

Structural characterization of gel-grown neodymium copper oxalate single crystals

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Abstract. Sparingly soluble neodymium copper oxalate (NCO) single crystals were grown by gel method, by the diffusion of a mixture of neodymium nitrate and cupric nitrate into the set gel containing oxalic acid. Tabular crystal, revealing well-defined dissolution figures has been recorded. X-ray diffraction studies of the powdered sample reveal that NCO is crystalline. Infrared absorption spectrum confirmed the formation of oxalato complex with water of crystallization, while energy dispersive X-ray analysis established the presence of neodymium dominant over copper in the sample. X-ray photoelectron spectroscopic studies established the presence of Nd and Cu in oxide states besides $(C_2O_4)^{2-}$ oxalate group. The intensities of Nd ($3d_{5/2}$) and Cu ($2p_{3/2}$) peaks measured in terms of maximum photoelectron count rates also revealed the presence of Nd in predominance. The inductively coupled plasma analysis supports the EDAX and XPS data by the estimation of neodymium percentage by weight to that of copper present in the NCO sample. On the basis of these findings, an empirical structure for NCO has been proposed. The implications are discussed.

Keywords. Neodymium copper oxalate; gel growth; characterization; XRD; IR; EDAX; XPS.

1. Introduction

The growth of sparingly soluble inorganic crystals employing gel technique (Henisch 1970) is well established and extensive work has been reported in the literature on the morphologies (Raju 1983a, b, c, 1986), nature of dislocations (Raju 1985), as well as on the mechanical behaviour (Raju *et al* 1984) in the case of gel-grown calcium sulphate dihydrate single crystals. It is well known that the rare-earth compounds exhibit high-temperature superconductivity and oxalate crystals show good ionic conductivity (George Verghese *et al* 1990), hence it is interesting to study the characteristics of rare-earth mixed oxalates. Caillaud *et al* (1988) have shown that superconducting compounds can be obtained by the controlled precipitation of oxalates followed by calcination. Further, researchers have proved that oxides like lanthanum copper oxide exhibit superconductivity up to 40 K (Beille *et al* 1987).

We report here the work carried out on the gel-grown mixed oxalate crystals of copper and neodymium (neodymium copper oxalate, NCO) and their characterization employing X-ray diffraction (XRD), IR, energy dispersive X-ray analysis (EDAX), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma (ICP)

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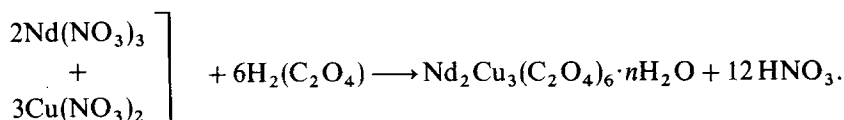
studies, which throw light on the kinetics of chemical reactions, the qualitative and quantitative analyses of heavy elements present in the mixed oxalates, besides the presence of their chemical states.

These results help in speculating on the empirical structure of NCO sample.

2. Experimental observations and results

2.1 Growth of NCO in gels

Acidified silica gel of specific gravity 1.03 g cm^{-3} was used as the reacting medium. A mixed solution of neodymium nitrate and cupric nitrate with nitric acid was used as the outer reactant above the gel at room temperature. The outer reactant diffused into the set gel containing oxalic acid. The following reaction takes place, producing bluish pink colloidal precipitate of mixed oxalates of neodymium and copper ($\text{Nd}_2\text{Cu}_3(\text{C}_2\text{O}_4)_6 \cdot n\text{H}_2\text{O}$) and nitric acid:



The nitric acid present in the gel medium may induce nucleation from the precipitate resulting in crystallization. A large number of well-defined bluish pink transparent microcrystals were observed just below the interface, while isolated crystals of relatively bigger sizes appeared at greater depths in the gel. The optimum conditions for the growth of good single crystals were found to be pH 5 of the gel and 0.5 molarity of each of the nitrates in 1:1 by volume in the outer reactant.

The proposed empirical structure of neodymium copper oxalate is given in figure 1.

Figure 2 shows an SEM of the basal plane of an NCO crystal (of size $5 \times 3 \times 0.5 \text{ mm}^3$) grown at greater depth in the gel. The basal plane can be seen to have relatively curved edges and corners. Careful examination of microstructures on the basal plane reveals crystallographically oriented dissolution figures (figure 3) suggesting thereby the single-crystalline nature of the NCO sample.

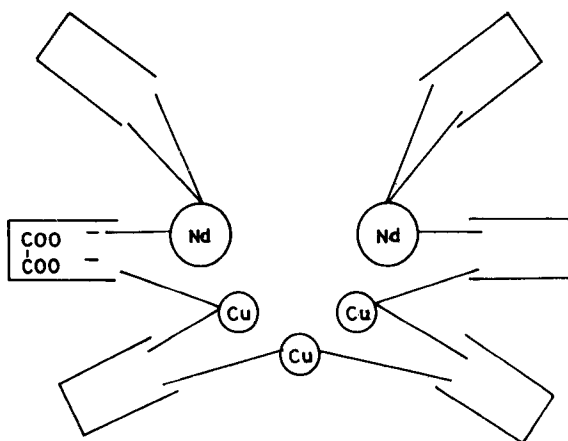


Figure 1. Proposed empirical structure of NCO.



Figure 2. SEM picture of gel grown NCO.

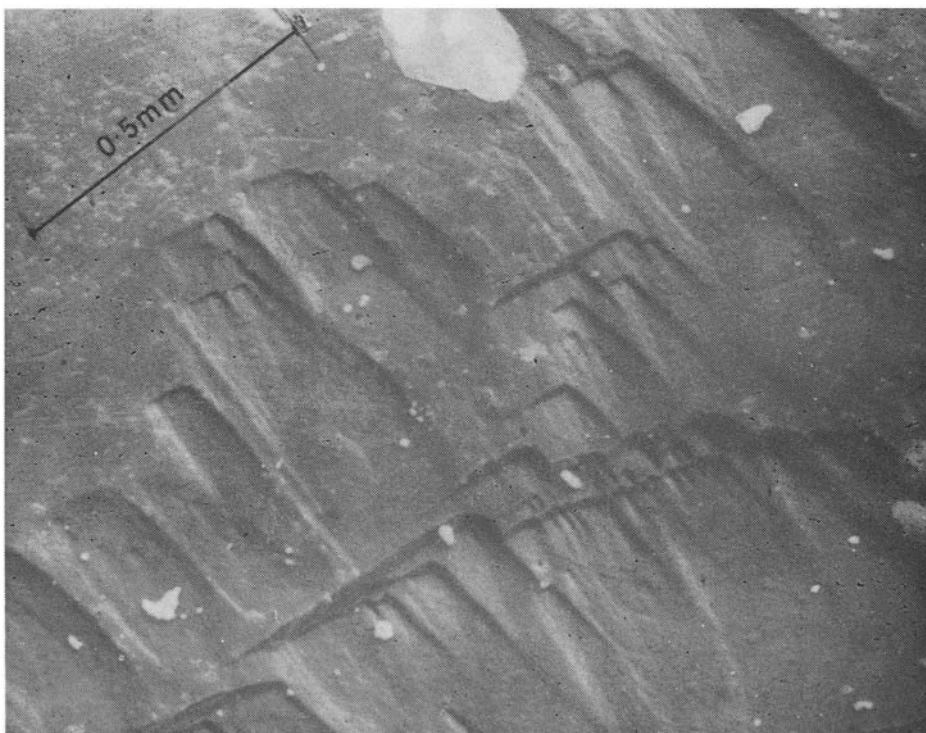


Figure 3. SEM picture showing dissolution figures on basal plane of NCO.

2.2 Characterization of NCO

2.2a XRD studies: In order to confirm the crystallinity, the powder X-ray diffraction pattern of NCO sample (figure 4) was taken in a Philips XRD PW 1050/70 with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The revelation of well-defined Bragg peaks at specific (2θ) angles suggests that NCO is ordered, meaning crystalline nature of the sample. It is worth mentioning here that the d values of the Bragg peaks in the XRD pattern of powdered NCO (figure 4) match quite well with the d values of the Bragg peaks relating to the XRD pattern recorded for powdered neodymium oxalate dodecahydrate.

2.2b IR absorption studies: The IR absorption spectrum of NCO sample (figure 5) in KBr matrix was recorded in a Perkin Elmer model 530.

The sample has water of crystallization as evidenced by the broad peak at $3000\text{--}3800 \text{ cm}^{-1}$ (relating to antisymmetric and symmetric OH stretchings) and at 1630 cm^{-1} (relating to HOH bending).

That the NCO sample has oxalate (C_2O_4)²⁻ ions is supported by the revelation of well-pronounced peaks at 1720 cm^{-1} [$\gamma_a(\text{C}=\text{O})$], 815 cm^{-1} [$\delta(\text{O}-\text{C}=\text{O}) + \gamma(\text{MO})$], 610 cm^{-1} , 500 cm^{-1} [ring deformation + $\delta(\text{O}-\text{C}=\text{O})$], 390 cm^{-1} [$\delta(\text{O}-\text{C}=\text{O}) + \gamma(\text{CC})$] (perhaps crystal water) and $335 \text{ cm}^{-1}(\pi)$.

2.2c Energy dispersive X-ray analysis (EDAX): In order to establish the elemental incorporation (like Nd and Cu) in the NCO crystals, EDAX was done. The integrated counts of X-ray photoelectrons relating to the elemental peaks taken for a definite time interval have been helpful in getting the approximate quantitative content of their respective elements reported in the present investigation.

The tiny crystals of NCO were mounted on to an aluminium stub, the surfaces of which were coated with a thin layer of gold to make them electrically conducting. The surfaces were examined in the EDAX analyser No. 711, an accessory to the Philips SEM model 501. The EDAX picture of NCO so recorded is shown in figure 6.

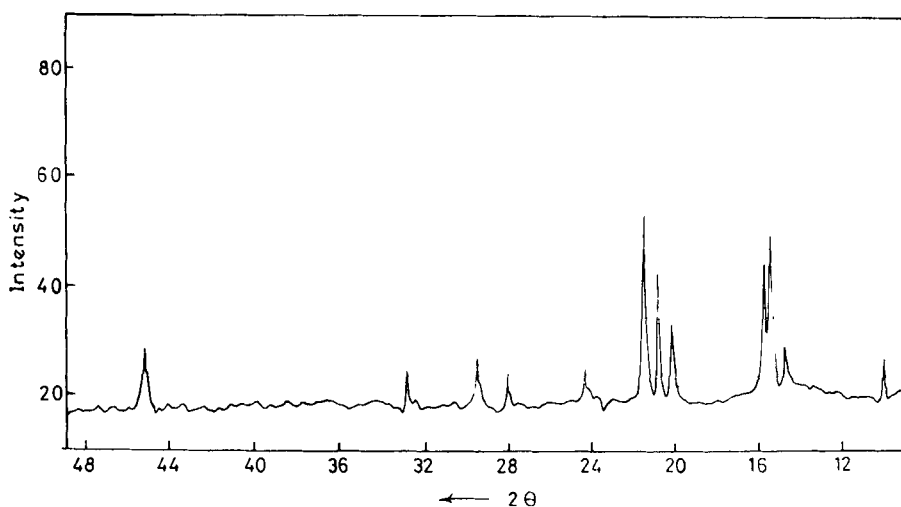


Figure 4. Powder XRD pattern of NCO.

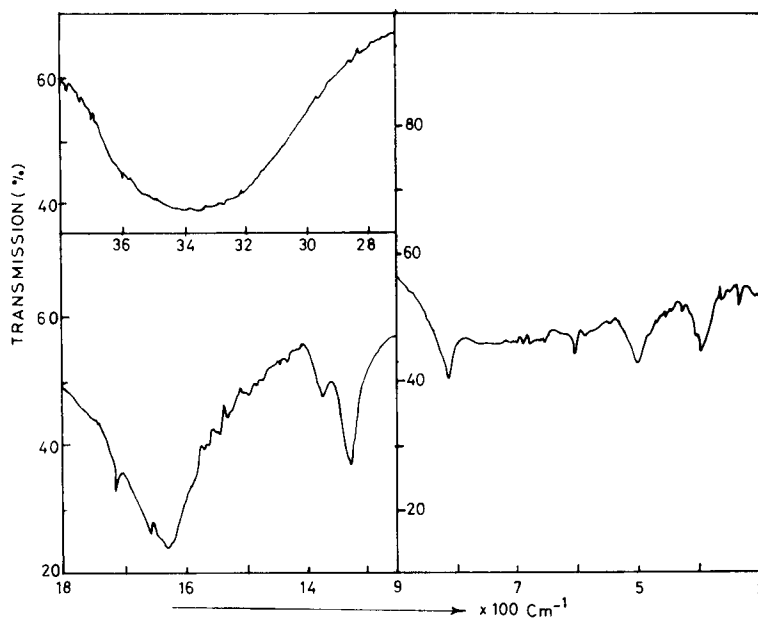


Figure 5. IR absorption spectrum of NCO.

79 8040EV K Z29 CU
 VS : 2500 HS : 20 EV/CH

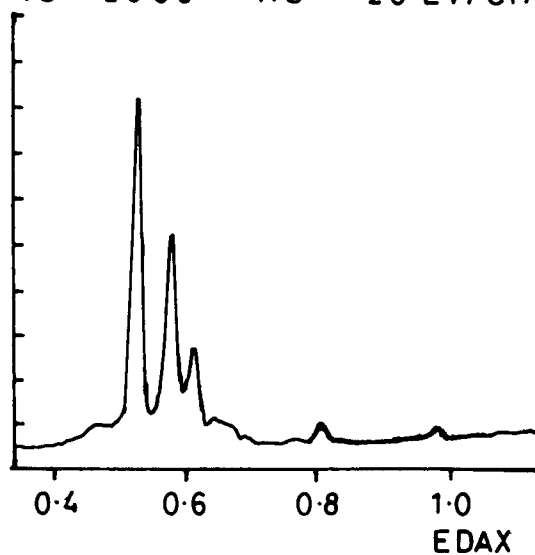


Figure 6. EDAX pattern of NCO.

The three dominant peaks positioned at 5.23, 5.72 and 6.088 keV (in the left hand side of figure 6) correspond quite well to the L_{α} , L_{β} and L_{γ} energies of neodymium, while a small hump at 8.04 keV corresponds to K_{α} line of copper (reported in the EDAX international chart), thereby establishing the presence of heavy elements (like

Nd and Cu) in NCO sample. A comparison of heights/areas relating to L_{α} peak of Nd and K_{α} of copper gives a strong clue that neodymium is dominant over copper in the sample.

The integrated count of X-ray photoelectrons relating to neodymium (L_{α}) collected for 150 sec was found to be 60,094 while for copper (K_{α}) the integrated count was 6144.

A very small hump for copper K_{α} at 8.04 keV compared to neodymium L_{α} at 5.23 keV observed in figure 6 is supported by the smaller integrated count of X-ray photoelectrons for copper K_{α} relative to neodymium L_{α} .

2.2d XPS studies: In order to further establish the constituents incorporated in NCO sample besides their chemical states, XPS studies are undertaken.

For the sample preparation, NCO is nicely powdered and a pellet of 1 cm diameter and 1 mm thickness was formed using a hydraulic press by applying a pressure of 1.1 tons per cm^2 . XPS spectra were taken in VG scientific ESCALAB MK II, by irradiating the sample with monochromatic soft X-rays (Mg K_{α} ; photon energy 1253.6 eV). The constant analyser energy was 50 eV and the resolution of the system was about 0.7 eV.

Figure 7 shows the XPS peak relating to Nd $3d_{5/2}$ with the binding energy centred at 980 eV, with the maximum count rate (MCR) of photoelectrons 8958, while figure 8 relates to the XPS peak of Cu $2p_{3/2}$ having binding energy around 933.6 eV (MCR 215).

It is well known that the count rates of photoelectrons relating to an XPS peak,

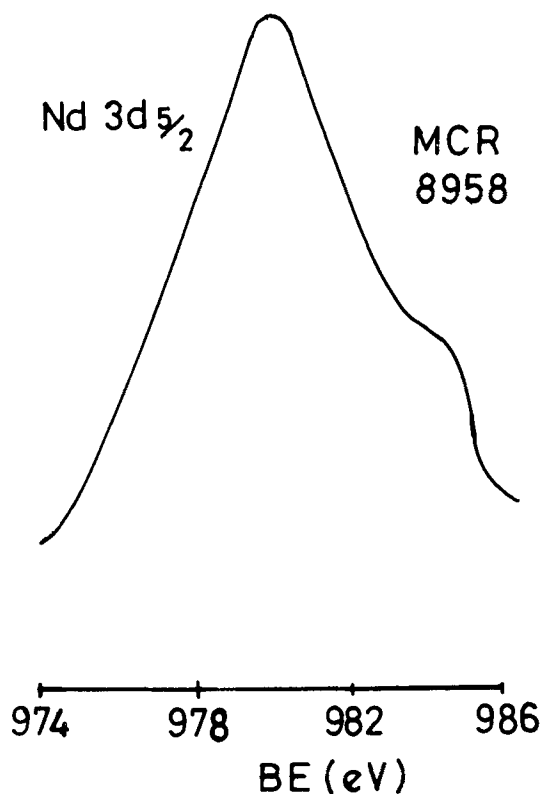


Figure 7. XPS peak of Nd ($3d_{5/2}$) of NCO.

meaning thereby intensity, is a measure of the quantity of the concerned element present in the material (Riggs and Parker 1975). The XPS observation regarding the MCRs of Nd and Cu supports the EDAX observation that Nd is more dominant than copper in the NCO sample.

The binding energy values relating to Nd ($3d_{5/2}$) and Cu ($3p_{3/2}$) in figures 7 and 8 agree quite well with the literature values (Wagner *et al* 1978) corresponding to their oxide states (Nd_2O_3 and CuO in the present case).

Figure 9 is the XPS region of carbon 1s of NCO sample in which it is clear that there are two peaks at binding energy values 287 and 290 eV. The first peak at 287 eV is attributed to the adventitious hydrocarbon being contributed from the laboratory environment or from the glove box, while the latter peak at the higher binding energy (290 eV) relates to the oxalate (C_2O_4)²⁻ group. This shift towards the higher binding energy corresponding to the oxalate group with respect to the first peak (287 eV) is due to the higher electronegativity of (C_2O_4)²⁻.

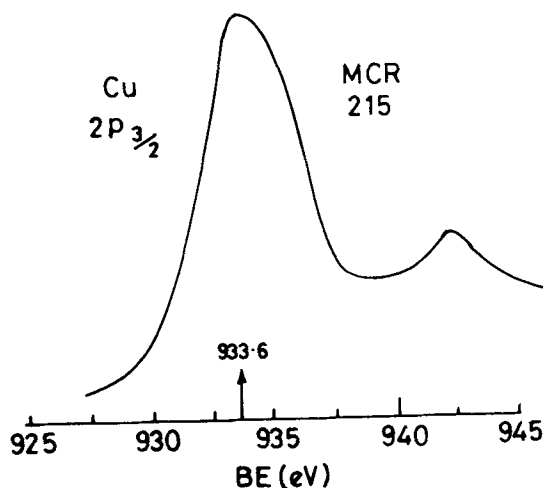


Figure 8. XPS peak of Cu ($2p_{3/2}$) of NCO.

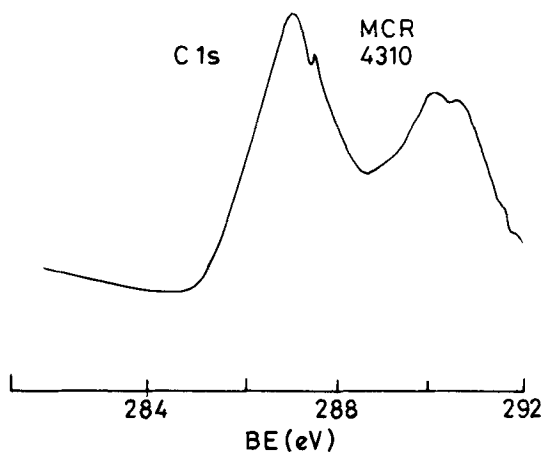


Figure 9. XPS peak of C 1s of NCO.

Thus XPS, though a method for surface analysis, is a powerful technique in identifying not only the constituents present in the sample but also their respective chemical states.

2.2e Inductively coupled plasma (ICP) analysis: The atomic emission spectrum of NCO by inductively coupled argon plasma was studied. Fifty to 55 mg of NCO was dissolved in HCl and the solution made up to 25 ml. The quantitative analysis of neodymium and copper was carried out with the calibration standards of Nd_2O_3 and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the range 0, 10, 20, 50 and 100 ppm. The concentrations of neodymium and copper (in ppm) were found to be 1170 and 6 ppm respectively. These computations are in very good agreement with the findings of EDAX and XPS confirming the dominance of neodymium over copper in NCO sample.

3. Discussion

The observation that NCO grown by gel is crystalline in nature is obviously evident by the revelation of tabular crystal at the greater depths in the gel, having geometrical edges and corners. On careful examination of the basal plane of the crystal, a large density of crystallographically oriented dissolution figures was observed. After the cessation of growth, during harvesting of the crystals, the acidic resultant (HNO_3) in the gel might have sparingly dissolved the sharp edges and corners thereby rounding them (figure 2) and also the basal plane producing crystallographically oriented dissolution figures (figure 3). The crystallinity of the NCO sample was further ascertained by powder XRD (figure 4) which revealed well-defined Bragg peaks whose d values match well with the d values of Bragg peaks relating to powdered neodymium oxalate, which is reported as crystalline (Weast and Lide 1990). The IR absorption spectrum of NCO (figure 5) establishes the presence of oxalato complexes in the sample besides its crystallinity as evidenced by the broad peak ($3000\text{--}3800\text{ cm}^{-1}$) relating to the water of crystallization, agreeing quite well with the reported values in the literature (Nakamoto 1978). A small hump at 8.04 keV (K_α peak of copper) in EDAX of NCO sample (figure 6) relative to the predominant peak L_α of Nd is well in agreement with the integrated count of photoelectrons of L_α of neodymium as 60,094 compared to 6144 for K_α of copper, both collected for 150 sec. The XPS results support well that Nd and Cu are in their oxide states (figures 7 and 8) getting linked to O^- of $(\text{C}_2\text{O}_4)^{2-}$, the latter being evidenced by the XPS of C 1s (figure 9). These results are in excellent agreement with the proposed empirical formula for NCO (figure 1). The MCRs of photoelectrons relating to $3d_{5/2}$ peak of neodymium (8958) and $3p_{3/2}$ peak of copper (215) reestablish the EDAX and ICP results that Nd is dominant over copper in NCO sample.

The dominance of Nd over copper is explained as follows.

The rare earth neodymium is a hard acid and oxalate is a hard base and hence has stronger affinity for neodymium oxalate formation. Copper belongs to soft acid and in presence of neodymium has a very weak role in the formation of copper oxalate. This may be the reason for the dominance of neodymium over copper in the NCO sample (Huheey 1983).

4. Conclusion

It is concluded that the gel-grown NCO sample reported in the present work (i) is crystalline in nature as evidenced by the well-defined edges and corners (though curved later) as well as by the revelation of crystallographically oriented dissolution figures (figures 2 and 3), (ii) is ordered and crystalline (XRD), (iii) accounts for the presence of oxalato complex by the revelation of its characteristic peaks and of lattice water by the broad peak at $(3000\text{--}3800\text{ cm}^{-1})$ (IR), (iv) has Nd and Cu established qualitatively and quantitatively (EDAX), (v) has Nd and Cu in their oxide states (XPS) getting linked to O^- of oxalate groups (figure 1), and (vi) has Nd in abundance relative to Cu as evidenced by the integrated counts of their X-ray photoelectrons (in EDAX and XPS) and by their quantitative presence estimated by ICP analysis.

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