Low Temperature Fluorination of Super Conducting and Non-superconducting Compounds Using NH₄F

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Abstract

Compounds Y₂Ba₄Cu₇Ox, Pr₂Ba₂Cu₂O₇ and La₂CuO₄ were fluorinated by a low temperature fluorination method using NH₄F. The fluorinated samples were analysed by x-ray diffraction and resistivity measurements. The x-ray diffractogram of the fluorinated samples indicated broadening of the peaks. None of the fluorinated samples showed any superconducting behaviour.

1. Introduction

Since the discovery of high temperature superconductivity in ceramic materials, extensive studies have been carried out on the effect of the substitution by impurities on the physical properties. While substitution at the rare earth site or alkaline earth site has not changed the Tc considerably (Fisk et al. 1987, Hor et al. 1987, Crabtree et al. 1987), introduction of vacancies at the oxygen sites reduces Tc drastically (Mc Kinnon et al. 1987). Theoretically many of these results have been accounted for as due to reduction of density of states at the Fermi level (Herman et al. 1987). This indicates that substitution at the oxygen site will be very crucial in the formation

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of superconductors. Ovshinsky et al. (1987) have reported substantial increase in Tc value of Y$_1$Ba$_2$Cu$_3$O$_7$ (Y-123) system by fluorine substitution. Among the conventional methods of fluorination, the most effective one involved the use of F$_2$ gas. But the complexity involved in handling the highly corrosive and poisonous F$_2$ gas prevented its free use as a fluorinating agent. The fluorides of the constituent elements of the compounds are widely used to fluorinate many systems (Ovshinsky et al. 1987, Radhakrishnan et al. 1987, Young et al. 1987, Bansal et al. 1988, Lee et al. 1991, Gao et al. 1995). These fluorides, taken as one of the starting materials, undergo the process of calcination and sintering at high temperatures. But in some cases, this high temperature ceramic technique of preparation will not help the formation of oxy-fluorides (Tyagi et al. 1988). A low temperature fluorination method using NH$_4$HF$_2$ was used by Rao et al. (1986) in fluorinating metallic oxides like V$_2$O$_5$, Nb$_2$O$_5$. This method was tried for fluorination of Y-123 system by Tyagi et al. (1988), but was unsuccessful. Slater et al. (1995) used NH$_4$F to fluorinate Sr$_2$-xAxCuO$_3$ (A=Ca,Ba) system in which a superconducting transition at 46 K was reported on as-prepared samples. In this paper we present the results of our attempts to fluorinate the compounds Y-123, Pr-123 & La$_2$CuO$_4$ at low temperatures using NH$_4$F.

2. Experimental

The adopted general method of fluorination using NH$_4$F is as follows. The compound to be fluorinated is prepared initially by any standard method and characterised by x-ray diffraction analysis. Ammonium fluoride (4 to 6 moles of NH$_4$F per mole of the compound) is then added to the compound and the mixture is ground, pressed into pellets and heated at 100°C per hour to 225-250°C; the sample is held at this temperature for 6 hrs and then cooled to room temperature. The resulting products are further characterised by powder x-ray diffraction. Using the above preparation method, Y$_1$Ba$_2$Cu$_3$O$_7$-d (Y-123), Pr$_1$Ba$_2$Cu$_3$O$_7$-d (Pr-123) and La$_2$CuO$_4$ had been fluorinated.

Stoichiometric amounts of high purity Y$_2$O$_3$, PrO$_2$, La$_2$O$_3$, BaCO$_3$ & CuO were mixed thoroughly in agate mortar. The mixed powders of Y-123 and Pr-123 were calcined at 950°C for 12 h, ground well and pelletised. Pellets of Y-123, Pr-123 and mixed powders of La$_2$CuO$_4$ were taken in separate boats and were sintered at 950°C for 24 hrs with one intermediate grinding. X-ray diffractograms of all the samples were recorded on Rigaku DMAX 1C diffractometer using CuKa radiation (l = 1.5405 Å).
The diffractograms of Y-123, Pr-123 and La$_2$CuO$_4$ (Fig. 2, 3, and 4) indicate that single phase compound have formed in the three cases. The Y-123 pattern was indexed with a cell having $a = b = 3.86\,\text{Å}$ and $c = 11.78\,\text{Å}$. The indexing of Pr-123 XRD pattern yielded an orthorhombic cell with $a = 3.56\,\text{Å}$, $b = 3.92\,\text{Å}$ and $c = 11.71\,\text{Å}$. La$_2$CuO$_4$ pattern was indexed with an orthorhombic cell having $a = 5.35\,\text{Å}$, $b = 5.40\,\text{Å}$ and $c = 13.15\,\text{Å}$. The resistivity of Y-123 and Pr-123 samples were measured from room temperature down to liquid nitrogen temperature. Y-123 sample showed a superconducting transition at 90 K while Pr-123 remained as a semiconductor down to 77 K (Fig. 1).

Fig. 1 Resistivity temperature curve of Y-123 & Pr-123 samples sintered at 950°C for 24 hrs.

Fig. 2 XRD of (a) unfluorinated and (b) fluorinated samples of Y-123 compound
Fig. 3 XRD of pure (a) fluorinated (b) samples of Pr-123 compound

Fig. 4 XRD of pure (a) and fluorinated (b) samples of La$_2$CuO$_4$
One pellet each of the prepared compounds (Y-123, Pr-123, and \( \text{La}_2\text{CuO}_4 \)) was separately mixed with \( \text{NH}_4\text{F} \). Four moles of \( \text{NH}_4\text{F} \) were used per mole of the compound. After thorough mixing, the samples were pressed as pellets. These pellets were heated at the rate of 100°C per hour to 235°C in air, held at this temperature for 6 h and furnace cooled to room temperature.

### 3. Results and discussion

The x-ray diffractograms (XRD) of the fluorinated and unfluorinated Y-123 samples are shown in figure 2. As evident from the pattern, the fluorinated sample also shows the same features as compared to the unfluorinated sample. The relative intensity of the [0 1 3] and [1 0 3] reflections has changed. There are broad and weak peaks at \( 2q = 26^\circ, 30.5^\circ \) and \( 42.5^\circ \) (see figure 2b). These three peaks fall in the vicinity of the characteristic BaF\(_2\) peaks. Rao et al. (1988) had observed the same kind of features in Y-123 compound, when fluorinated with NH\(_4\)HF\(_2\) and attributed the broad peaks as due to the incorporation of F atoms into the lattice such that a BaF\(_2\) type sublattice with a distortion in the planes occurs. Also the peaks at \( 2q = 38.5^\circ \) and \( 40.5^\circ \) are found to be slightly broadened. It is interesting to note that the room temperature resistance of this sample (Y-123) has gone up from a few ohms to 180 kW range even when the general features of the XRD pattern has not changed. The room temperature resistance of the fluorinated Pr-123 sample was in 1 MW range and \( \text{La}_2\text{CuO}_4 \) remained as an insulator before and after fluorination.

In the case of Pr-123 compound the general features of the XRD pattern (figure 3) are similar before and after fluorination. Here also, three broad and weak (BaF\(_2\)-like) peaks at \( 2q = 26^\circ, 30.5^\circ \) and \( 42.5^\circ \) are observed after fluorination. In addition, the resolution of the doublet peak around \( 2q = 46.5^\circ \) are very broad in the fluorinated sample.

Figure 4 represents the XRD pattern of fluorinated and unfluorinated \( \text{La}_2\text{CuO}_4 \) sample. In this case also, in addition to the peak broadening, the loss of resolution of the doublet peaks at \( 2q = 33^\circ, 43.5^\circ, 54^\circ \) and \( 58^\circ \) is observed in the fluorinated samples.

The results of our investigations of fluorination on Y-123, Pr-123 and \( \text{La}_2\text{CuO}_4 \) compounds were not encouraging because we could not get superconducting compounds. This method of low temperature fluorination using NH\(_4\)F seems to be very tricky [as reported by Slater et al. (1994) in Sr\(_2\)-\( x\)AxCuO\(_2\)F\(_2\)+\( x\) compounds]. The fluorinated compounds, contain some amount of BaF\(_2\) or SrF\(_2\) impurities as long as Ba or Sr are constituents of the compound.
4. Conclusion

Using NH₄F as the fluorinating agent, compounds can be fluorinated at low
temperatures (200 – 250°C). But in the case of Y-123 compound, superconducting
properties are not shown by the fluorinated samples. The XRD of the fluorinated
samples indicated the presence of the fluorides of the constituent elements. This
method of low temperature fluorination cannot be used as a general procedure of
fluorination of superconducting compounds.

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