



# Crystallochemical characterization of Ce/RE substituted phases of T' structure type: Quantitative analysis of Cu valence ( $V$ ) and its content ( $1 - y$ ) in superconducting sample of nominal composition $\text{Nd}_{1.95-x}\text{Ce}_x\text{CuO}_4$ ( $x = 0.15$ )

R. Horyń\*

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2 Okólna Str., 50-420 Wrocław, Poland

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## ABSTRACT

New explanation is given concerning phase separation i.e., consequences of  $\text{Cu}(1 - y)$  deficiency, generally observed in samples of nominal stoichiometry  $\text{RE}_{2-x}\text{Ce}_x\text{CuO}_4$  (RE = lanthanide), reported to happen in T' structure phases during synthesis in air above  $1000^\circ\text{C}$ . Contrary to some literature data, it is assumed herein that phase separation mentioned takes place not during reductive annealing but already during synthesis in air. Accompanying evaporation of Cu, this process leads to RE-site deficient T' skeleton(s). Based on literature available phase equilibria in  $\text{Nd}_2\text{O}_3\text{-CeO}_2\text{-CuO}$  system, plausible structure deficiencies are presented and discussed. It is shown that reductive annealing of so defected T' matrices leads to removal of only tiny amounts of oxygen, the latter resulting from higher than +2 Cu valence and from Cu deficiency factor ( $1 - y$ ). As confirmed on  $\text{Nd}_{1.95-x}\text{Ce}_x\text{CuO}_4$  sample ( $x = 0.15$ ), doping of Cu ions with electrons appears not to be a crucial factor for appearance of superconductivity in T' phase.

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## 1. Introduction

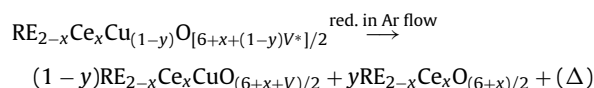
There are several factors which may efficiently disturb precise characterization of Ce/RE substituted  $\text{RE}_2\text{CuO}_4$  type samples, concerning final content of Cu ( $1 - y$ ), its valence ( $V_{\text{Cu}}$ ) and the resulting overall structure oxygen index ( $\sum O$ ). These factors are:

- (1) the experimentally proven loss of Cu [1–6], caused by its volatility taking place during sample synthesis at the temperature range above  $1000^\circ\text{C}$  and
- (2) precisely unknown contribution of Ce structure element to the effective oxidative ability of  $\text{RE}_{2-x}\text{Ce}_x\text{Cu}_{1-y}\text{O}_{[6+x+(1-y)V]/2}$  samples (determined iodometrically), caused by incomplete solubility of this element in diluted (1 N) HCl. The latter becomes evident if to look at the relation which determines the overall oxidative ability of T' structure phase, namely:  $V_{(\text{Cu}+\text{Ce})} = [(1 - y)V_{\text{Cu}} + SxV_{\text{Ce}}]/[(1 - y) + Sx]$ .

No matter the meaning of appropriate terms in the above equation, it is easy to find out quite essential difference in  $V_{(\text{Cu}+\text{Ce})}$  factor of analyzed sample if calculated depending on total insolubility

of Ce ( $S = 0$ ) or its total solubility ( $S = 1$ ). Here, the coefficient ( $S$ ) reflects atomic fraction of nominal  $\text{Ce}_x$  really dissolved in 1 N HCl. It becomes evident that coefficient ( $S$ ) has to be applied while determining exact measure of the  $V_{\text{Cu}}$  factor.

Evaporation of Cu and its effect on crystallochemical nature of Ce/RE substituted  $\text{RE}_2\text{CuO}_4$  samples has been recently discussed in detail in [7]. It is shown therein that deficiency of Cu ( $y$ ) in samples of  $\text{LaPr}_{0.88}\text{Ce}_{0.12}\text{CuO}_4$  stoichiometry, prepared in air at  $T \geq 1000^\circ\text{C}$ , reaches  $\sim 2\text{--}3$  at.%. For this reason, they are not superconducting though being single phased. Superconductivity appears in these samples after their reductive annealing at  $\sim 900^\circ\text{C}$ , consisting of following phase separation reaction;



As seen, the reaction results in repairing the Cu deficiency and leads to restoration of the stoichiometric structure skeleton, the latter being realized through precipitation of appropriate amount of impurity phase  $y\text{RE}_{2-x}\text{Ce}_x\text{O}_{(6+x)/2}$  as epitaxial intergrowths. Here  $\Delta = (1 - y)\text{O}_{(V^*-V)/2}$  and indicates quantity of oxygen expected to be removed to fulfill doping of Cu ions with electrons to the level ( $V = V^* - x$ ). According to [7], this separation process is fully reversible.

\* Tel.: +48 071 3435021; fax: +48 71 3954 222.  
 E-mail address: [R.Horyn@int.pan.wroc.pl](mailto:R.Horyn@int.pan.wroc.pl)

Let suppose that valence of Cu( $V^*$ ) in samples prepared in air is not higher than 2+ (typical value reported in literature is around  $V^* = 2.04\text{--}2.07$ ). Then even so, ( $\Delta$ ) would represent easy measurable quantity namely,  $\Delta = (1 - y)8x$ . Note, that applying the lowest value for  $V^* = 2.04$ , the oxygen reduction caused loss of sample weight is going to reach  $\sim 3$  mg/g of the tested sample, quite high to be easily detected gravimetrically.

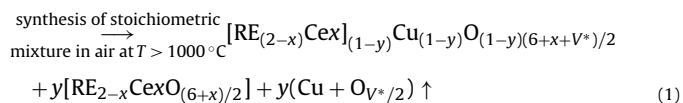
At this point we are facing the enigmatic property of the electron doped T'-type phases, widely reported in numerous literature reports [8,9] i.e., experimentally proven bulk superconductivity, appearing after removal negligible (if not to say immeasurable) quantity of oxygen.

Admittedly, the phase separation process proposed in [7] explains several important problems nevertheless, it stays in a contradiction to the enigmatic property mentioned. The minute quantity of oxygen would be obtainable if negligible doping of Cu ions with electrons is assumed. However, this would mean ( $V \sim 2$ ) and would stay in an evident contradiction to the commonly accepted idea of the electron doping of Cu ions in these materials. Moreover, the mechanism of phase separation proposed in [7] is still incorrect in certain other aspects. The main of them refers to the fact that stoichiometric mixture of  $(2 - x)\text{REO}_{1.5} + x\text{CeO}_2 + \text{CuO}$ , if synthesized in air, is hardly believed to result in Cu deficient  $(1 - y)$  single phase state of the formula  $\text{RE}_{2-x}\text{Ce}_x\text{Cu}_{(1-y)}\text{O}_{[6+x+(1-y)V^*]/2}$ . Such a scenario is possible but under the condition that domain of T' phase in the ternary systems of  $\text{RE}_2\text{O}_3\text{--CeO}_2\text{--CuO}$  type is wide enough to cover, with increasing temperature and Ce content, some Cu deficient compositions.

To our knowledge, there are no literature reports on T' phases exhibiting so deviated domains of homogeneity.

## 2. New approach to the problem of phase separation in T' structure phases

Much more realistic scenario is that Cu evaporation caused phase separation, specified in [7], takes place not upon oxygen reductive annealing but, in fact, already in air. As the result, the secondary phase  $\text{RE}_{2-x}\text{Ce}_x\text{O}_{(6+x)/2}$  appears with the quantity growing up in function of increasing deficiency ( $y$ ). Worth mentioning is that, regarding precipitation of the secondary phase, several of them may appear dependent on the system considered. Simultaneously, the resulting T' structure phase has to undergo a proportional deficiency, namely;



Assuming molar quantities of the starting oxides used being equal to  $(2 - x)\text{REO}_{3/2} + x\text{CeO}_2 + \text{CuO}$ , one can see that molar content of the resulting T' phase remains unchanged, but both of its Me sub-lattices start to exhibit the decreasing content  $(1 - y)$ , caused by evaporation of Cu. Due to this, the excess oxygen in T' phase practically disappears and, in spite of Cu valence  $V^* > 2$ , its stability remains secured. The above becomes evident if to apply;  $(1 - y) = 0.98$ ,  $x = 0.15$  and  $V^* = 2.04$ . Then, oxygen content in T' phase of the air synthesized samples (see reaction (1)) may reach quite a safe value;  $\text{O}_{\text{oxyg.}} = \text{O}_{(1-y)(6+x+V^*)/2} = 4.013$ . The same parameters, if applied to the scheme proposed in [7], give  $\text{O}_{\text{oxyg.}} = \text{O}_{[6+x+(1-y)V^*]/2} = 4.074$ , in our opinion too large for T' structure oxygen sub-lattice to accommodate the resulting excess oxygen.

The hypothesis posed in this paper assumes also that, subsequent annealing in oxygen free environment of the samples prepared in air (so called oxygen reduction), does not change the T' structure deficiency already created. The only effect of this

treatment lies in a steady decrease of the resulting oxygen content to  $\text{O}_{\text{reduc.}} = \text{O}_{(1-y)(6+x+V)/2}$ . However, to prevent so defected structure against its unavoidable destruction and, to induce in it ability to superconduct, the oxygen reduction process should be stopped on the level close to  $\text{O}_{\text{reduc.}} \leq 4$ , which is not an easy task. The latter means decrease of Cu valence value from  $V^* \sim 2.04$  to  $V = 2.00$ , since only  $\text{Cu}^{2+}$  ions (not a mixture of  $\text{Cu}^{2+}$  and  $\text{Cu}^{1+}$  ones) can ensure a satisfactory strong bonding of  $\text{O}^{2-}$  ions within deficient  $\text{CuO}_2$  layers. Note that, as far as stability of T' structure is concerned, these layers are the most crucial ones. Consequently, very small loss of sample weight  $\Delta = 8(1 - y)(V^* - V)$  is expected which, for the case of the air synthesized samples  $\text{Nd}_{2-x}\text{Ce}_x\text{Cu}_{1-y}\text{O}_{[6+x+(1-y)V^*]/2}$  of  $x_{\text{Ce}} = 0.15$  and of molecular weight  $\sim 415$  g, appears not exceeding  $\sim 0.8$  mg/g, i.e., exactly what comes from the literature reports.

Thus we have an explanation to the mentioned already enigmatic property of so called electron doped T'-type phases. Moreover, concerning basic property of these phases i.e., superconductivity, a crucial conclusion arising from the hypothesis posed is – absence of electron doping of Cu ions to the level  $V = (V^* - x)$ . Instead, a specific electronic configuration of T' structure, resulting of the overall structure deficiency created, seems to be the most probable determinant of the property considered.

Finally, the hypothesis posed clarifies also the problem of AF order of Cu ions. Just thanks to the overall deficiency of T' phase skeleton (see Eq. (1)) (not to the stoichiometric one), a suppression of the long-range AF order of these ions can come to true easier. Providing itinerant carriers to appear, this can lead to superconductivity.

Considering the secondary phase(s) which accompanies the T' one during synthesis in air, its quantity may indeed reach a value close to  $y \approx 2\text{--}3$  mol%. Small amount means a high dispersion and, for this reason, X-rays confirmation of its presence at this stage of sample synthesis difficult (if possible at all). This explains sensibly single phase state of the samples prepared in air, reported in [7] and also in Refs. [18–21]. Thanks to the mineralization effect (larger grains), subsequent oxygen content reduction applied to these seemingly single phase samples, may reveal their multi-phase state, however, the state created already during synthesis in air.

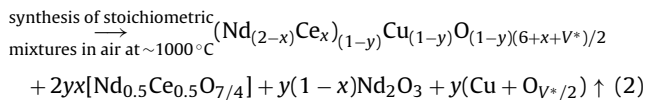
### 2.1. Evaluation of possible T' structure defectiveness based on $\text{Nd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$ system

As mentioned above, the phase separation reflected by the reaction (1) cannot be considered as obligatory one for each ternary system of  $\text{RE}_2\text{O}_3\text{--CeO}_2\text{--CuO}$  type. The lack of literature data concerning phase equilibria diagrams in these systems does not permit for such a generalization. The  $\text{Nd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$  phase diagram published in [10] may serve as a good example. Provided that this diagram is precisely determined, one can notice that this system does not contain solid solution of the C-type sesquioxide i.e.,  $(\text{Nd}_{2-x}\text{Ce}_x)\text{O}_{(6+x)/2}$ .

Consequently, Cu evaporation caused shift of the overall composition of tested samples may locate them within either three-, or one of two-phase fields of coexistence (there are two such fields) namely; into T' +  $\text{Nd}_2\text{O}_3$ , into T' +  $\text{Nd}_2\text{O}_3 + (\text{NdCe})\text{O}_{7/2}$  or to T' +  $(\text{NdCe})\text{O}_{7/2}$ , all depends on the substitution parameter  $\text{Ce}_x$  applied. Here  $(\text{NdCe})\text{O}_{7/2} = 2(\text{Nd}_{0.5}\text{Ce}_{0.5})\text{O}_{7/4}$ , and reflects solid solution of fluorite structure, based on  $\text{CeO}_2$  and containing  $\sim 50$  at.% of Nd component [10].

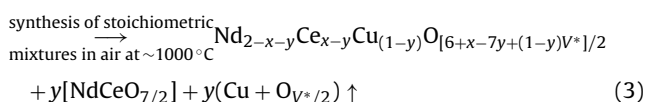
Let us consider in detail phase separation, which would probably take place in 214 type samples of  $\text{Nd}_2\text{O}_3\text{--CeO}_2\text{--CuO}$  system when synthesized in air. Taking into account absence of the C type  $(\text{Nd}_{2-x}\text{Ce}_x)\text{O}_{(6+x)/2}$  solid solution in this system, three scenarios may happened to stoichiometric mixture of appropriate oxides. They are

- (a) location of the overall sample composition within the field of three co-existing phases namely,  $T' + Nd_2O_3 + (Nd_{0.5}Ce_{0.5})O_{7/4}$ . Assuming that the shift is going to proceed along the line of constant Ce/Nd ratio  $= x/(2-x)$ , which begins from CuO corner through the sample analyzed, total quantities of the secondary phases  $(NdCe)O_{7/2}$  and  $Nd_2O_3$  can be determined via proportional splitting of the hypothetical C type solid solution mentioned above i.e.,:



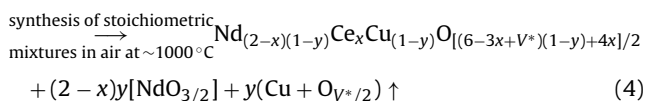
As a result, the sample would become composed of somewhat deficient but still stoichiometric  $T'$  phase of slightly decreased density, which in case of the substitution factor  $(x)=0.15$  and typical loss of Cu  $(y)=0.025$  at/formula, would remain in equilibrium with 0.375 mol% of  $CeO_2$  based fluorite solid solution  $(Nd_{0.5}Ce_{0.5})O_{7/4}$  and with 2.125 mol% of  $Nd_2O_3$ .

- (b) the scenario in which the nominally stoichiometric sample happens to be shifted to the field of two co-existing phases i.e.,  $T'$  and fluorite type solid solution  $(Nd_{0.5}Ce_{0.5})O_{7/4}$ :



Appearance of  $y=0.025$  quantity of  $CeO_2$  based fluorite type solid solution  $(NdCe)O_{7/2}$ , when corrected for its formal formula  $(Nd_{0.5}Ce_{0.5})O_{7/4}$ , gives real contribution of this secondary phase two times larger (5 mol%) than that resulting from the reaction (3). Then, occupancy of Nd sub-lattice in  $T'$  phase would appear to be decreased by equal quantities ( $y$ ) of Nd and Ce, altogether also by 5 mol%.

- (c) the scenario in which the nominally stoichiometric sample happens to be shifted to the field of another two co-existing phases i.e.,  $T' + Nd_2O_3$



According to this scenario, Nd content in  $T'$  phase would exhibit 2.5 mol% deficiency in relation to the nominal one, with preservation of Ce content on the nominal level ( $x$ ).

Considering oxygen reduction performed in an inert atmosphere at  $\sim 900^\circ\text{C}$  it is necessary to point out that, no matter which scheme of the phase separation presented above would be practically realized, this procedure should lead to identical loss of sample weight equal to  $\Delta_{\text{oxyg.}} = 8(1-y)(V^* - V)$  per molecular weight of  $T'$  phase.

To satisfy already mentioned experimental evidence concerning tiny amount of oxygen, removable from  $T'$  phases during oxygen reduction, this means very small difference between Cu valence factors  $(V^* - V)$ .

Consequently, if the hypothesis posed is correct then superconductivity, eventually detected in oxygen reduced samples, would not be induced due to appropriate doping of Cu ions with electrons to the level  $V_{Cu} = (V^* - x_{Ce})$  but, as already expressed in Section 2, thanks to a specific electronic structure of  $T'$  defected skeleton. Here we have in mind deficient occupancy of its all sub-lattices with the oxygen sub-lattice inclusively, created during both; synthesis in air at  $\sim 1050^\circ\text{C}$ , as well as after reductive annealing at  $900^\circ\text{C}$ . Note that a secondary importance of the electron doping of Cu ions within the systems under discussion is also expressed in [11–13].

## 2.2. Final remarks concerning the hypothesis posed

Exact indication which of the phase separation scenarios considered above takes place in real samples is impossible to be done in advance because, depending on the Cu deficiency factor  $(1-y)$  created, and on the Ce substitution parameter ( $x$ ) applied, each of them has a chance to appear in given system. That is why quantitative analytical methods such as sample hydrogen reduction and its re-oxidation at  $\sim 850^\circ\text{C}$  as well as iodometric titration, have to be performed to determine not only the  $(1-y)$  factor but also the overall oxidative ability ( $V_{Cu+Ce}$ ) of  $T'$  phase. However, due to the multi-phase state of the products resulting from the synthesis in air, application of the methods mentioned is highly complicated. This refers mainly to the main parameters i.e., to final Cu valence factor ( $V$ ), and to real Ce content ( $x$ ) in  $T'$  phase, both resulting from iodometric titration. Note that, with exception of the scheme of phase separation presented in (c) which predicts  $Nd_2O_3$  as the only secondary phase, those expected via the (a) and (b) type separations contain Ce. So, titration of such samples cannot give a precise measure of the Cu valence value ( $V$ ) in  $T'$  phase, unless assuming total insolubility of Ce, no matter which phase(s) Ce is located in. However, as indicated below (Section 3), such an assumption is completely wrong. It occurs that, even if total  $Ce_x$  remains bonded within  $T'$  structure (as in the scenario (c)), its partial solubility in non-oxidative acid such as HCl is unquestionable. That is why, appropriate correction should be applied.

A general conclusion that comes from the phase separation scenarios presented above is that, a precise characterization of the variable parameters of  $T'$  phase considered encounters serious difficulty, mainly caused by the secondary phase(s) precipitation. In this respect, the best situation would be dealing with samples composed of single  $T'$  phase.

Such a possibility exists and seems to stay in setting up nominal composition of samples (those subjected for synthesis in air) already off-stoichiometric i.e., charged with the Nd sub-lattice deficiency (generally RE sub-lattice) expected. Similar approach has already been successfully tested in our previous paper [14], discussed in detail below.

## 3. Experimental

### 3.1. Contribution of Ce to oxidative ability of $T'$ structure $Nd_{2-x}Ce_xCuO_4$ samples

We faced the Ce contribution problem when trying to dissolve much larger quantities of such-samples (about 100 mg), subjected for titration to evaluate valence of Cu ions. Note that in this respect, typical quantities reported in numerous papers are 3–5 times smaller.

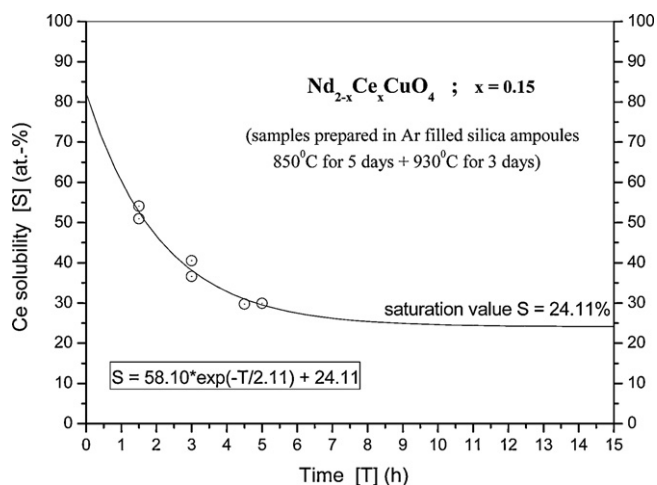
As the result, a pale-yellow deposit could be detected, finally proved by X-ray analysis to be  $CeO_2$ . Moreover, when trying to determine if  $CeO_2$  deposit appears because of its less significant solubility in HCl (compared to the remaining structure components), appropriate time dependence was recorded (see Fig. 1).

The procedure consisted of application of an adequately longer time passing between dissolution of given portion of analyzed sample and of its subsequent iodometric titration. Thanks to non oxidative sintering conditions applied, the ( $S$ ) values presented in Fig. 1 were collected under the assumption that valence of Cu and its content in the sample tested were invariable vs. time, having nominal values  $V=2$  and  $(1-y)=1$ . Note that, even if the above assumption was not precise enough, a very important fact emerges from Fig. 1 that, solubility of  $CeO_2$  never reaches 100% and that, instead of an increase expected with time, it shows a steady decrease, up to a saturation level close to  $\sim 24$  at.% (0.24 fraction of nominal  $Ce_x$ ).

The only explanation for the decrease noticed is hydrolysis of  $Ce^{4+}$  ions to  $CeO_2$  via some oxy-chlorides or hydroxyl-oxides and means necessity of taking into account, variable with time, contribution of  $Ce^{4+}$  ions ( $S_{x_{Ce}}$ ) towards  $I^1$  ions, to be applied in Eq. (1) to reflect the overall oxidative ability ( $V_{Cu+Ce}$ ) of  $Nd_{2-x}Ce_xCuO_4$  type samples.

Easy to imagine that, by neglecting real contribution of  $Ce_x$  in oxidation of  $I^1$  to  $I^0$  performed iodometrically, and of eventual deviation of the sample Cu content  $(1-y)$  from its nominal value, a serious error concerning Cu valence factor ( $V_{Cu}$ ) may arise.

Another problem which may essentially complicate precise characterization of the  $T'$  type samples refers to the effect of phase separation discussed in Sections 1 and 2.



**Fig. 1.** The time dependent decrease of  $\text{CeO}_2$  solubility, resulting from hydrolysis of  $\text{Ce}^{4+}$  ions after dissolution of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  sample in 1 N HCl.

No matter at which step of sample preparation this effect takes place (either during reductive annealing in oxygen free environment [7] or, as postulated in this paper, already during synthesis in air), the multi-phase state of these samples, may create undesired distribution of the nominal Ce content ( $x$ ) among the secondary phases. This, in turn, may make estimation of Cu valence factor ( $V_{\text{Cu}}$ ) in deficient major T' phase, erroneously determined.

To avoid such a possibility, the scheme of phase separation presented in Eq. (4) of Section 2.1 as (c) was tried as the simplest one in analytical characterization. First of all, this scenario ensures no redistribution of Ce among any secondary phase(s). Secondly, the only secondary phase expected of this scheme is  $\text{Nd}_2\text{O}_3$ . Then, in order to get rid of eventual precipitation of  $\text{Nd}_2\text{O}_3$ , nominal composition of the starting sample was, in advance, set up to be Nd deficient, equal to  $(2-x)(1-y)$ . Assuming Cu evaporation factor  $y \sim 2.5$  at.%, and the Ce substitution parameter  $x = 0.15$ , the deficiency applied was fixed as  $\sim 0.05$  mol.%  $\text{NdO}_{1.5}$ . Consequently, a mixture composed of  $0.9\text{Nd}_2\text{O}_3 + 0.15\text{CeO}_2 + \text{CuO}$  was used for synthesis in air, in a hope to result as single T' phase of the formula  $\text{Nd}_{1.80}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{O}_{[6+(1-y)V^*]}/2$ . Subsequent oxygen reductive annealing of this sample was expected to induce nothing else but a slight decrease of its oxygen index, thus resulting in sample of the composition  $\text{Nd}_{1.80}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{O}_{[6+(1-y)V]}/2$ , may be superconducting. Once again we remind that ( $V^*$ ) and ( $V$ ) factors mean valence of Cu ions in T' phase, before and after the reductive annealing, respectively.

By the way, there are several reports in literature [1,2,15–17] which indicate that the best superconducting parameters are observable in samples whose nominal compositions are slightly enriched in Cu (this means RE-site deficient).

### 3.2. The details of sample preparation and the methods of its analysis

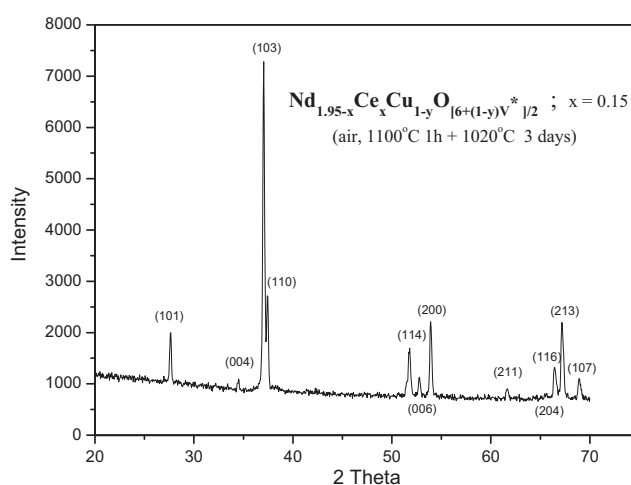
The sample specified above, of  $\sim 4$  g in weight, has been prepared by solid state reaction of appropriate quantities of  $\text{Nd}_2\text{O}_3$ ,  $\text{CeO}_2$  and  $\text{CuO}$  oxides, preheated overnight at  $900^\circ\text{C}$ . The synthesis was performed in air and consisted of calcinations at  $950^\circ\text{C}$  for 3 days, re-grinding and pelletizing, then sintering at  $1050$ – $1100^\circ\text{C}$  for 1 h, repetition of the re-grinding and pelletizing, and final sintering at  $1020^\circ\text{C}$  for another 3 days.

The resulting product (see Fig. 2), analyzed by X-ray diffraction (DRON-3 diffractometer with Fe filtered  $\text{Co K}\alpha$  radiation), confirmed its single phase state.

The dc-magnetic susceptibility data of this sample, collected with the use of the Quantum Design MPMS-5 (see Fig. 3), proved typical, although very weak (cf. the scales of Figs. 3 and 5) paramagnetic behavior of the sample. This agrees with the explanation given in Section 2 concerning suppression of AF ordering of Cu ions which, according to the hypothesis posed, has to have a higher probability to appear in T' deficient skeleton (already after synthesis in air) than in a stoichiometric one, as suggested in [7].

Then, the sample was subjected for reduction of its overall oxygen index by applying a stream of 3 N Ar at  $900^\circ\text{C}$ . The reductive annealing was repeated several times until the appropriate temperature dependencies of dc-magnetic susceptibility showed significant (bulk) transitions to superconducting state. Final characterization of the sample consisted of

- X-ray diffraction, to determine lattice parameters (DRON-3 diffractometer with Fe filtered  $\text{Co K}\alpha$  radiation) and with DHN-PDS program for lattice dimensions refinement,
- iodometric titration, to find out effective oxidation ability and, consequently, Cu valence factor ( $V$ ), properly corrected for time dependent solubility of Ce ions. For this reason, the sample was dissolved in 1 N HCl and, after  $\sim 15$  h counting



**Fig. 2.** X-ray diagram of sample;  $\text{Nd}_{1.95-x}\text{Ce}_x\text{Cu}_{1-y}\text{O}_{[6+(1-y)V^*]}/2$ , resulting of its synthesis in air at  $1100^\circ\text{C}$  for 1 h +  $1020^\circ\text{C}$  for 3 days.

from its dissolution up to application of KI, subjected for titration. As it comes from Fig. 1, 15 h was necessary to reach the saturated solubility of Ce,

- gravimetry, consisting of total reduction of the sample oxygen index using a stream of  $\text{H}_2$  at  $750^\circ\text{C}$ , and then of its recovery by oxidation the post reduction residue in air at  $850^\circ\text{C}$ . The hydrogen reduction and the re-oxidation of the resulting product were made to determine the excess oxygen  $(1-y)\text{O}_{(V^*-V)}/2$  removed. Precisely, to evaluate quantity of oxygen  $(1-y)\text{O}_{V/2}$  present in the structure which exhibits superconductivity and the oxygen  $(1-y)\text{O}_{V^*/2}$ , present in it before reductive annealing.

### 3.3. The analytical expressions used

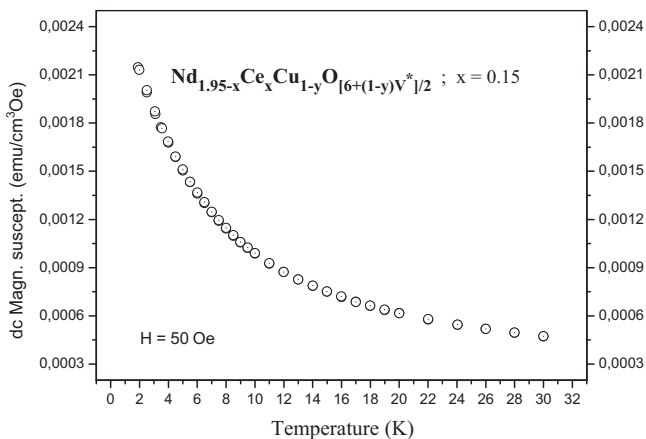
#### 3.3.1. Iodometry

The analytical formula resulting from iodometric titration of the final preparation product of the composition  $\text{Nd}_{1.95-x}\text{Ce}_x\text{Cu}_{1-y}\text{O}_{[6+(1-y)V]}/2$ , recalculated for the valence of Cu ions ( $V$ ), looks as follows;

$$V = \frac{[M + (1-y)\text{Cu}]N\nu + m^\#[(1-y) - xS]}{(1-y)(m^\# - 8N\nu)} \quad (5)$$

The appropriate symbols in the above equation mean  $M = \text{Nd}_{1.95-x}\text{Ce}_x\text{O}_3$  (equal to 328.65) i.e., the weight of invariable term free of  $(1-y)\text{CuO}_{V/2}$  factor, separated from the sample molecular formula of the particular ( $x$ ) then,  $(1-y)$  = real atomic content of Cu (variable during sample synthesis), Cu is the atomic weight of copper,  $V$  is the final valence of Cu,  $m^\#$  is the sample mass used for titration,  $xS$  is the contribution of  $\text{Ce}^{4+}$  ions in oxidation of  $\text{I}^-$  to iodine (available from Fig. 1),  $N$  is the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  (here  $\sim 0.01$  mol/l, standardized against  $\text{K}_2\text{Cr}_2\text{O}_7$ ), and  $\nu$  = volume of  $\text{Na}_2\text{S}_2\text{O}_3$  (in liters), used to reduce  $\text{I}^0$  back to  $\text{I}^-$ .

As already mentioned above, in order to minimize an error in estimation of the ( $S$ ) factor, iodometric titration was performed after  $\sim 15$  h from dissolution of the sample in 1 N HCl i.e., applying its saturated value  $S = 0.24$  (in Fig. 1; 24.0 at.%).



**Fig. 3.** The dc-magnetic susceptibility data for  $\text{Nd}_{1.95-x}\text{Ce}_x\text{Cu}_{1-y}\text{O}_{[6+(1-y)V^*]}/2$  sample, resulting of its synthesis in air at  $1100^\circ\text{C}$  for 1 h +  $1020^\circ\text{C}$  for 3 days.

To simplify Eq. (5), following terms (all available from the iodometry), were applied to it, namely;  $A = (NvM - m^{\#}xS)$ ,  $B = (m^{\#} + NvCu)$ , and  $C = (m^{\#} - 8Nv)$ . Thanks to this, the analytical expression for the Cu valence factor ( $V$ ) becomes dependent on Cu deficiency factor ( $1 - y$ ) only namely;

$$V = \frac{A}{C(1-y)} + \frac{B}{C} \quad (6)$$

### 3.3.2. Reduction with $H_2$

The analytical expression resulting from hydrogen reduction of the sample considered, recalculated for the Cu content ( $1 - y$ ), looks as follows;

$$(1 - y) = \frac{M(m' - m'')}{8Vm'' - Cu(m' - m'')} \quad (7)$$

Here,  $m'$  and  $m''$  correspond to weights of the sample specimen used for reduction, and that resulting after reduction, respectively. The symbols Cu,  $V$  and  $M$  are having the same meanings as those used in Eq. (5).

Inserting for the parameter  $(1 - y)$  of Eq. (6) its value which stays in Eq. (7), permits to determine the effective valence of Cu ions ( $V$ ) and, consequently, the remaining independent variable i.e., the real Cu content ( $1 - y$ );

$$V = \frac{(m' - m'')[MB - ACu]}{(m' - m'')MC - 8Am''} \quad (8)$$

As mentioned, re-oxidation of the hydrogen reduced sample  $Nd_{1.95-x}Ce_xCu_{1-y}O_{6+(1-y)V/2}$  (probably consisting of appropriate mixture of  $Nd_2O_3$  and  $(CeNd)O_{7/2}$  oxides + free Cu), permits to recover its state resulting from the synthesis in air i.e.,  $Nd_{1.95-x}Ce_xCu_{1-y}O_{6+(1-y)V^*/2}$  and to determine the Cu valence factor ( $V^*$ ). The simplest way to do it leads through already defined Cu deficiency factor ( $1 - y$ ) (see Eq. (7)). The appropriate final formula looks following;

$$V^* = V \frac{m - m''}{m' - m''} \quad (9)$$

in which, the term ( $m$ ) means sample weight resulting of the re-oxidation in air at  $850^\circ C$  applied to the specimen  $m''$  i.e., to the residue obtained from hydrogen reduction of the starting  $m'$  specimen.

## 4. Results and discussion

X-ray diffraction pattern of the sample, resulting after its reductive annealing at  $900^\circ C$  with the use of Ar flow, is presented in Fig. 4.

The diagram is satisfactory clean and confirms presence of  $T'$  type phase only. Lattice parameters of this phase are:  $a = 3.9472 \text{ \AA}$ ,  $b = 3.9472 \text{ \AA}$ ,  $c = 12.0793 \text{ \AA}$ . The values obtained agree very well with those reported in [18] for sample of the  $x = 0.15$ . Standard deviations of the parameters obtained are:  $\Delta a = 0.0004 \text{ \AA}$ ,  $\Delta c = 0.0014 \text{ \AA}$  and  $\Delta 2\theta = 0.0012^\circ$ .

Results of dc-magnetic susceptibility measurements of this samples are presented in Fig. 5. As seen, the volume fraction of superconducting phase in this sample is high enough to consider it as superconducting in bulk. More precisely, it stays within the

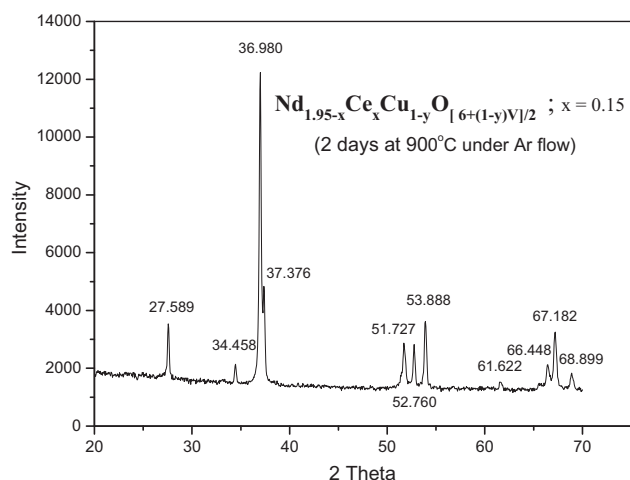


Fig. 4. X-ray diagram of  $Nd_{1.95-x}Ce_xCu_{1-y}O_{[6+(1-y)V]/2}$  sample, after reduction of its oxygen content using Ar flow at  $900^\circ C$  for 2 days.

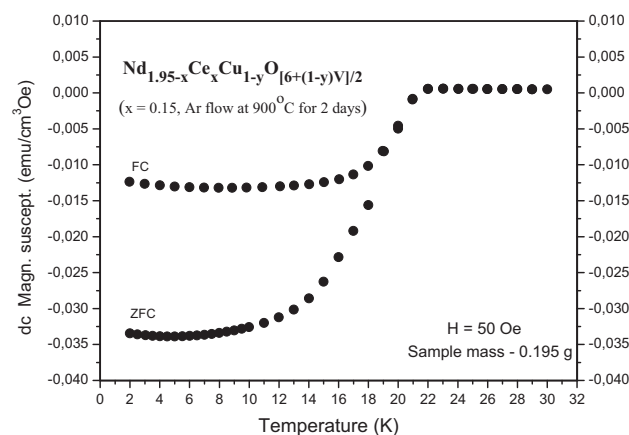
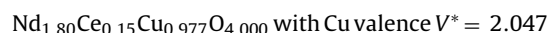


Fig. 5. The dc-magnetic susceptibility data for  $Nd_{1.95-x}Ce_xCu_{1-y}O_{[6+(1-y)V]/2}$  sample, resulting after subjecting it to oxygen reduction in Ar flow at  $900^\circ C$  for 2 days.

range of 20–40% as deduced based on (FC) and (ZFC) data, respectively, consistent with numerous reports, even those quite recently published [19]. Appropriate values found for all the remaining parameters considered in Eqs. (5)–(9) for the sample analyzed are given in Table 1.

Worth mentioning are the parameters  $V^*$ ,  $V$  and  $(1 - y)$ , whose values fully confirm sensibility of the modification applied to the (c) type scenario of phase separation. The results presented in Table 1 allow to describe formulae of the sample analyzed, before and after its reductive annealing under Ar flow. They are:

After synthesis in air :



After the reductive annealing :



We remind that nominal Nd-site deficiency of this sample was ( $Nd_{1.95}$ ) and, as earlier stated, this deficiency was applied tentatively in a view to avoid precipitation of  $Nd_2O_3$ , expected in the (c) type scenario of phase separation discussed in Section 3.1. Eventual incorrectness resulting of this fact and of its effect on final values of the parameters determined, is bound to be much smaller (if not to say none) in comparison to that which would result in case of no correction applied. That is why, we can state that, superconductivity observed in  $T'$  phase of the sample considered, defected according to the modified scheme (c), cannot be explained as induced by appropriate doping of Cu ions with electrons. It

Table 1

Results of chemical analysis of Nd deficient sample of the composition;  $Nd_{1.95-x}Ce_xCu_{1-y}O_{[6+(1-y)V]/2}$ ,  $x = 0.15$ , resulting of oxygen content reduction (Ar flow at  $900^\circ C$  for 2 days).

Analytical methods	Parameters		
	Considered	Determined	Available
Iodometry	$\nu$	0.02330	
	$m^{\#}$	0.10116	
	$A$	0.0789335	$M = 328.65$
	$B$	0.1171263	$S = 24 \text{ at.}\%$
	$C$	0.0991500	$x = 0.15$
	$V$	2.00	$N = 0.01083$
	$(1 - y)$	0.977	
	$V^*$	2.047	
	Hydrogen reduction and re-oxidation	$m'$	1.14650
	$m''$	1.10238	
	$m$	1.14753	

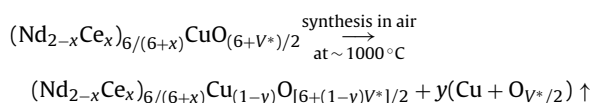
means that doping of Cu ions is practically absent in this phase and confirms our conviction expressed earlier that, geometrical factors such as length of Nd–O and/or Cu–O bonds, as well as their specific nature (covalent/ionic character), resulting of the specific Nd-site, Cu-site and O-site deficiencies, seem to be the most essential ones.

#### 4.1. A supplementary note concerning the (a)–(c) phase separation schemes

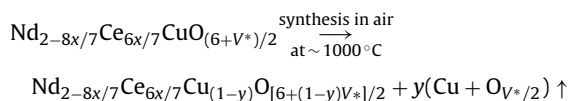
Comparing the results obtained in our previous paper [14] with the presented herein, a supposition emphasized in [14] on quite different nature of RE<sub>2–x</sub>Ce<sub>x</sub> type substitution that may really proceed in these systems, becomes more convicting. Note, that when realized under the oxidizing sintering conditions, this type of substitution cannot induce appropriate decrease of Cu valence state, all due to instability of Cu<sup>1+</sup> ions in oxygen environment. So, according to [14], Ce/RE substitution is probably realized through an exchange of the equal number of electrons between RE and Ce, instead of equal atomic fractions of these elements. Thanks to this, RE sub-lattice becomes charged with no more than 6 holes, and for full stability of the T' structure, i.e., for its oxygen index free of any excess oxygen, another two holes are necessary. These two holes are offered by Cu ions, in spite of (1–y) deficient occupancy of this element caused by evaporation. The above condition becomes satisfactory fulfilled, since according to numerous literature reports, valence of Cu in air synthesized samples (V\*) is indeed higher than 2+. Hence, two necessary holes resulting from (1–y)V\* = 2.

Consequently, in order to avoid precipitation of any secondary phase(s), the (a)–(c) scenarios of phase separation discussed in Section 2.1, if modified according to the idea specified above, should lead to more reliable results. Precisely, nominal compositions of samples before their synthesis in air should be charged with the following deficiency in Nd sub-lattice;

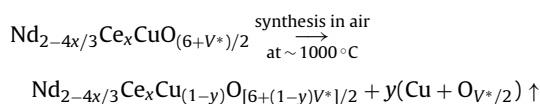
(a\*) by applying the coefficient 6/(6+x) to the (Nd<sub>2–x</sub>Ce<sub>x</sub>) term, instead of (1–y) as in (a);



(b\*) by extracting (x/7) fraction of Nd and Ce from the terms (2–x) and (x) of the (b) scheme, respectively;



(c\*) by extracting x/3 fraction of Nd instead of (2–x)y as in (c), leaving Ce content (x) intact;



Easy to find out that, no matter what kind of site deficiency is a priority created in Nd sub-lattice, its charge is always equal to 6 holes and does not depend on Cu evaporation factor (y). However, to set up this factor on the proper level, the deficiency of Cu cannot exceed the range of 0.020 < y < 0.025. This means 2.04 < V\* < 2.05 and stays in an agreement with the experiment. Numerous tests, reported till now in literature indicate that, for samples of the substitution parameter x = 0.15, the interval given above is the optimal one, though not easy to achieve. The oxygen reduction treatment applied to such samples usually appears to result with high volume fraction of superconducting T' phase.

Higher (y) factors may evoke a steady destruction of this skeleton, due to too deep deficiency in O-sublattice. On the other hand, lower (y) factors may lead to insufficient deficiency in this sublattice. Consequently, both the cases mentioned may result in either a substantially decreased volume fraction of superconducting phase or, in no superconductivity at all.

A satisfactory results obtained in this paper, concerning crystallochemical state of the nominally Nd site deficiency (1.95–x) sample i.e., its single phase T' structure, the final Cu content (1–y) = 0.977, the valence factor V = +2 and the slight deficiency in oxygen sub-lattice (3.977), all these data are promising enough to undertake appropriate tests on reality of the remaining scenarios predicted in this paper i.e., (a\*) and (b\*), based on samples of the substitution parameter (x) different than 0.15.

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