GROWTH AND PROPERTIES OF $M_{2-x}Ce_xCuO_{4+d}$ SINGLE CRYSTALS *

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1. INTRODUCTION

The recent discovery of the new electron superconductivity in doped cuprates of general formula $M_{2-x}Ce_xCuO_{4+d}$ (where M is a rare earth ion like Nd, Pr etc.) by Tokura et al. [1] contributes to understanding the mechanism of high T_c–superconductivity. The Nd_2CuO_4 phase melts inconguently at about 1240 ° C and a liquidus line below this temperature lies in a composition range between 82 and 93 mol% CuO according to the phase diagram of the $Nd_2O_3 - CuO$ system determined from DTA and X–ray phase analysis byu Oka and Unoki [2]. From DTA measurements of other M_2CuO_4 (M = Sm, Eu and Gd) compounds performed by the same authors and from the comparison of the phase diagrams of $Nd_2O_3 - CuO$ and $La_2O_3 - CuO$ system reported earlier [3] it follows that the width of the liquidus line increases with increasing ionic radius of the M atom. Oka and Unoki [2] have also prepared crystals of $(NdCe)_2CuO_4$ in accordance with the phase diagram of the $Nd_2O_3 - CuO$ system using the flux method and/or the travelling–solvent floating–zone method. The crystals grown by the use of slow–cooling method (15 K/h) in a platinum crucible had dimensions of 2mm x 2mm x 0.5mm. In contrast, a crystal with the dimensions of 6mm in diameter and 22mm in length and 3.7g in weight was obtained using the second method in an infrared–radiation–convergence–type furnace. Growth of platelet like crystals of n–type phase $Nd_{2-x}Ce_xCuO_{4+d}$ with x ranging from 0 to 0.12 using flux technique in the platinum crucibles and with x from 0.12 to 0.18 in the alumina crucibles was reported by Tarascon [4],[5].

2. PREPARATION

The $M_{2-x}Ce_xCuO_{4+d}$ crystals were prepared by modified flux method using the following procedures:

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a) CuO, CeO_2 and calcinated M_2O_3 powders having 99.99% purity or better were mixed in the molar ratios 90.01: 1.78: 8.21 mol%. Charges of about 40g were placed into high purity Al_2O_3 crucibles and premelted in air in a muffle furnace at 1150° for 6 hours; then the temperature was decreased at a rate of 2.5°C per hour to 950°C.

Crystals of the compounds $M_{2-x}Ce_xCuO_{4+d}$ were found into cavities of the melt only at a rather well defined distance from the top surface (3 : 6 mm): these crystals show thin platelet shape and maximum dimensions are 2 x 2 x 0.005 mm. The size of the crystal is typically decreasing with the increase of the mass of the M ion.

b) The same reagents were mixed at the ratios 82.31:2.47:15.22 mol%. Charges of about 50 g were pre–melted in air at 1250°C into a Pt crucible. The temperature was lowered at a rate of 2°C/Hour to 1050°C. At this temperature the upper part of the melt (approximately 30% in weight) was still liquid and could be poured out of the crucible: platelet–like crystals of $M_{2-x}Ce_xCuO_{4+d}$ were found after passing the liquid through porous Al_2O_3. The rest of the melt contained much larger and thicker crystals which could be extracted by dissolving the melt with diluted HNO_3. The typical dimensions of these crystals were 1 x 1 x 0.1 mm and a few individuals exceeded 3 x 3 x 0.2 mm. The acid attack texturizes the surfaces parallel to the c axis.

3. SEM INVESTIGATION

SEM inspection and EDAX microanalysis of the $M_{2-x}Ce_xCuO_{4+d}$ crystals showed some interesting features:

a) Crystals from the same batch but different positions in the crucible have different values of x. The range within which x varied turned out to be dependent upon the nature of the ion M as it is reported in the following Table:

Table I

	x_{min}	x_{max}
$Nd-Ce$	0.08	0.16
$Sm-Ce$	0.04	0.13
$Eu-Ce$	0.01	0.10

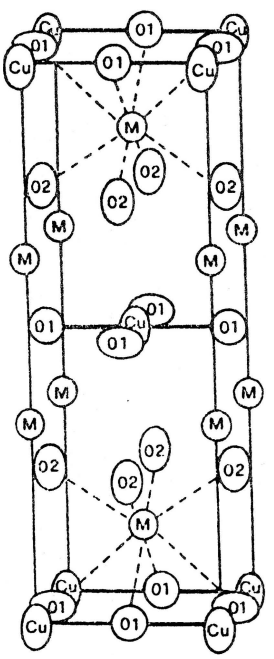
b) The surface of some crystals revealed dendrite–like inhomogeneities detectable only by secondary electron emission.

According to the intensity of the e^- beam the contrast is reversed, erased or just smoothed. The two phases can be characterized by $Nd : Ce$ ratio fluctuations or to oxygen stoichiometry fluctuations; the erasing effect in vacuum suggests the latter cause to be more probable. It is extremely interesting, however, that in both cases the system admits two distinct phases rather than smooth fluctuations.

4. STRUCTURAL DATA

X–ray data were collected on a CAD4 single crystal diffractometer using MoKα radiation. A total of 278 independent reflections having $I > 3\sigma$ were used in the calculations for each structure. The final anisotropic refinement resulted in a R index equal or better than 0.05 for 12 independent parameters. The relative occupancies of the M and Ce ions at the same site were derived from EDAX measurements on the same crystals used for the diffraction experiment.

The resulting structure, cell parameters, bond lengths and atomic distances are given in Fig. 1 and Tables II and III.



Unit cell
(ORTEP drawing)

M = Nd, Ce

a = 3.9479(3) Å
c = 12.039(1)

M = Sm, Ce

a = 3.9219(3) Å
c = 11.8885(7)

M Eu, Ce

a = 3.9169(5) Å
c = 11.897(2)

Fig. 1

Crystal structure and cell parameters of $M_{2-x}Ce_xCuO_4$ ($M = Nd, Sm, Eu$)

Table II

Bond Distances (Å) with Esd's in parentheses

	$M = Nd, Ce$	$M = Sm, Ce$
$M - 0(1)$	2.6522(4)	2.6338(4)
$M - 0(2)$	2.3302(3)	2.3062(3)
$Cu - 0(1)$	1.9739	1.9609(3)
$Cu - 0(2)$	3.5993(3)	3.5607(3)

Table III

Table of positional parameters and their estimated standard deviations

$Nd1.85Ce0.15Cu04$

Atom	x	y	z	B(A2)
Nd	0.000	0.000	0.35286(5)	0.444(4)
Ce	0.000	0.000	0.353	0.4
Cu	0.000	0.000	0.000	0.52(2)
0(1)	0.000	0.500	0.000	0.9(1)
0(2)	0.000	0.500	0.250	0.66(7)

$Sm1.85Ce0.15Cu04$

Atom	x	y	z	B(A2)
Sm	0.000	0.000	0.35210(5)	0.357(4)
Ce	0.000	0.000	0.353	0.4
Cu	0.000	0.000	0.000	0.43(2)
0(1)	0.000	0.500	0.000	1.1(2)
0(2)	0.000	0.500	0.250	0.48(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a2 * B(1,1) + b2 * B(2,2) + c2 * B(3,3) + ab(cos\ gamma a) * B(1,2) + ac(cos\ beta a) * B(1,3) + bc(cos\alpha) * B(2,3)]$

5. ELECTRICAL MEASUREMENTS

Four probe electrical resistivity measurements were performed on a number of crystals of suitable size of $Nd_{2-x}Ce_xCuO_{4+d}$ and $Sm_{2-x}Ce_xCuO_{4+d}$ (the Eu–based crystals being always too small). Gold wire contacts were attached on the a–b plane surface using silver paint and cured for 5 min at 400°C in flowing O_2. This method provides a low and stable contact resistance but it is not clear if it may affect significantly the oxydation state at the surface of the crystals.

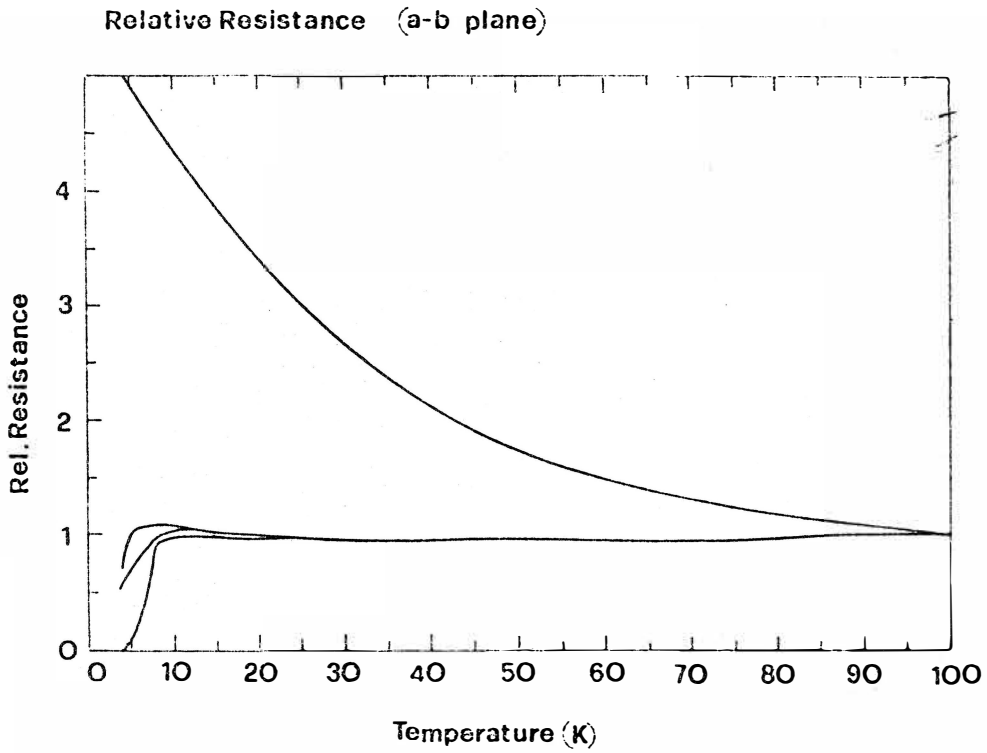


Fig. 2

Relative resistance $R(T)/R$ (look) of four crystals of $Nd_{2-x}Ce_xCuO_4$ (a – b–plane values)

Among all the measured crystals, metallic behaviour and superconductivity above 4.2K was detected only when $M = Nd$; in all cases the onset of T_c was below 10K and the zero resistance state was never achieved above 4.2K (Fig. 2). The different nature of the conduction of crystals grown in the same batch is again testifying the crucial effect of the oxygen content and the $M : Ce$ stoichiometry; the starting inhomogeneity of the samples masked the effect of heat treatments in Ar atmosphere which had proved to be effective in the optimization of the superconducting properties of the corresponding policrystalline compounds. Fig.3 reveals a strong anisotropic behaviour of the electrical conductivity.

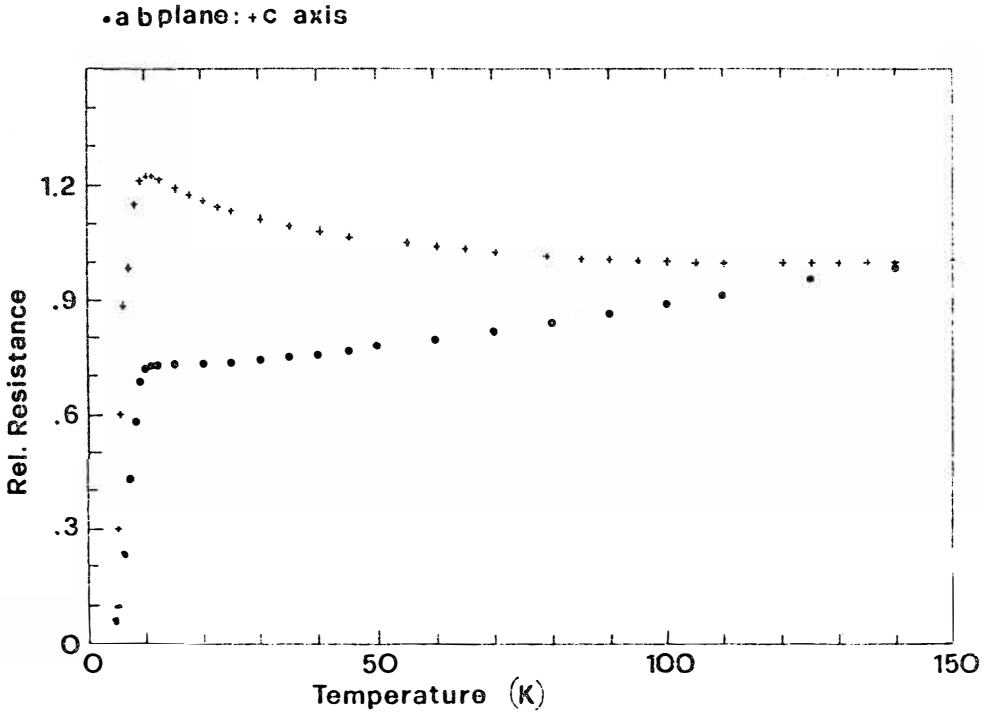


Fig. 3

Relative resistance $R(T)/R(150\,K)$ on the same $Nd_{2-x}Ce_xCuO_4$ crystal: $a-b$–plane; $+c$–axis

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