriented samples. For Gd1212, a melting peritectic reaction⁹ that was very similar to Y123's reaction was first hypothesized with $\text{GdSr}_2\text{RuO}_6$ (Gd1210) in the role of Y211 and L(Cu) a Cu-rich liquid:



On the other side, observations of Gd1212, high-temperature processing in O_2 atmosphere¹⁰ led to the proposition of another reaction, where, due to the high volatility of Ru:



It is apparent that the occurrence of Eq. (2) would make

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the growth of any kind of oriented sample very difficult, except in a high-pressure RuO₂ atmosphere.

Anyway, by performing top-seeded MTG in air on pellets obtained from Gd1212–Gd1210 precursor powders, our group achieved the growth of 0.5 mm size oriented Gd1212 samples.^{11,12} In these samples a certain CuO production was observed, whereas the initial composition was globally preserved. The same results were obtained also by varying the initial composition, adding CuO powder instead of Gd1210, to increase the liquid phase in the melt.¹³ This suggests there is an interval of temperature and of O₂ partial pressure (p_{O_2}) in which reaction Eq. (1) is dominant over Eq. (2).

A better understanding of high-temperature behavior of Gd1212 is then necessary to improve the fabrication of bulk MTG samples and single crystals.

For this purpose, a scan of the entire CuO–Gd1212–Gd1210 coexistence line of the Gd–Sr–Ru–Cu–O phase diagram is advisable.

The parameter we used to associate our results to the points of this line is the x parameter:

$$x = \frac{n(\text{Gd1210}) + n(\text{Gd1212})}{n(\text{Gd1210}) + n(\text{CuO}) + 3 \cdot n(\text{Gd1212})} \quad (3)$$

where $n(S)$ is the molar amount of the substance S . Parameter x in Eq. (3) is equivalent to the relative molar concentration of Gd1210 with respect to CuO, as better explained in the appendix.

II. POWDER SYNTHESIS

The synthesis of Gd1210 was achieved by directly mixing Gd₂O₃, RuO₂, and SrCO₃ in the required amounts and firing them in a muffle furnace at 1200 °C for 24 h.¹⁴

During their turn, Gd1212 powders were synthesized starting from the produced Gd1210 and commercial CuO powders, weighed, and mixed in the proper amount.¹¹ This mixture was repeatedly reacted in pure O₂ flux in an horizontal tube furnace at 1020 °C for several 10 h dwell cycles, with intermediate grinding, up to a maximum total duration of 70 h.

After each cycle, θ -2 θ x-ray diffraction (XRD) analysis was performed on ground powders to check their phase composition and ensure the absence of spurious phases.

Finally, the mixtures to be analyzed by thermogravimetric and differential thermal analysis (TG–DTA) were obtained by mixing the desired amounts of powders of Gd1212 and of the added phase (Gd1210 or CuO) in an agate mortar.

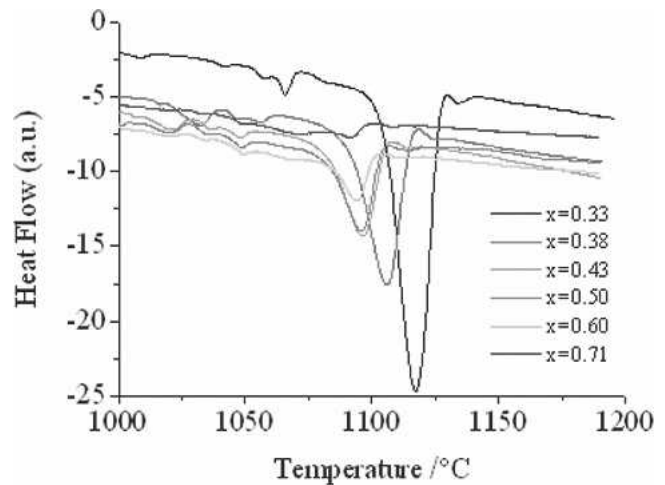


FIG. 1. DTA measurements in air (heating ramp) for Gd1210–Gd1212 mixtures (for pure Gd1212, $x = 0.33$).

III. TG–DTA ANALYSIS

To investigate the CuO–Gd1212–Gd1210 stability line, we chose to analyze, besides the pure CuO, Gd1212, and Gd1210 [whose x parameters, following Eq. (3), are $x = 0.00$, $x = 0.33$, and $x = 1.00$, respectively], two Gd1212/CuO mixtures, and five Gd1212/Gd1210 mixtures. The chosen stoichiometric ratios were $n(\text{Gd1212})/n(\text{CuO}) = 4/1$ and $1/1$ ($x = 0.31$ and 0.25), and $n(\text{Gd1212})/n(\text{Gd1210}) = 4/1$; $2/1$; $1/1$; $1/2$; and $1/4$ ($x = 0.38$; 0.43 ; 0.5 ; 0.6 and 0.71). We focused our investigation principally on the Gd1210-rich side of the stability line because, from our previous work, best MTG samples were obtained starting from Gd1212 + 0.25 Gd1210 ($x = 0.38$) precursor powders.^{6–8} On the other side, CuO-rich mixtures might be used to attempt single-crystal growth by flux-flow crystal growth.¹⁵

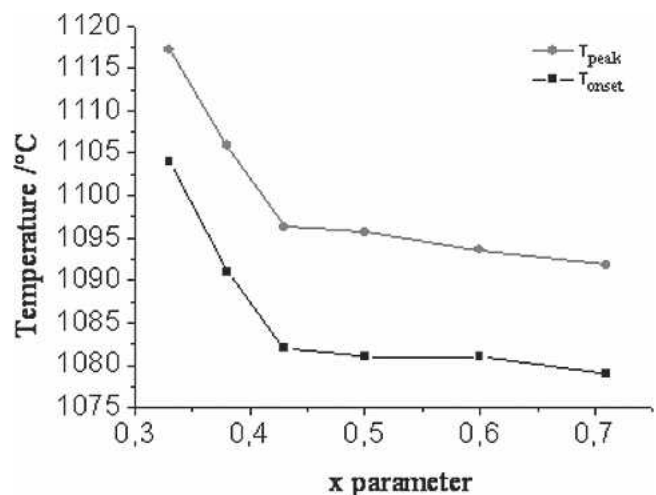


FIG. 2. Peritectic melting temperatures of Gd1212/Gd1210 mixtures in air from DTA measurements (peak temperatures T_{peak} are in gray, and extrapolated onset temperatures T_{onset} in black).

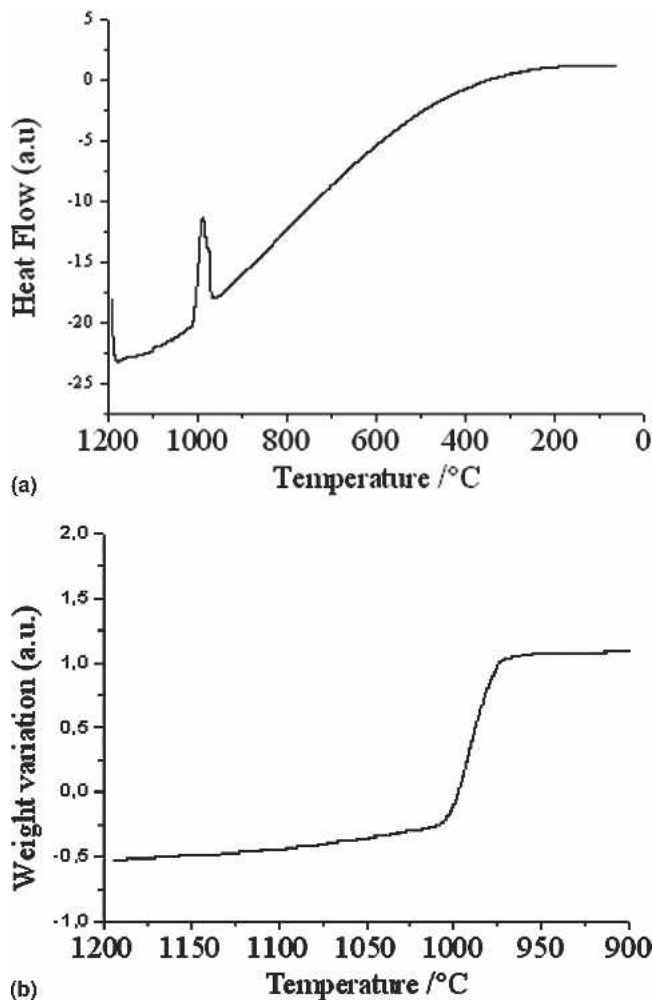


FIG. 3. (a) DTA and (b) TGA analyses (cooling ramp) for $x = 0.38$ mixture in air: the decrease of the resolidification temperature and the weight increase due to oxygen absorption are visible.

Using SETARAM SETSYS-Evolution 1750 equipment (Pennsauken, NJ) for TG-DTA, the melting temperatures and the occurrence of high-temperature reactions were analyzed for the prepared mixtures. About 100 mg of the prepared mixtures were put in an alumina crucible, measurements were performed in flowing air (at a flow rate of 10 mL/min, 1 atm pressure, $p_{O_2} = 21\%$), the schedule was: a first (heating) ramp from 40 °C up to 1200 °C at 5 °C/min rate, a dwell phase of 10 h and a last (cooling) ramp from 1200 °C back to 40 °C at 5 °C/min rate. The collected data were analyzed by the SETARAM SETSOFT 2000 program.

For the Gd1210-rich mixtures, TG-DTA analysis of the heating ramp (Fig. 1) has shown a progressive decrease of Gd1212 melting temperature T_p (Fig. 1, we assume $T_p = T_{onset}$, but we report also the temperature T_{peak} of the negative peak). This is a typical “solution” behavior and reveals chemical interaction between the components. T_p shows a tendency to saturate at about

1080 °C (1090 °C for T_{peak}), that means a decrease of about 24 °C (27 °C for T_{peak}) for the highest Gd1210 contents (Fig. 2).

The resolidification process, observed in the cooling ramp, occurs at about 990 °C for all the Gd1212/Gd1210 and Gd1212/CuO mixtures, which implies an undercooling of 100 to 110 °C below the melting temperature. Such a big undercooling may be a cause for the difficulties found in growing melt-textured samples with domain size larger than 0.5 mm.¹² In effect, for MTG the appropriate growth temperature window lies between the heterogeneous nucleation undercooling temperature (resolidification temperature in the presence of a seed) and the homogeneous nucleation undercooling temperature (resolidification temperature in absence of any seed).¹⁶ The MTGs, up to now, have been then, probably, performed at too high temperatures. More measurements of the heterogeneous nucleation undercooling temperature, adding a seed in the mixture, will be necessary to better clarify this point.

Moreover, although there is evidence of oxygen loss during the melting process, it seems to be completely reabsorbed during the resolidification process. Total mass balance, in fact, is almost 0.00 ± 0.05 mg after the performed cycles: clear proof that there is a temperature window, for a certain oxygen partial pressure range around air composition, in which a peritectic melting process, analogous to Y123 one, is dominant above the RuO₂ sublimation process.

To exemplify and summarize all these results, Figure 3 shows DT-TGA curves of the $x = 0.38$ sample presenting a single resolidification process at 990 °C, associated with an abrupt weight increase at the same temperature, going up slightly above the initial weight. As an enforcement to this observation, XRD analysis performed on the

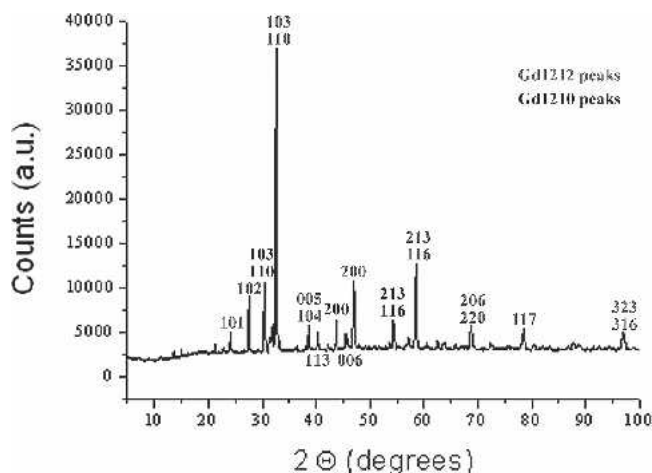


FIG. 4. XRD diffractogram for $x = 0.38$ mixture after a TG-DTA thermal cycle in air: after the resolidification only peaks belonging to Gd1210 and Gd1212 phases are visible, with peak relative intensities very near to those of the initial mixture (only the highest peaks are indicated).

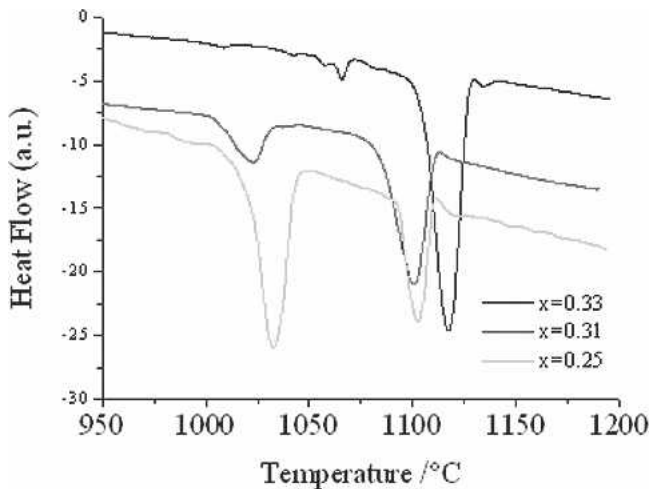


FIG. 5. DTA measurements (heating ramp) for CuO-Gd1212 mixtures in air (for pure Gd1212, $x = 0.33$).

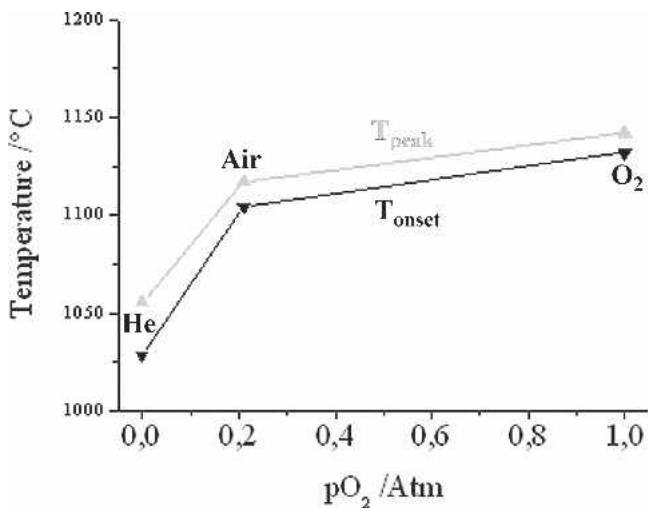
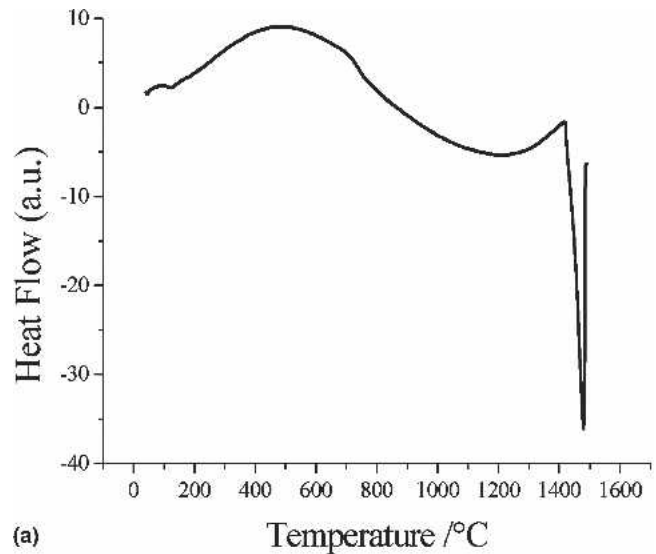


FIG. 6. Gd1212 T_p dependence on the oxygen partial pressure (T_{onset} in black, T_{peak} in bright gray).

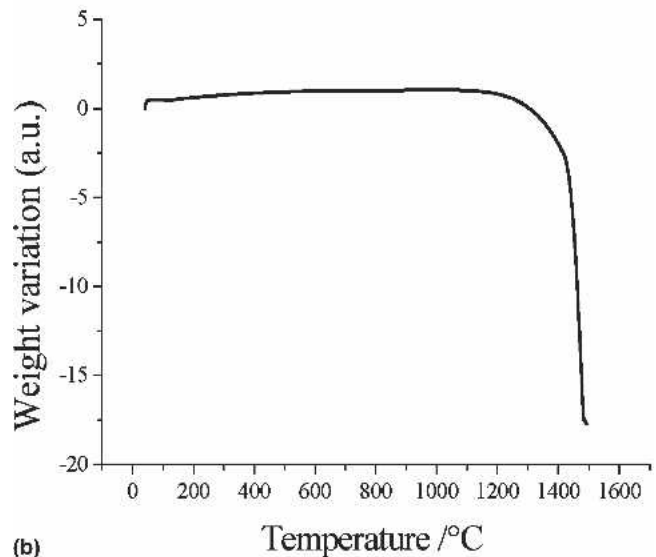
processed powders show the presence of only Gd1212 and Gd1210 phases (Fig. 4) and no evidence of the Gd1202 phase or others compatible with Eq. (2).¹⁷ This behavior is a good sign of the fact that our experiment has been performed inside a temperature and p_{O_2} window in which Eq. (1) is the dominant process.

Cu-rich mixtures, analyzed under the same conditions (Fig. 5), also present a T_p lowering with respect to Gd1212, probably characterized by a steeper decrease with CuO addition, and by a saturation temperature around 1090 °C (1100 °C for T_{peak}), 14 °C lower than T_p (17 °C for T_{peak}). Anyway, more points will be needed to obtain more precise indications about high-temperature properties of these mixtures.

By using the same schedule, the dependence of Gd1212 T_p on atmosphere was also analyzed (Fig. 6). We performed TG-DTA measurements on pure Gd1212



(a)



(b)

FIG. 7. (a) DTA and (b) TGA analyses (heating ramp up to 1500 °C) of pure RuO₂ in air, showing the sublimation temperature at 1439 °C and the onset of evaporation for temperatures higher than 1200 °C.

in flowing He ($p_{\text{O}_2} \leq 2 \times 10^{-4}$ atm) and in flowing O₂ ($p_{\text{O}_2} = 1.00$ atm), and we compared the results with the analysis already made in air ($p_{\text{O}_2} = 0.21$ atm). T_p appears to be very sensitive to p_{O_2} : its value in O₂ atmosphere being $T_{\text{onset}} = 1132$ °C ($T_{\text{peak}} = 1142$ °C), that means 28 °C higher than the value in air (25 °C for T_{peak}), and 104 °C higher than the value of 1028 °C ($T_{\text{peak}} = 1055$ °C, so the difference is 87 °C) measured in inert (He) atmosphere. For O₂ atmosphere resolidification peak is split in three, with their onset at 1062, 1034, and 1023 °C ($T_{\text{peak}} = 1049$, 1031, and 1021 °C, respectively). For He atmosphere, resolidification peak is split in two ($T_{\text{onset}} = 1008$ and 980 °C, $T_{\text{peak}} = 1002$ and 964 °C, respectively) strongly inhibited ones (the total enthalpy is

about one-tenth than in air). An appreciable weight loss (about 3%) at the end of the cycle is observed for the powders analyzed in He, that appears due to O₂ loss, whereas a slight decrease in weight due to RuO₂ sublimation (about 0.5%) has been observed for O₂ atmosphere. No significant weight loss has been observed, as already said, at the end of the cycle for powders analyzed in air. So, at these temperatures, RuO₂ sublimation should become relevant starting from a p_{O_2} higher than 0.21 (as shown by our data) but lower or equal to 0.35 as reported in Ref. 17 (that show huge weight losses for high p_{O_2} atmospheres).

TG-DTA measurement in air have been also performed on RuO₂ with a schedule analogous to the previous one, but going up to 1500 °C. Measurements have shown that sublimation onset occurs at 1439 °C ($T_{\text{peak}} = 1478$ °C), although a slight vapor generation appear to start around 1200 °C (Fig. 7). This last result suggests that, for Gd1212, in O₂ atmosphere the temperature window in which Eq. (1) dominates over Eq. (2) may be too narrow, so that high-temperature processing may lead to partial Ru sublimation. On the other side, as seen for He atmosphere, a too low p_{O_2} leads to O₂ losses. The variation of T_p with CuO or Gd1212 mixing and the huge difference between T_p and the observed spontaneous resolidification temperature suggest that MTG process parameters must be calibrated depending on initial composition.

IV. CONCLUSIONS

The obtained results show that, for thermal processes reaching a maximum temperature of 1200 °C, the peritectic melting reaction in Eq. (2) is the dominant process for Gd1212 powders in air ($p_{\text{O}_2} = 0.21$). As an evidence of this fact, TGA mass balance after any melting-resolidification cycle in air results equal to 0 within experimental errors. This occurs both for the pure material and for mixtures of Gd1212 plus one of its melting reactions products: Gd1210 or CuO. To enforce this observation, TG-DTA measurements performed on pure RuO₂ in air, up to 1500 °C, have shown that, for the pure compound this process occurs at quite higher temperatures than those used in the MTG processes, so that probably its importance is quite low.

Gd1212 melting temperature decreases about 20 °C, depending on CuO, and about 30 °C, depending on Gd1210 addition. Resolidification temperatures show a huge undercooling, occurring around 990 °C, that should be considered in the objective of growing macroscopic oriented samples, giving suggestions for more effective thermal schedules of MTG processes.

RuO₂ sublimation has proved to be more important for Gd1212 in pure O₂ atmosphere ($p_{\text{O}_2} = 1.00$). On the contrary, for Gd1212 in inert atmosphere (He, $p_{\text{O}_2} \leq 2 \times$

10^{-4}) oxygen-loss processes seem to be more important and are probably the cause of the observed partial suppression of the resolidification process. More measurements, performed coupling a mass spectrometer to TG-DTA, are in progress for a better evaluation of evolved gases. A huge dependence of Gd1212 T_p on atmosphere has been observed, with a difference of about 100 °C between the values measured in O₂ and in He atmosphere.

Further investigations will be necessary to better analyze the CuO-Gd1212 side of the coexistence line.

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APPENDIX

Having a mixture made of three substances (CuO, Gd1212, and Gd1210) a generic order parameter x may be written, for our case, as

$$x = \frac{\alpha \cdot n(\text{CuO}) + \beta \cdot n(\text{Gd1212}) + \gamma \cdot n(\text{Gd1210})}{a \cdot n(\text{CuO}) + b \cdot n(\text{Gd1212}) + c \cdot n(\text{Gd1210})} \quad , \quad (\text{A1})$$

where α , β , γ , a , b , c are linear coefficients to be determined. Working on the CuO-Gd1210 coexistence line, if only these two compounds were present, the more natural x parameter would be the relative molar concentration of one of the two compounds (for example, Gd1210) with

respect to the total molar composition of the mixture. This can be written as

$$x = \frac{n(\text{Gd1210})}{n(\text{CuO}) + n(\text{Gd1210})} \quad . \quad (\text{A2})$$

The presence of Gd1212 leads us to search for a more complicated parameter, of the form Eq. (A1), that reduces to Eq. (A2) in the absence of Gd1212. The coefficient must be then determined in a way that will satisfy this condition. This leads us to immediately write $\alpha = 0$; $\gamma = 1$; $a = 1$; and $b = 1$ (any other linear proportionality factor will be introduced in the Gd1212 coefficients). Moreover, we want the parameter associated with Gd1212 to correspond to its position in the coexistence line. We must, then, use Eq. (1), that is, explicitly writing the L(Cu) composition:

$$\text{Gd1212} = \text{Gd1210} + 2\text{CuO} \quad , \quad (\text{A3})$$

we impose $x(\text{Gd1212}) = x(\text{Gd1210} + 2\text{CuO}) = 1/3$, implying $b = 3\beta$. So, to preserve the original parameter for every composition, we formally write $x(\text{Gd1212}-2\text{CuO}) = x(\text{Gd1210}) = 1$; that means:

$$\frac{\beta}{3\beta - 2} = 1 \quad , \quad (\text{A4})$$

so that finally $\beta = 1$ and we obtain formula shown in Eq. (3).