

New synthesis method of superconducting $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$, $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$

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Abstract

The first example of anion doped high T_c material $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ was recently discovered by James, Zahurak et al. In order to increase the amount of superconducting material we used new preparation routes. A two step process was used: preparation of $\text{T Nd}_2\text{CuO}_4$ and Pr_2CuO_4 phases and then fluorination. The preparation of T rare earth cuprates used are: oxides, hydroxide, oxalic and propionate synthesis method. The fluorination was done by reaction with NH_4F under neutral gas. Using the previous way, large diamagnetism signal was observed as well on $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ as on $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$. X-ray and magnetic studies show as evidence an improvement of compounds.

1. Introduction

The first synthesis of $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ has been described by James et al [1]. This method was based on reaction between copper and neodymium oxide powders mixed with NdF_3 . Magnetic measurements show a small diamagnetic effect corresponding to evidence of a superconducting fraction volume (10 to 15% reported by M.E. Lopez-Morales and P. M. Grant [2]) in non-supra material. We investigated other preparation routes in order to increase the amount of superconducting material. It proceeds in two separate steps: preparation of Ln_2CuO_4 using several low temperature synthetic ways and then, fluorination by NH_4F under neutral gas.

2. Preparation of Ln_2CuO_4 ($\text{Ln} = \text{Nd, Pr}$)

Firstly the preparation of Nd_2CuO_4 was done by three methods: hydroxide coprecipitation, oxalate coprecipitation, and preparation of Nd, Cu propionates, and compared with classical solid state reaction between oxides. Propionic method is considered as the most convenient method for Pr_2CuO_4 .

2.1 Hydroxyde preparation

Nd_2O_3 and CuO are dissolved in a HNO_3 water solution and precipitation occurs by adding potassium hydroxide solution at 85°C – 90°C . Hydroxide suspension pH is adjusted at 11 and kept at this value for 45 minutes. The precipitate is filtered and washed several times with warm distilled water in order to eliminate potassium. After filtration and water washing the precipitate is heat treated at 900°C for 14h in air.

2.2 Oxalic preparation

An oxalic water solution is prepared (ratio 1:4) as described by Hiss et al. [3]. As in hydroxide preparation, oxides are dissolved in nitric solution and added to oxalic solution. The precipitate is kept at $\text{pH}=4$ for four hours with continuous stirring and then filtered. The lack of copper in the filtrate is checked using ammonia solution. The precursor is heat treated at 900°C in gold crucible for 14h in air.

2.3 Propionic preparation

Oxides in ratio $\text{Nd}/\text{Cu}=2/1$ are dissolved in propionic acid [4]. The excess of solvent is evaporated to dryness. We obtain a resinic precursor. The resinic precursor is heat treated at 900°C in gold crucible for 14h in air.

2.4 Fluorination

The fluorination was done by reaction between NH_4F and the previous prepared oxides with ratio $\text{NH}_4\text{F}/\text{oxide}=0.5/1$ whatever the precursor. Chemical analysis on annealed sample prepared by oxalate method gave the amount of fluorine $x=0.30$. The reaction occurs in an Inconel tube at 350°C under neutral gas (argon). A final heat treatment at 890°C during 14H under flowing argon leads to superconducting material.

3. Experimental

Unit-cell constants has been determined by X-ray powder diffraction using a Kristalloflex Siemens diffractometer with graphite monochromator. The lattice

parameters were refined using a least square program with accuracy better than 0.01%. A mass spectrometer (Thermolab VG Instrument) coupled to T.G.A. device enabled to analyze the loss of weight. Magnetic susceptibility measurements have been carried out in

range 4.2K to 40K in a calibrated a.c. susceptometer using a lock-in amplifier. Resistivity has been measured using the four point d.c. technique. Specific heat measurements have been performed between 1.3K and 40K using a calorimeter based on the adiabatic method.

Table 1 : Lattice parameters and cell volume of compounds prepared by different precursors.

Compounds	Precursors	Lattice parameters (Å)		Volume (Å ³)
		a	c	V
Nd ₂ CuO ₄	Oxides	3.942(0)	12.165(7)	189.05
Nd ₂ CuO ₄	Hydroxides	3.941(8)	12.166(2)	189.05
Nd ₂ CuO ₄	Propionates	3.941(9)	12.165(4)	189.04
Nd ₂ CuO ₄	Oxalates	3.932(4)	12.150(2)	187.89
Nd ₂ CuO _{4-x} F _x	Oxalates	3.935(7)	12.120(1)	189.37
Pr ₂ CuO ₄	Propionates	3.936(9)	12.283(1)	190.38
Pr ₂ CuO _{4-x} F _x	Propionates	3.938(9)	12.247(2)	190.01

4. Results and discussion.

4.1 Nd₂CuO₄ powders

Table 1 gives lattice parameters and volume. We notice that only oxalate route powder has the smaller lattice volume. This is due to smaller lattice parameters a and c probably related to a copper deficiency inherent to preparation method (copper oxalate losses during washing). For other powders, hydroxide and propionate, lattice parameters correspond to those given by literature.

4.2 Fluorinated Nd₂CuO₄

The lattice parameters and lattice volume of Nd₂CuO₄ and Pr₂CuO₄ fluorinated and annealed under argon at 900°C are given in table 1. These results show a and c-axis variation whatever the precursor. It can be assumed to a slight expansion of CuO₂ square layer (~0.05%) and interlayer distance reduction (~0.3%). Powder diffraction patterns indicate that all samples are single phase and show the same peaks as tetragonal Nd₂CuO₄ but shifted, corresponding to a contraction along c-axis and an expansion of a and b axis. Thermogravimetric analysis under argon on Nd₂CuO₄ freshly fluorinated at 350°C shows a fast loss of weight of 0.08 % at 870°C. A loss 0.2% at 870°C is observed for Pr₂CuO₄ freshly fluorinated. This loss was identified as oxygen loss by mass spectrometer device in agreement with the oxygen diffusion in Nd₂CuO₄ reported by

Yasushi et al. [5]. This heat treatment corresponds to the final annealing of powders for obtaining superconducting material.

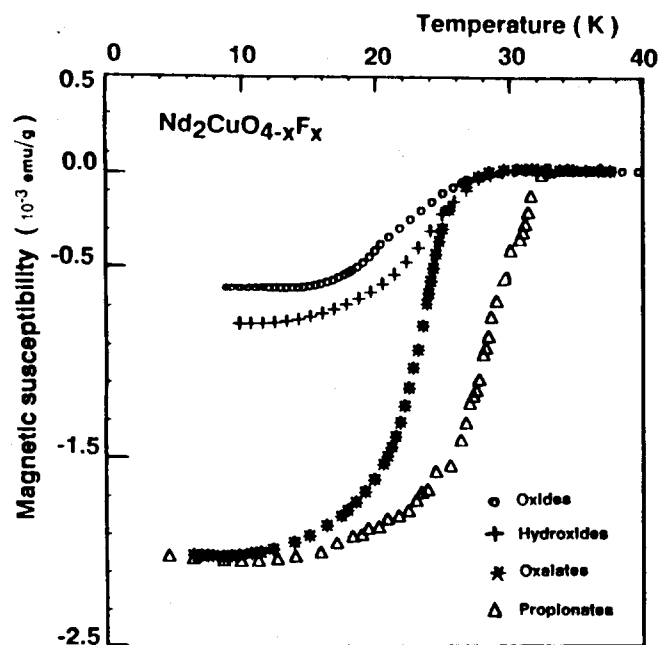


Figure 1. magnetic susceptibility of Nd₂CuO_{4-x}F_x prepared by: ○ oxide, + hydroxide, * oxalic, and Δ propionic routes.

The superconductivity is induced by partial substitution of oxygen ions by fluorine ions on the oxygen sites and a loss of oxygen by the annealing treatment under argon. This suggests that partial reduction of copper is done and introduces mobile electrons in the CuO_2 - layers.

4.3. Magnetic properties

Figure 1 gives the diamagnetic susceptibility of $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ for oxide, hydroxide, oxalate and propionate precursors under the same condition of fluorination. Figure 2 gives the diamagnetic susceptibility of $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ for oxide and propionic precursors. We notice that oxalate and propionate precursors lead to the same magnitude of diamagnetic signal below 10K. The superconducting temperature is around 27K. The hydroxide derived compound exhibits a weaker diamagnetism (-0.8×10^{-3} emu/g instead of -2×10^{-3} emu/g at 4K) while is identical to that found for oxide precursors. This corresponds to a superconducting fraction volume of 25%. Corrections due to sample demagnetization and porosity imply that the actual Meissner fraction is somewhat higher than this value; this indicates a bulk superconductivity in nature. The diamagnetic effect increases with the sintering temperature as shown in figure 3 whatever the rare-earth cuprate, and can be related to a grain growth. The samples heated at 900°C exhibit an agglomeration of small grains with an average grain size of $1 \mu\text{m}$. At 1000°C , the sintering process is achieved and grain size grows up to $6 \mu\text{m}$.

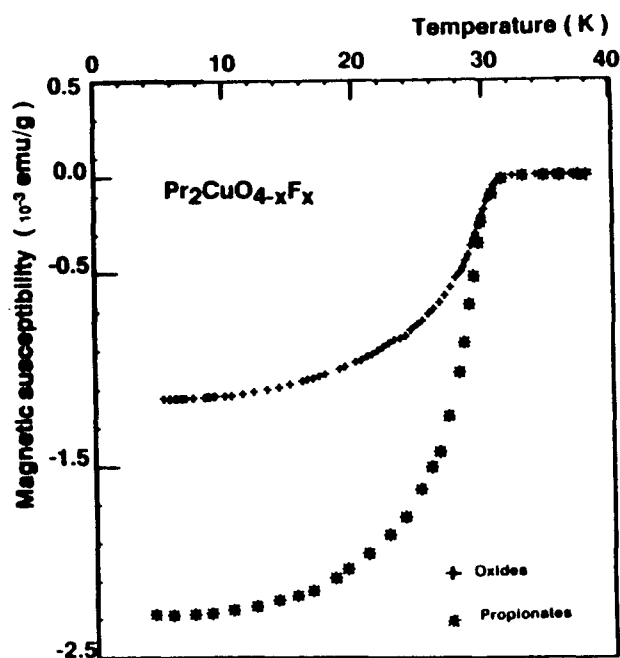


Figure 2. Magnetic susceptibility of $\text{Pr}_2\text{CuO}_{4-x}\text{F}_x$ for different precursors: + oxides and * propionates.

Figure 1 shows the striking differences between investigated routes. Such results may be analysed from

powder morphology of the materials under consideration. Indeed it is well known that oxalate and propionate methods lead to submicronic grains. For oxide preparation the grain size and the low reaction temperature result in a poor grain homogeneity and also to large grain size. SEM observation shows a grain size $\sim 0.2 \mu\text{m}$ for oxalate and propionate preparations. In despite the oxide and hydroxide preparations lead to a grain size $\sim 10 \mu\text{m}$. Fluorination by NH_4F is solid gas reaction. Thus, surface area and grain size and aggregation state play a great role. If we assume that fluorination takes place from the grain shell to the core, large grain size will impede the oxide/fluor ratio. It seems to be the case for hydroxide and oxide preparations.

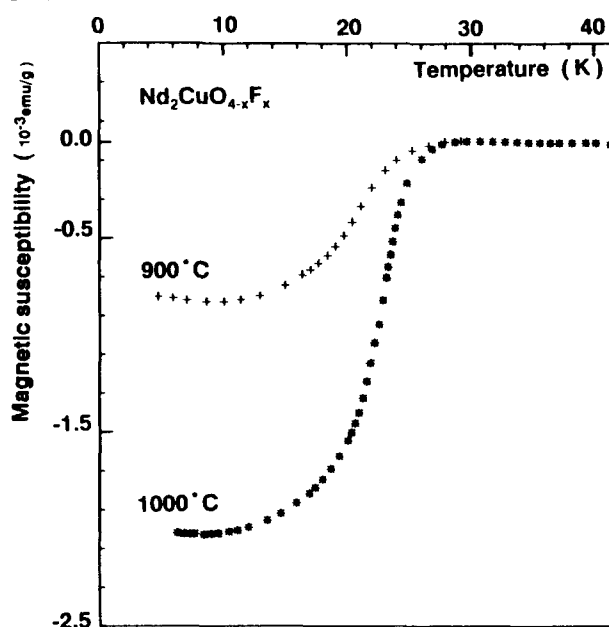


Figure 3. Temperature dependence of magnetic susceptibility of $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ prepared by propionate method. The samples are heated at temperatures 900°C and 1000°C .

The final heat treatment entails a diffusion of fluorine in grain core. Thus ratio F/Cu is lowered and leads to small Meissner effect. The same results are obviously observed for $\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$ prepared by hydroxide method in spite of the fact that homogeneity is insured by the preparation method. The sensitivity of neodymium hydroxide to CO_2 combined with the use of potassium hydroxide can lead to impurity phases. Even in small amount this may drive a grain growth in Nd_2CuO_4 or inhibit the fluorination. The last point is the sintering temperature effect after fluorination. We notice a large increase of diamagnetic susceptibility with sintering temperature. As emphasized above the sintering process entails grain growth, promoting the homogenization of fluorine in the grain core but also it reduces grain interface, and hence increase of diamagnetism.

In the case of propionic preparation, the most homogeneous compound, but also with the small grain size, the T_c onset shifts to 32K for $Nd_2CuO_{4-x}F_x$.

The resistivity measurements of $Nd_2CuO_{4-x}F_x$ (oxalates) and $Pr_2CuO_{4-x}F_x$ (propionates) show a sharp transition at 27K for the former and 30K for the latter. In the case of $Pr_2CuO_{4-x}F_x$ a large peak is observed at the T_c onset 30K in the heat capacity and no magnetic ordering of Pr^{3+} for the temperature ranging between 1.3K and 40K. For $Nd_2CuO_{4-x}F_x$, the heat capacity measurements show only one peak at 1.5K due to the antiferromagnetic ordering of Nd^{3+} as in the case of Nd_2CuO_4 [6, 7].

5. Conclusion

The purpose of this paper is to illuminate some of the issues involved in preparation of fluorinated superconducting Nd_2CuO_4 and Pr_2CuO_4 . The preparation methods and thus ceramical properties of oxide powder are shown to be related to amount of fluorine reacting with grain surface and, hence to superconducting properties. For a small grain size of Nd_2CuO_4 and Pr_2CuO_4 , as far as fluorine reacts with grain shell, large Meissner effect can be obtained. However a more detailed crystal structure, for determining fluorine position would be needful for

further study with aim of understanding and optimizing superconducting properties.

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