

Copper Deficiency — a Crystallochemical Nature of Ce-Doped Gd_2CuO_4 Phase. Part II

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Two samples of nominal composition $\text{Gd}_{1.80}\text{Ce}_{0.15}\text{CuO}_{4.0}$ and $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.075}$ were subjected for a long-term treatment in air at 1100°C , comprised with a precise control of their weights vs. time of the treatment applied. The gravimetric analysis and the iodometric titration, both showed a deficiency on Cu-site, steadily increasing vs. time with a slight tendency to a saturation. The X-ray analysis of the resulting products showed that even after 272 h of sintering, the samples remained single phase of the “214” structure type. Refinement of their crystal structures as well as density measurements, both allowed confirming Cu deficient structure constitution of these samples. Results of dc-magnetization measurements, performed prior to reduction of the sample’s overall oxygen content, did not show any sign of superconductivity down to 4.2 K. These preliminary results indicate that copper deficiency, developing during synthesis, may occur to be a decisive factor for the reported lack of superconductivity in Ce-doped Gd_2CuO_4 phase. Oxygen content reduction and further tests on the samples obtained are in progress.

PACS numbers: 64.75.+g, 81.40.Rs, 75.50.-y, 72.20.My

1. Introduction

In Part I [1] we present results of our study on phase equilibria in $\text{Gd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$ system prevalent for isothermal cross-section of 980°C . Because of seriously restricted solubility of CeO_2 in Gd_2CuO_4 binary phase at 980°C , we could not construct satisfactorily precise the domain of Ce doped Gd_2CuO_4 solid solution. Nevertheless, an important result concerning crystallochemical constitution of this solid solution, consisting of deficiency on Cu-site, is given therein.

The aim of this work was to recognize more precisely real constitution of Ce-doped Gd_2CuO_4 solid solution, based on samples of much higher Ce content. We hoped to get some additional evidences that would help understanding so essential differences in electronic and transport properties of this phase reported in relation to those of the Ce-doped Nd_2CuO_4 one.

2. Experimental

Two samples of nominal composition $\text{Gd}_{1.80}\text{Ce}_{0.15}\text{CuO}_{4.0}$ and $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.075}$, each of about 2 g, were prepared by classical solid state reaction using appropriate oxides of the Johnson–Matthey 4N purity. The preliminary sintering procedure consisted of 2 days at 800°C , then 2 days at 850°C and finally 3 days at 900°C , each time comprised with regrinding and palletizing of the samples before application of higher sintering temperature.

On passing the above procedure, the samples were subjected for a long-term (≈ 12 days) ageing in air at 1100°C , comprised with a precise control of their weights vs. time of the treatment applied. Then they were quenched to room temperature and X-ray analyzed (DRON-3 diffractometer and Fe filtered $\text{Co } K_\alpha$ radiation). Any decrease in the sample weights, observed vs. time at 1100°C , was assumed to result entirely from volatility of either copper or copper oxides. Volatility of the remaining elements was neglected.

Parallel to the samples under gravimetric control, two reference samples of the same composition were used to verify, by X-ray, the phase composition of the gravimetrically controlled samples and its time dependent variation.

The overall content of Cu and its oxidation state in the samples analyzed were deduced based on double titration with sodium thiosulphate of known concentration (N), applied to the solutions obtained by dissolving them in HCl, both “on cold” and “on boiling”, all according to the procedure given in [2].

Additional tests applied to the gravimetrically controlled samples were determination of their density, performed according to the procedure described in [3], as well as refinement of their crystal structures by the Rietveld technique. For this purpose, the X-ray powder patterns recorded in SIEMENS D5000 diffractometer ($\text{Cu } K_\alpha$ radiation with Si internal standard) and the FULLPROF program [4] were used.

Concerning contribution of Ce, we assumed that this element takes part as well in the oxidation of iodide ions to free iodine. The algebraic matrices used for estimation of Cu final content ($y\text{Cu}$) and its valence (V_{Cu}) were as follows:

$$\begin{array}{llll} \text{titration on} & (A + y\text{Cu} + 8yV_{\text{Cu}}) & \longrightarrow & y(V_{\text{Cu}} - 1) + 0.15 \\ \text{cold solution} & m_c & \longrightarrow & NU_c \\ \\ \text{titration on} & (A + y\text{CuO}) & \longrightarrow & y + 0.15 \\ \text{boiled solution} & m_b & \longrightarrow & NU_b \end{array}$$

Physical meaning of the individual factors given in these matrices is following: A — invariable and known part of the overall molecular weight of each tested sample, i.e. either $\text{Gd}_{1.8}\text{Ce}_{0.15}\text{O}_3$ or $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{O}_{3.075}$, expressed in g, then $(y\text{Cu} + 8yV_{\text{Cu}})$ — unknown part of the molecular weights in which y — atomic fraction of copper and V_{Cu} — effective valence of copper. The remaining factors are known and represent: N — concentration of sodium thiosulphite, U_c and U_b — volumes of sodium thiosulphite used in the titration processes. Finally, m_c and m_b — masses of solid state samples used to prepare their “on cold” and “on boiling” solutions, respectively.

At this point we should admit that the m_b value is unavailable since it is referred to “214” structure type sample of $V_{\text{Cu}} = 2$. This valence state appears exclusively in course of “on boiling” dissolution of the samples available, i.e. those of $V_{\text{Cu}} \neq +2$, used to perform titration of their “on cold” solutions. For this reason we can only deduce the m_b value, namely $m_b = m'_c [1 - 8y(V_{\text{Cu}} - 2) / (A + y\text{Cu} + 8yV_{\text{Cu}})]$. Easy to see why the m_b portion cannot be weighed experimentally, and why, dependent on the V_{Cu} factor, the m_b can be either larger or smaller than the m'_c .

3. Results and discussion

In Fig. 1 we present the time dependent loss of sample weights, taking place at 1100°C in air. The sharp jumps seen at the beginning of the thermal treatment applied seem atypical. Let us note that at this stage, the samples were not single phase yet (as an example see Fig. 2a), and the jumps may reflect dissociation of CuO to Cu_2O , comprised with evaporation of the latter.

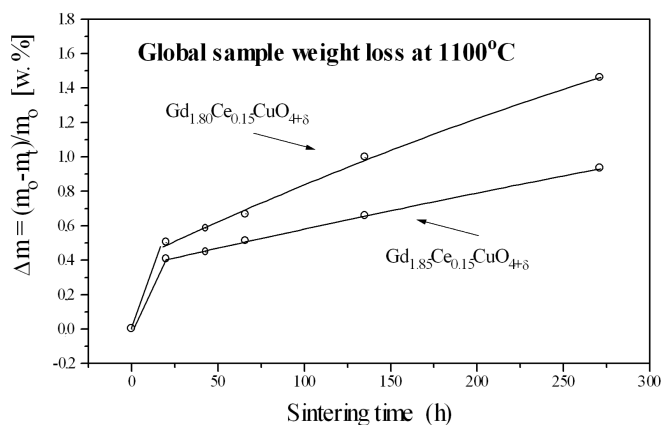


Fig. 1. The time dependent loss of weight, taking place in air at 1100°C for samples of the nominal composition $\text{Gd}_{1.80}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, expressed in wt. %.

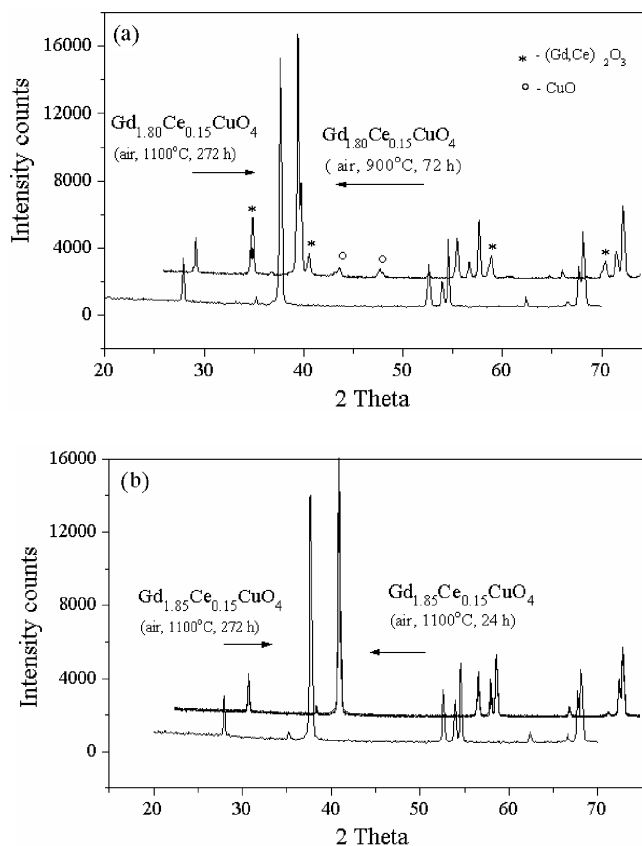


Fig. 2. The X-ray ($Co K_{\alpha}$) diffraction patterns of Ce-doped Gd_2CuO_4 samples; (a) sample of nominal compositions $Gd_{1.80}Ce_{0.15}CuO_4$, after sintering at 900°C for 72 h and at 1100°C for 272 h, (b) sample of nominal compositions $Gd_{1.85}Ce_{0.15}CuO_4$, after sintering at 1100°C for 24 h and for 272 h, respectively.

As proved by X-ray diffraction of the reference samples, already after ≈ 24 h at 1100°C, the samples under control became single phase (somewhat later in case of the sample $Gd_{1.80}Ce_{0.15}CuO_4$), hence further smooth loss of their weights vs. time is seen. In case of the Gd deficient sample $Gd_{1.80}Ce_{0.15}CuO_4$, its weight loss is much quicker (see Fig. 1). Interesting to note is that, even after 272 h exposure to 1100°C, both the samples remain single phase in spite of a continuous loss of their weights (see for example Fig. 2b). This feature means that probably, beginning from the line of constant Cu content equal to 33.33 at.%, domain of Ce-doped Gd_2CuO_4 solid solution expands considerably towards Cu deficient compositions.

Results of chemical, gravimetric, and X-ray analyses of Ce-doped $Gd_2CuO_{4\pm\delta}$ type single-phase samples of the nominal composition $Gd_{1.80}Ce_{0.15}CuO_4$ and $Gd_{1.85}Ce_{0.15}CuO_4$, are presented in Table. Based on the iodometric titration and on density measurements, final structure constitution

TABLE

Results of chemical, gravimetric, and X-ray analyses of Ce-doped $\text{Gd}_2\text{CuO}_{4\pm\delta}$ type single phase samples of the nominal composition $\text{Gd}_{1.80}\text{Ce}_{0.15}\text{CuO}_4$ and $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$, obtained after sintering in air at 1100°C during 272 hours.

$\text{Gd}_{1.80}\text{Ce}_{0.15}\text{CuO}_4$ (Gd deficient sample)	$\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (stoichiometric sample)
1a) Atomic fraction of Cu found by gravimetry	
0.901*	0.936*
1b) Atomic fraction of Cu found by titration	
0.890	0.925
2) Valence of Cu (V_{Cu})	
1.978	2.017
3) Lattice parameters (\AA)	
$a = 3.903, c = 11.834$	$a = 3.902, c = 11.832$
4) Experimental density (g/cm^3)	
7.95	7.97
5) M-component's atomic fractions	
Gd (63.380), Ce (5.282), Cu (31.338)	Gd (63.248), Ce (5.128), Cu (31.624)
6a) Composition recalculated for Cu deficiency model	
$\text{Gd}_{1.846}\text{Ce}_{0.154}\text{Cu}_{0.913}\text{O}_{3.98}$	$\text{Gd}_{1.85}\text{Ce}_{0.15}\text{Cu}_{0.925}\text{O}_{4.01}$
calculated density (g/cm^3)	
7.989	8.014
structure reliability factor (R_{wp})	
3.68% ($R_w = 2.81\%$)	3.55% ($R_p = 3.05\%$)
6b) Composition recalculated for cationic-site full occupancy	
$[\text{Gd}_{1.9014}\text{Ce}_{0.0986}] [\text{Cu}_{0.9401}\text{Ce}_{0.0599}]\text{O}_{4.100}$	$[\text{Gd}_{1.8974}\text{Ce}_{0.1026}] [\text{Cu}_{0.9487}\text{Ce}_{0.0513}]\text{O}_{4.110}$
calculated density (g/cm^3)	
8.230	8.220
structure reliability factor (R_{wp})	
3.72% ($R_w = 3.13\%$)	3.64% ($R_p = 3.13\%$)

These data were obtained assuming the observed sample weight loss to be caused by evaporation of free Cu.

of these samples could be precisely determined. As it is suggested in [1], the distribution model ascribed to them consists of Cu deficiency, variable vs. time of sintering applied.

This model has been also confirmed by the crystal structure analysis (for the case of nominally stoichiometric sample the results are presented in Fig. 3), consisting of mutual comparison of the experimental intensity data $I_{(hkl)}$ with those calculated for each of the models considered. Appropriate reliability factors are given in Table.

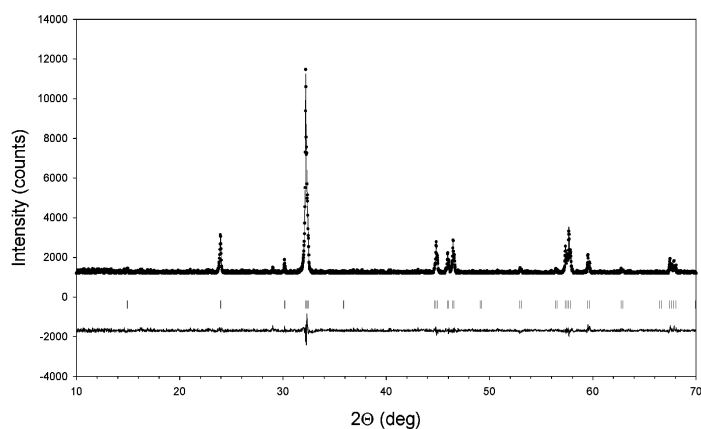


Fig. 3. Results of the Rietveld refinement of the nominally stoichiometric $\text{Gd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\delta}$ sample. Dots — the experimental data, the full line — the Rietveld fit. Below, the peak positions and the differential diagram are shown.

In light of the above result, the Ce doped Gd_2CuO_4 solid solutions reported in [5] seem to have identical structure constitution. As already stated in [1], lack of superconductivity in this material may be a direct consequence of its Cu deficient nature.

Concerning somewhat surprising behaviour of the Gd deficient sample, namely relatively large loss of copper noticed after 272 h exposure to 1100°C (see Fig. 1), its explanation is following. Let us suppose that the components of Gd deficient sample would undergo at 1100°C a full reaction without any visible loss of Cu. If so, then multiplying its nominal formula by a factor $2/1.95$ (to express it in Gd-site full occupancy form), this sample would be composed of two phases, namely $\text{Gd}_{1.846}\text{Ce}_{0.154}\text{Cu}_{1.00}\text{O}_{4+\delta} + 0.0256 \text{CuO}$. It is obvious that $\approx 2.5 \text{ mol.}\%$ content of CuO would not be seen through X-ray diffraction, and the sample would be considered as single phase. Certainly, if certain fraction of copper in this sample would remain as free CuO, then larger loss of its weight would have happened not only because of higher content of the overall copper. Easy to guess why final composition of this sample as well as valence of its Cu, both are so close to that of the stoichiometric one (see Table).

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