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# Effect of pressure and temperature on the resistivity of $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$

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**Abstract**

The effect of pressure and temperature on the electrical resistivity of the composition-controlled $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$ superconductor have been studied. Electrical resistivity measurements were carried out by a four-probe technique using a Bridgman opposed anvil high-pressure device and the high-temperature measurements were done using a heating coil arrangement. The measurements were done up to a pressure and temperature of 8 GPa and 523 K, respectively. The structure of the sample was confirmed by the theoretical calculation of the X-ray diffraction intensities. A gradual decrease in the electrical resistivity with increase of pressure was observed. The effect of pressure on the bonds causing the decrease in the resistivity has been confirmed by X-ray diffraction measurements. The temperature effect causes an upward shift in the electrical resistivity in the observed range of pressure.
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*Keywords:* Superconductors; Chemical synthesis; Electrical properties; Pressure; $NdCaBa_2Cu_3O_7$

## 1. Introduction

The main interest on doping the divalent calcium ion is to increase the hole concentration in the copper oxide layers of the Nd-123 ($NdBa_2Cu_3O_{7-\delta}$) system. When calcium is incorporated in an R-123 (R = rare-earth element) system it preferentially substitutes at R site. The calcium substitution at the yittrium site of the Y-123 ($YBa_2Cu_3O_{7-\delta}$) system leads to enhancement in the superconducting transition temperature and thermoelectric power [1]. Nd-123 is a promising material for its bulk applications due to its improved superconducting properties compared to Y-123, such as the high critical current density and magnetic irreversibility fields and is not affected even in the presence of intense external fields [2,3]. The composition-controlled $Nd_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ superconductors have evoked considerable interest mainly because of their wide homogeneity range. Extensive studies such as hole doping [5], fluctuation conductivity [5], flux pinning behaviour [6,7], microstructure [8] and neutron spectroscopy [4] have been made on this system with a view to understand the homogeneity. Thermoelectric power measurements at atmospheric pressure for Ca-doped Nd-123 bulk materials show an increase in the temperature coefficient of resistance indicating improved metallic properties [4]. The superconducting transition widths decrease with calcium substitution with resistance drop of 2.7 for pure Nd-123 and 2.0 for 3% doping of Ca at the Nd site, which shows a lowering of the transition width for the Ca-substituted sample; this may be an advantage for its applications. High-pressure experiments constitute a sensitive probe of the superconducting state because of the change in electronic and phononic properties [9].

Hence, $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$ was chosen for the present study and the effect of pressure and temperature on its electrical properties are studied at various pressures and temperatures up to a maximum of 8 GPa and 523 K, respectively.

## 2. Experimental details

The composition-controlled $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$ high-temperature superconductor was synthesised by a solid-

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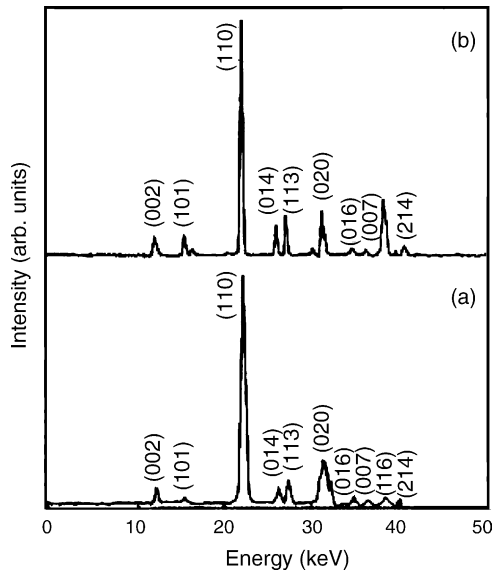


Fig. 1. (a) Experimental and (b) simulated diffraction pattern of $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$.

state method [4]. High-purity $Nd_2O_3$, $BaCO_3$, CuO and $CaCO_3$ in stoichiometric composition were ground finely and pelletised. They were then calcined at 1173, 1193 and 1193 K with intermediate grindings. They were annealed in flowing oxygen at 733 K for 3 days and the temperature was finally decreased to room temperature at the rate of 12 K $h^{-1}$.

Energy-dispersive X-ray powder diffraction study was carried out on the $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$ system using white X-rays produced by a copper target using a rotating-anode X-ray generator (Rigaku). The system was indexed with an orthorhombic structure with the space group Pmmm using an X-ray diffraction analysis software [10]. Diffraction simulation has been done using an X-ray powder diffraction software [11] and is found to match very well with that of the experimental pattern. The experimental pattern and the simulated pattern for the samples are shown in Fig. 1a and b, respectively.

High-pressure resistivity measurements were carried out on the samples up to 8 GPa by using an opposed anvil high-pressure device described elsewhere [12]. Pyrophyllite was used as the gasket and steatite as the pressure-transmitting medium. The pressure calibration was done by observing the Bi transitions.

Electrical resistivity studies at high pressure and high temperature were done using a heating coil arrangement in the opposed anvil high-pressure device [13] and is shown in Fig. 2. The temperature stability obtained was ±2 K. The power to the coil was controlled by a variac and the temperature has been maintained using a temperature controller. In this arrangement, a chromel–alumel thermocouple connected together by spot welding is used as temperature sensor. The spot-welded junction was hammered and made very thin and flat. A sample of 0.1 mm thickness has been used for the resistivity measurements. Necessary corrections for the effect of

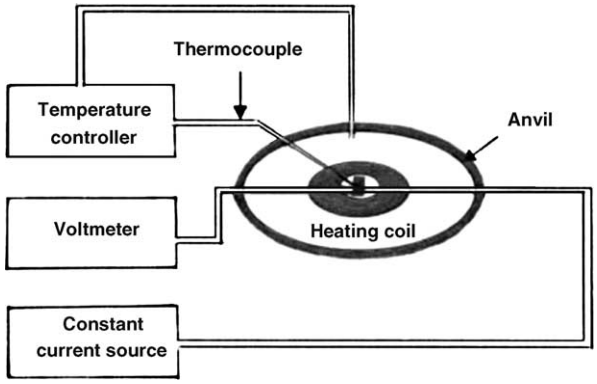


Fig. 2. High-pressure high-temperature electrical resistivity set-up.

pressure on the thermal emf were made according to Cheng et al. [14,15]. The thermocouples, sample and the heater were assembled for good thermal contact, and mica sheets and tapes were used for insulating purposes. Prior to the measurements, the temperature was stabilised for 15 min so as to ensure thermal equilibrium of the sample. From the obtained data, graphs were plotted between electrical resistivity and pressure. The position of the sample and the thermocouple in the high-pressure high-temperature set-up is shown in Fig. 2.

## 3. Results and discussion

The compound is found to be crystallised in orthorhombic structure with the lattice parameters $a = 3.87 \pm 0.01$ Å, $b = 3.92 \pm 0.01$ Å, $c = 11.74 \pm 0.01$ Å and volume $V = 178.7$ Å$^3$. The X-ray diffraction pattern shows the formation of a single phase. The lattice parameters obtained are in agreement with the literature [4,16]. A decrease in volume is observed on substitution of calcium at the Nd site. Diffraction simulation studies confirm the substitution of calcium at the neodymium site.

The relative electrical resistivity ($\rho/\rho_{0.3\,GPa}$) versus pressure of orthorhombic $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$ measured at various temperatures up to 523 K is shown in Fig. 3. Better contacts were established by giving a small load, which corresponds to 0.3 GPa at the sample site. Hence, resistivity at 0.3 GPa was chosen for the normalisation. The measurements were carried out for both loading and unloading pressures. It was found that the behaviour is reversible under pressure with small hysterisis, except for a small decrease in the $\rho$ value for the unloading curve. From the loading and unloading behaviour, it is also evidenced that the initial decrease in the resistivity is not mainly due to the compaction of the sample. Thus, it is a real effect caused due to the structural changes in the sample on application of pressure. $Nd_{0.97}Ca_{0.03}Ba_2Cu_3O_{7-\delta}$ shows an initial gradual drop up to 3 GPa. Above 3 GPa, it follows a nearly constant value of electrical resistivity, which continues up to 8 GPa. The change in the electrical resistivity at lower pressures is larger while at higher pressures the decrease in $\rho$ is small.

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