

Phase Relations in $\text{Gd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$ System at 980°C . Part I

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Phase equilibria in $\text{Gd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$ system were studied based on samples obtained from appropriate mixtures of the starting components, prepared by a conventional solid state reaction in air. The phase relations prevalent in this system have been deduced based on X-ray diffraction of well-equilibrated samples. An isothermal cross-section diagram through the system at 980°C is presented and chemical constitution of the Ce-doped Gd_2CuO_4 phase is proposed.

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1. Introduction

Although plenty of papers on crystallochemistry and superconductivity of Ce doped Nd_2CuO_4 and Gd_2CuO_4 compounds have been published to date, there are only a few concerning phase relations prevalent in appropriate ternary systems [1–3]. This refers mainly to $\text{Gd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$ system, to date treated only fragmentary [4, 5], perhaps for the reason that, contrary to Ce doped Nd_2CuO_4 compound, the Gd based counterpart does not exhibit superconductivity [6]. Considering the latter problem, several effects are proposed to explain the lack of superconductivity in Ce doped Gd_2CuO_4 . The main are: the orthorhombic distortion of the structure caused of CuO_4 -squares rotation [6], or/and the weak ferromagnetism associated with canting of Cu-ion moments, observed in all the T' 214-type phases with the lattice parameter $a < 3.92 \text{ \AA}$ [7].

The aim of this work was to recognise phase relations in $\text{Gd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$ system, especially the domain of the $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ -type solid solution and its close neighbourhood. With this we expected to get some additional evidences that would help understanding so essential differences in electronic and transport properties of this phase when related to those of Ce doped Nd_2CuO_4 .

2. Experimental

The Gd_2O_3 – CeO_2 – CuO samples were prepared by a conventional solid state reaction of appropriate mixtures of the starting components. The sintering conditions were: 900°C for 3 days, then grinding, compacting to pellets and final annealing at 980°C for 7 days, finished with quenching of the resulting products on a copper plate to room temperature.

Phase relations prevalent in these samples were deduced based on X-ray diffraction, performed in a Dron-3 diffractometer with the use of Fe-filtered $\text{Co } K_\alpha$ radiation.

The oxidation state of Cu-ions in single-phase samples was determined by iodometric titration assuming that Ce^{+4} -ions, present due to the oxidizing sintering conditions applied, act as oxidizers as well while titration.

3. Results and discussion

At the first stage, mutual solubility of pseudo-fluorite Gd_2O_3 ($a/2 \sim 5.406 \text{ \AA}$) and fluorite CeO_2 ($a \sim 5.410 \text{ \AA}$) was defined. Because of a substantial difficulty in precise recognition, by X-ray, of the appropriate solubility terminals, this problem has been solved based on composition dependence of the X-ray peak intensity ratios of $I_{(431)}^{\text{Gd}}/(I_{(440)}^{\text{Gd}} + I_{(220)}^{\text{Ce}})$ -type, collected before and after the synthesis of each subsequent sample. The result obtained (see Fig. 1) indicates that no more than 8 mole% of $\text{GdO}_{1.5}$ dissolves in CeO_2 . Solubility of CeO_2 in $\text{GdO}_{1.5}$ matrix at 980°C is much higher and corresponds to ~ 25 mole%.

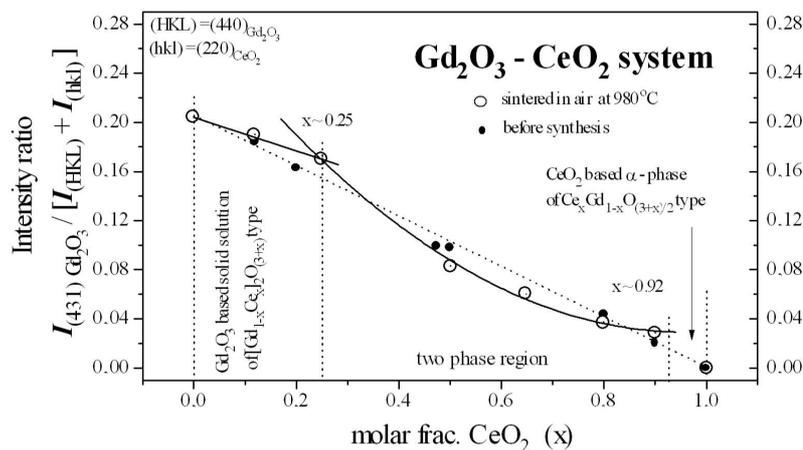


Fig. 1. Composition dependence of the X-ray peak intensity ratios of $I_{(431)}^{\text{Gd}}/(I_{(440)}^{\text{Gd}} + I_{(220)}^{\text{Ce}})$ -type; closed circles — collected before synthesis, open circles — collected after synthesis of each sample.

Concerning solubility of CeO_2 in 214-type binary phase Gd_2CuO_4 we have found it very restricted. At $980^\circ C$, it does not exceed 1.5 mole% (see Fig. 2) and for this reason, a precise determination of the domain of Ce doped Gd_2CuO_4 solid solution has not been possible. Of numerous samples containing Ce, and covering close neighbourhood of Gd_2CuO_4 , only one sample has been found to be a single phase, namely $Gd_{0.657}Ce_{0.014}Cu_{0.328}O_{3.20}$. None sample of the series $Gd_{2-x}Ce_xCuO_4$, i.e. containing 33.33 at.% Cu, has occurred to be a single phase. This means that the domain of Ce doped Gd_2CuO_4 phase is somewhat shifted and probably lies in some more Cu deficient regions of the $Gd_2O_3-CeO_2-CuO$ system.

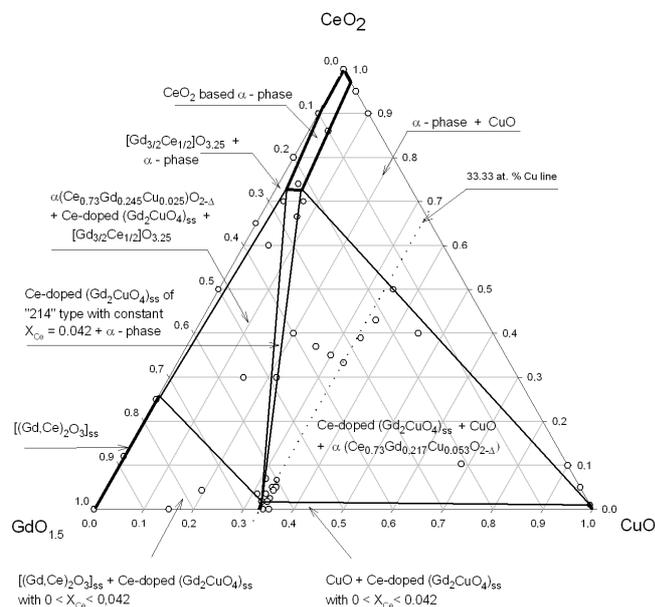


Fig. 2. The $Gd_2O_3-CeO_2-CuO$ system phase diagram at $980^\circ C$. For a better clarity, compositions of only some selected samples (open circles) are shown.

Like in case of Nd-based system [1], above $1000^\circ C$ the domain of Ce doped Gd_2CuO_4 phase expands considerably towards the ternary system. We have confirmed this fact experimentally. However, we have not tried a higher temperature region as the reference for the isothermal cross-section because of a liquid phase (probably CuO) appearing in growing quantities, mainly in a central part of the ternary system. Obviously, on soaking into alumina sample holders (observable in real samples), the liquid phase would unquestionably lead to some serious changes in final composition of these samples, mainly to Cu deficiency, the latter difficult in precise evaluation. Moreover, beginning up from $\sim 1050^\circ C$, a noticeable evaporation has been encountered in all samples of the series $Gd_{2-x}Ce_xCuO_4$, taking place even without a visible melting effect. This fact additionally justified a necessity

to perform the work at somewhat lower temperature. At this point it is sensible to mention that for the reason given above, the experimental data reported in [4] and concerning solubility of CeO_2 in Gd_2CuO_4 at 1100°C , seem not to correspond to the series 33.33 mole% CuO but to a less copper content one.

Coming back to the already mentioned only single phase sample of “214” structure type found in this system, there are two analytical expressions which can reflect a possible distribution of the structure components in this Cu deficient sample. These expressions are: $\text{Gd}_{2-x}\text{Ce}_x\text{Cu}_y\text{O}_4$, with $y = (2 - x)/V_{\text{Cu}}$ and $[\text{Gd}_{2-x}\text{Ce}_x\text{Cu}_y]_{3/(2+y)}\text{O}_4$ with $y = (2 + 3x)/(8 - 3V_{\text{Cu}})$, all valid if to neglect certain excess oxygen (δ), normally present in all Gd based “214”-type samples. Note that both the formulae are identical as for atomic percentage of the structure components. Moreover, provided that $y < 1$, the overall fraction of Cu in both of them appears to be decreased below 33.33 at.%, on behalf of those referred to Gd and Ce.

The distribution models resulting from the formulae given above differ, however, essentially one from the other. While the first formula reflects a deficient occupancy of “214”- type Cu sublattice, the second one represents a free of any deficiency model in which not only Gd-site, but also Cu-site, both exhibit mixed occupancy. Of total Ce content equal to $3x/(2 + y)$ in this model, the fraction $2(1 - y)/(2 + y)$ is subjected for full compensation of appropriate deficiency on Cu-site.

The first indication which of the models considered may occur to be a real one for the “214” structure type samples of given X_{Ce} is the V_{Cu} factor and its behaviour vs. Y_{Cu} . In case of the Cu-deficient model, the V_{Cu} factor should exhibit an increase vs. Y_{Cu} , while in case of the mixed occupancy model, it should show a sharp decrease.

Expressing composition of the sample considered in frame of the Cu deficient model we obtain: $\text{Gd}_{1.9583}\text{Ce}_{0.0417}\text{Cu}_{0.9773}\text{O}_4$ with the factor $V_{\text{Cu}} = \sim 2.004$, while in frame of the free of any deficiency model, we have: $[\text{Gd}_{1.971}\text{Ce}_{0.028}][\text{Cu}_{0.984}\text{Ce}_{0.014}]\text{O}_4$ with the Cu valence $V_{\text{Cu}} = \sim 1.950$.

The average valence of Cu ions experimentally found for this sample via its titration ($V_{\text{Cu}} = 2.04$) indicates on the Cu deficient distribution model rather than on the mixed occupancy one. A little higher V_{Cu} factor obtained (as compared with the calculated one) may indicate the presence of the excess oxygen $\delta \sim 0.02$.

To summarise, no matter which of the models considered is a real one, both sensible explain the reason for the lack of superconductivity in Ce-doped $\text{Gd}_2\text{CuO}_{4+\delta}$ samples. Certainly, the presence of either Cu deficiency, or some Ce^{+4} ions on Cu-site was found. In any case this must lead to a strong weakening of the AF-magnetic interactions between Cu-ions within the Cu–O planes, the interactions which are decisive for superconductivity to appear.

In Part II [8] we present results of more detailed study on the problem of crystallochemical constitution of $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ -type solid solution (signalised

with the preliminary data herein), based on single phase samples of higher Ce content.

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