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Interaction of Yttrium–Barium Cuprate with Fluorine

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The interaction of yttrium–barium cuprate with fluorine (0.1–1 atm) has been studied at 20–310 °C, the intensity (rate) of the interaction showing a deep minimum near 100 °C; our observations indicate that below 100 °C the interaction mechanism is dominated by fluorine intercalation in the vacant oxygen sites of yttrium–barium cuprates.

Several studies of the interaction of yttrium–barium cuprate with gaseous fluorine have been published recently.[1–7] Interest in fluorinated cuprates originally arose in connection with the possibility of obtaining enhanced T_c values in these materials. It has also been found that fluorinated phases acquire stability to atmospheric degradation. This observation has attracted considerable attention since degradation processes present serious obstacles to the practical application of these superconductors.

The results obtained so far[1–7] are as follows. Treatment of cuprates with fluorine results in an increase in the weight of the samples, *i.e.*, addition of fluorine occurs. The interaction takes place even at 20 °C. At temperatures below 100 °C no impurity phases are observed, the crystal lattice parameter and T_c values remaining unchanged. At temperatures 200–300 °C and above the initial orthorhombic structure is destroyed in order to produce the fluorides. Fluorination at 200 °C results in the formation of Cu^{3+} ions.[5]

These results indicate[1,3–5] that during a moderate interaction of yttrium–barium cuprate with fluorine an amorphous phase of fluorides and oxyfluorides is formed on the particle surfaces of the initial orthorhombic phase. The formation of amorphous species on the crystallite surfaces has been observed by electron microscopy.[1,3] This layer of amorphous fluorides protects the initial phase from interaction with water vapour and other gases, preventing degradation of its superconducting properties.[1,3–5]

More recently,[6] it was shown that the proposed formation of an amorphous phase of fluorides (and oxyfluorides) on the grain surfaces of the Y–Ba cuprates is not quite in agreement with the available experimental evidence (*e.g.*, X-ray diffraction data). We now report new data on the mechanism of the interaction of yttrium–barium cuprate with fluorine.

The starting oxide $YBa_2Cu_3O_{6.9}$ was obtained by the standard procedure of solid-state sintering of a compressed mixture of Y_2O_3, BaO_2 and CuO powders at 950 °C followed by slow cooling. The samples obtained were single-phase (orthorhombic structure), $T_c = 91$–93 K, full transition width 2–4 K. By annealing these samples under vacuum at 500 °C tetragonal samples of composition $YBa_2Cu_3O_{6.3}$ were obtained. The powdered samples for fluorination had a specific surface area of about 0.6 $m^2\,g^{-1}$ (± 10%, as measured by low temperature argon adsorption). Each sample, in a nickel container, was placed in an apparatus made of nickel. After evacuation, the apparatus was filled with fluorine at a preset pressure, the fluorine being obtained by the decomposition of K_2NiF_6. The part of the apparatus containing the sample was heated in a furnace. The fluorination occurred in a hermetically sealed volume with a large excess of fluorine (approximately five times the amount necessary for complete fluorination of the sample). The relative change in the amount of superconducting phase for a given sample was determined from the change in its magnetic susceptibility at 10 kHz.

The interaction of Y–Ba cuprate with fluorine was studied in the temperature interval 20–310 °C and fluorine pressure 0.1–1 atm. In most cases the properties of the reaction products differed very little from those of the starting compound. Weight control is thus important as the method of investigation.

Fig. 1(*a*) shows the dependence of the relative gain in weight of the powdered sample $YBa_2Cu_3O_{6.9}$ on fluorine pressure at different temperatures. For all reactions the starting powder weighed about 150 mg and the interaction time was 4 h. In the reaction at 20 °C at $p_{F_2} = 1$ atm the weight of the sample increases by about 10%. This corresponds to a bulk chemical composition of the sample $YBa_2Cu_3O_{6.9}F_{3.5}$ (assuming that only fluorine addition takes place). At higher temperatures the weight gain of the samples sharply decreases to only 1.4% at 107 °C. Analogous results were obtained at lower fluorine pressures [Fig. 1(*a*)]. Above 107 °C the weight gains in equal time intervals again increase.

This behaviour can be observed more clearly in Fig. 1(*b*), constructed from the data in Fig. 1(*a*). All three isobars have a minimum at 100 °C. It should be noted that at $p_{F_2} = 1$ atm the tetragonal samples are more difficult to fluorinate than the orthorhombic ones.

Fig. 2(*a*) shows X-ray diffraction patterns for samples fluorinated at $p_{F_2} = 1$ atm. The diffraction patterns at points B, C and D are practically identical with that of the initial sample A. There is only a noticeable decrease in the line intensities at D. The orthorhombic lattice parameters at points B, C and D do not differ, within the measurement errors, from those of the initial sample A [$a = 3.821(2)$, $b = 3.894(3)$, $c = 11.677(6)$ Å]. At point E the lines of the initial orthorhombic phase are replaced by those of fluorides (YF_3, CuF_2).

One possible reason for the absence of lines due to impurity

Mendeleev Commun., 1991, 1(1), 30–33

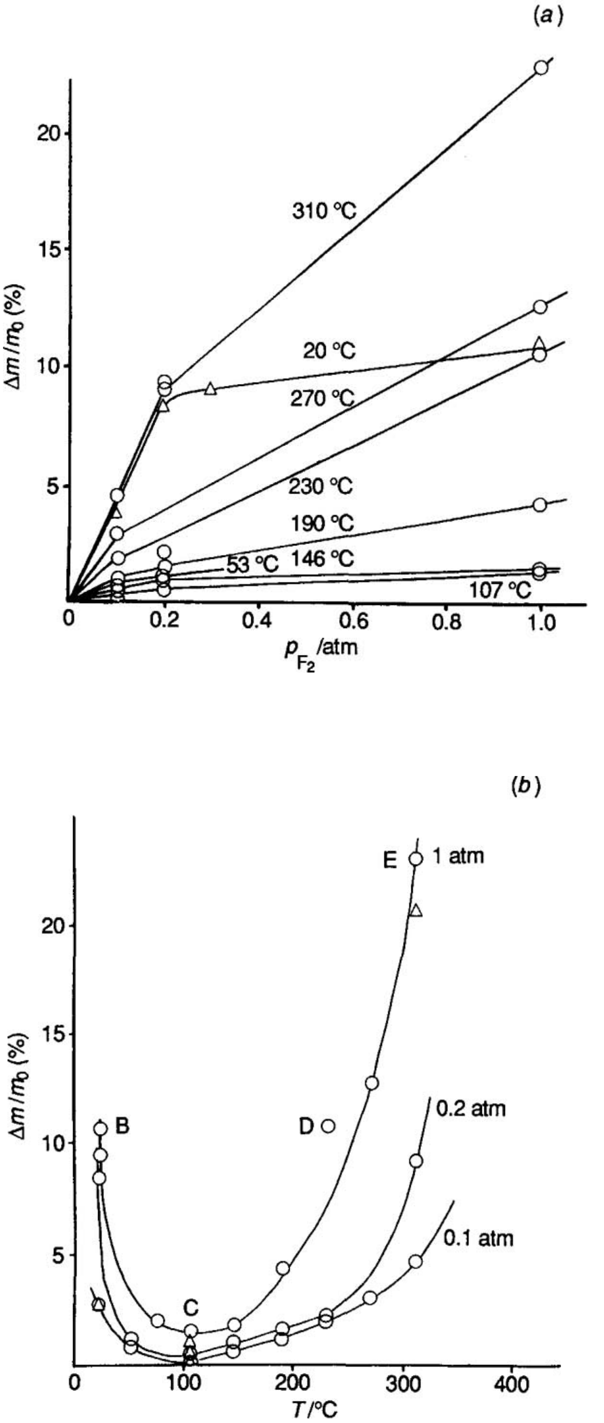

Fig. 1 (*a*) Isotherms and (*b*) isobars for the interaction of yttrium–barium cuprate with fluorine. Δm: change in sample weight, m_0: initial weight. (◯) Orthogonal sample, (△) tetragonal sample. Fluorination temperatures: B, 20; C, 107; D, 230 and E, 310 °C.

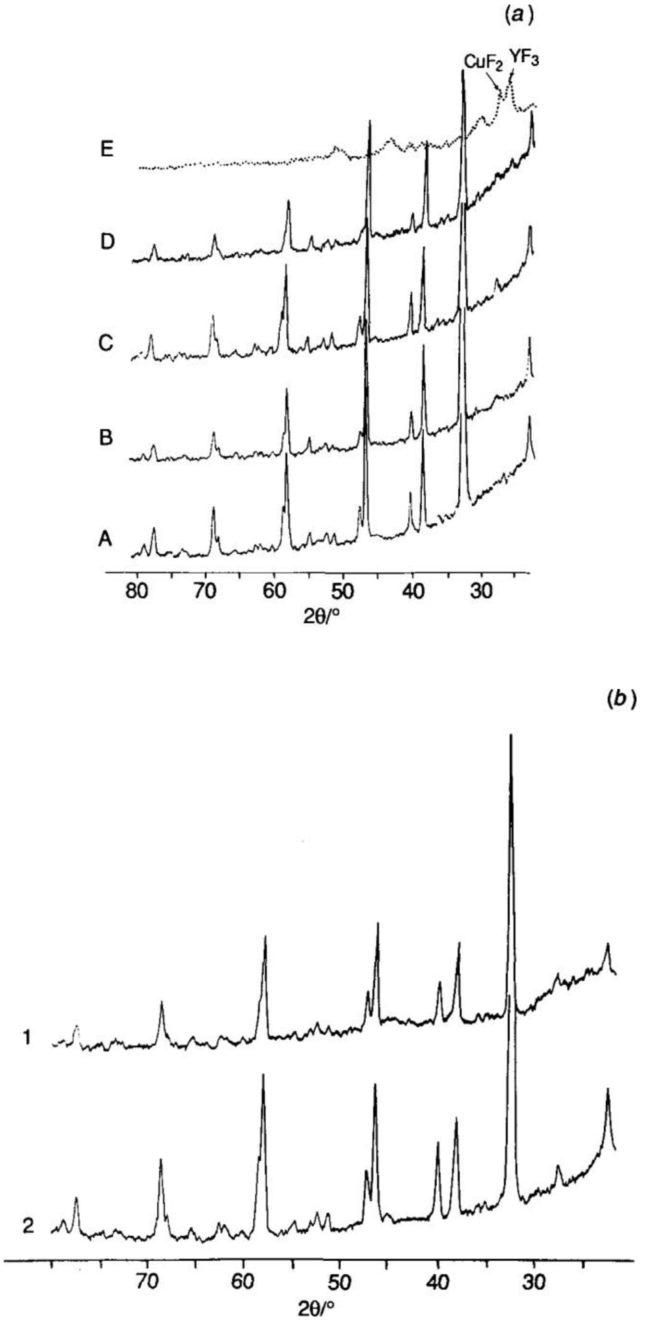

Fig. 2 Diffraction patterns: (*a*) for the initial $YBa_2Cu_3O_{6.9}$ (A) and for samples after fluorination at points B, C, D and E [Fig. 1(*b*)]; (*b*) for the flat surface of a ceramic plate of $YBa_2Cu_3O_{6.9}$, 1, after treatment with fluorine at 20 °C; 2, initial untreated surface

phase at considerable fluorine contents (⩾ 10 wt. %) is that the fluorides are present as an amorphous phase. With such a fluorine content the volume fraction of the amorphous phase must be considerable: 30% or more. The amorphous phase must be located on the surface of the grains of the initial phase. For a uniform distribution of the amorphous phase over these surfaces the thickness of the layer formed by this phase should be 5–10 μm or more. This will considerably weaken the diffraction line intensities[6] (partly due to the decrease in the amount of the main phase). Comparison of curves A and B in Fig. 2(*a*) (measured under identical conditions) indicates that the weakening of the main line intensities does not exceed 20–30%.

A similar result was obtained when the diffraction patterns were measured for the flat surface of an orthorhombic $YBa_2Cu_3O_{6.9}$ ceramic plate. It can be seen in Fig. 2(*b*) that after treatment with fluorine at 20 °C for 20 h (curve 1) the decrease in the line intensities is only 25–30% relative to those before fluorination (curve 2).

It is known that the fluorides and oxyfluorides of yttrium, barium and copper are thermally stable compounds (the least stable one, CuF_2, decomposes at temperatures above 600 °C).[8] The thermal stability of the fluorinated samples was checked as follows. By treatment with fluorine at 20 °C, a sample of nominal composition $YBa_2Cu_3O_{6.9}F_{4.2}$ was obtained for which the weight increase was 11.8%. This sample was kept under a vacuum of 10^{-2} Torr at 20 °C and weighed periodically. After 8–10 h the weight of the sample was decreased by more than 1%. In a previous study[6] it was shown that such treatment at 200 °C resulted in weight losses as large as 40–50% of the amount of fluorine taken up by the sample. Thus, it appears that a considerable portion of the fluorine taken up at 20 °C is easily lost upon evacuation. This is unexpected if the fluorine does indeed enter into the composition of the fluorides (or oxyfluorides).

The model of the interaction which is based only on the formation of an amorphous film of fluorides on the surface of the solid phase does not agree readily with the data in Fig. 1(*a*, *b*). According to this model, the rate of formation of the fluorides must increase with increasing temperature and the minimum at 100 °C is thus difficult to explain.

The perovskite-like crystal structure of Y–Ba cuprate is known to contain a considerable number of oxygen vacancies. In the orthorhombic modification $YBa_2Cu_3O_7$, more than 20% of the oxygen sites are unoccupied. Since the oxygen ions are the largest species in this structure, the lattice has a large unoccupied vacancy volume of 10–15% of the phase volume. An unoccupied volume within the structure of a substance is necessary for intercalation. Taking into account these considerations, the interaction of Y–Ba cuprate with gaseous fluorine can be represented by reactions (1) and (2). The reversible reaction (1) is the insertion of fluorine molecules into the free volume of the solid phase. Reaction (2) is the interaction of fluorine with the atoms of the crystalline matrix.

$$YBa_2Cu_3O_y + iF_2 \rightleftharpoons YBa_2Cu_3O_y(F_2)_i \qquad (1)$$

$$YBa_2Cu_3O_y + zF_2 \rightarrow z_1YF_3 + z_2BaF_2 + z_3CuF_2 + y/2\,O_2\uparrow \qquad (2)$$

Reaction (1) appears to be favoured by the convenient ratio of the oxygen ion radius (1.4 Å) to the Van der Waals radius of fluorine (1.35 Å). This process proceeds rapidly even at 20 °C.† With increasing temperature the rate of the reverse reaction (1) increases, *i.e.*, the number of intercalated molecules must decrease. For example, the portion ABC of the isobar in Fig. 2 corresponds to this. It can be assumed that at point C the rates of the forward and reverse reaction (1) are the same, *i.e.* the intercalation is at a minimum.‡ With further increase in temperature the process occurs mainly by reaction (2) which terminates at point E with destruction of the initial crystal structure [Fig. 2(*a*), E]. It appears that the amorphous phases of fluorides found on the grain surfaces are formed at this stage.[1,3]

The fluorine molecules in the oxygen vacant sites do not seem to cause any substantial distortions in the crystal structure, and the lattice parameters practically remain unchanged. Thus, the intercalation model of the interaction of Y–Ba cuprate with fluorine is in satisfactory agreement with the experimental data.

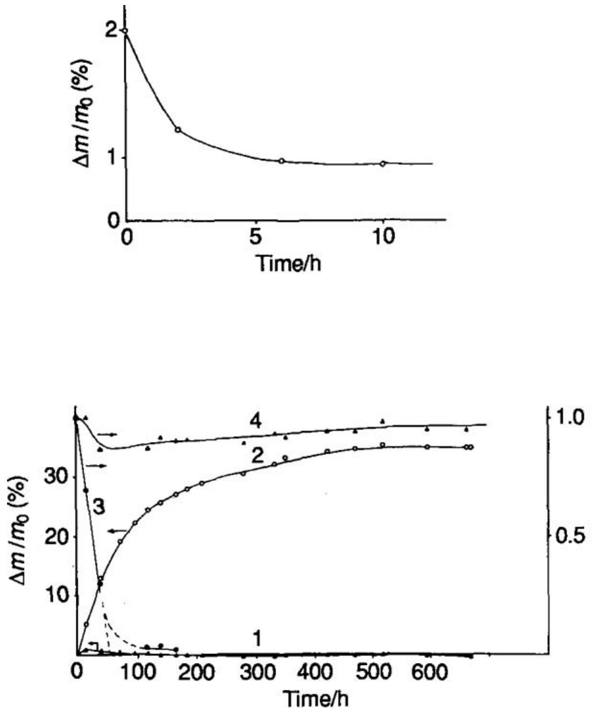

Fig. 3 (*a*) Relative change in weight of a fluorinated sample in vacuum of 10^{-2} Torr at 20 °C [a probable manifestation of the reversible reaction (1)]. (*b*) Relative changes in weight and amount of superconducting phase for initial and fluorinated (powder) samples on exposure to saturated water vapour at 30 °C: 1 (△), change in weight of fluorinated sample; 2 (○), change in weight of initial orthorhombic sample; 3 (●), change in superconducting phase content for initial sample; 4 (▲), change in superconducting phase content for fluorinated sample.

Fluorine intercalation effectively inhibits the degradation processes caused by water vapour. Fig. 3(*b*) compares the interaction of powdered samples of $YBa_2Cu_3O_{6.9}$ and $YBa_2Cu_3O_{6.9}F_{2.54}$ with saturated water vapour at 30 °C. In the initial sample superconductivity is completely destroyed after approximately four days, with the sample weight increasing by about 15%. The fluorinated sample shows almost no change in weight or properties 30 days or more.

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References

1 A. Tressaud, J.P. Chaminade, K. Amine, L. Nganga, J.M. Dance, M. Lahaye, J.P. Bonnet, B. Chevalier, J. Etourneau and R. Tournier, *J. Less Common Met.*, 1989, **151**, 237.

2 J.A. Stuart, P.K. Davies and T.P. Feist, *Solid State Ionics*, 1989, **32**, 1100.

3 S.M. Zahurak, D.W. Murphy, S. Nakahara, W.W. Warren, D.M. Krol, A.M. Thayer, D.C. Douglass, G.F. Brennert, S.H. Glarum, E.M. Gyorgy, S.M. Fine and M. Greenblatt, *Solid State Ionics*, 1989, **32**, 1104.

4 A. Tressaud, B. Chevalier, B. Lepine, K. Amine, J.M. Dance, L. Lozano, J. Darriet, J. Etourneau, R. Tournier, A. Sulpice, P. Lejay, J.L. Diot and P. Maestro, *Solid State Ionics*, 1989, **32**, 1109.

5 J.M. Dance, A. Tressaud, B. Chevalier, J. Darriet and J. Etourneau, *Solid State Ionics*, 1989, **32**, 1188.

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† For comparison, $YBa_2Cu_3O_{6.9}$ does not interact with chlorine at 20 °C (the chlorine Van der Waals radius is 1.80 Å).

‡ The presence of fluorine in the reaction products may be due to (*i*) the presence of 'residual' intercalation compounds or (*ii*) binding of fluorine by reaction (2).

Mendeleev Commun., 1991, 1(1), 30–33

6 V.V. Lisitsa and Yu.I. Vesnin, *Vzaimodeistvie kuprata ittria–baria s ftorom pri 20 °C*, (The interaction of yttrium–barium cuprate with fluorine at 20 °C). Preprint No. 89-23, Institute of Inorganic Chemistry, Academy of Sciences of the USSR, Siberian Branch, 1989.

7 C. Perrin, O. Pena, A. Dinia, M. Sergent, G. Fonteneau, P. Christensen, J. Lucas, P. Burlet and J. Rossat-Mignot, *Physica C*, 1989, **162**, 889.

8 *Gmelins Handbook*, SN 60, vol. 1B, Verlag Chemie, Weinheim Lif. 1, p. 199.