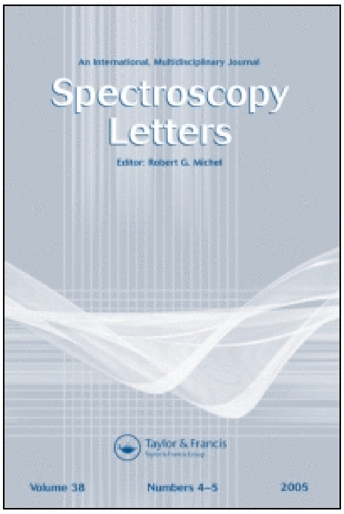

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Y. M. Guo[a]; R. A. Condrate Sr.[a]; J. A. Taylor[a]; J. R. Lagraff[a]; E. C. Behrman[a]
[a] Institute for Superconducting Ceramics NYS College of Ceramics at Alfred University, Alfred, NY

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RAMAN SPECTRA OF $YBa_2Cu_3O_{7-y}$ WITH DIFFERENT TYPES OF FLUORINE ADDITIONS

KEY WORDS: Raman spectra, superconductors, cuprates, fluorine additions, NF_3 annealing, structure

Y.M. Guo, R.A. Condrate, Sr., J.A. Taylor, J.R. LaGraff and E.C. Behrman
Institute for Superconducting Ceramics
NYS College of Ceramics at Alfred University
Alfred, NY 14802

ABSTRACT

Raman spectra have been measured and structurally interpreted for $YBa_2Cu_3O_{7-y}$ treated by different types of fluorine additions, including both initially doping appropriate fluorides into the starting materials to be fired, and NF_3 treating of the pure superconductor oxide. Both x-ray diffraction and low-temperature inductance measurements have also been conducted. All presented data indicated that phase impurities were generated during the former processes. However, related data indicated that NF_3 treatment of the pure oxide samples generated no new crystalline phases, but caused substitution or addition of F at O sites in the oxide phase.

INTRODUCTION

Recent investigations have shown that the fluoridation of $YBa_2Cu_3O_{7-y}$ materials can favorably influence their properties, depending upon the nature of the treatment.[1-3] For instance, NF_3 treatment of the pure superconducting oxide will not degrade its superconductivity.[4] Moreover, its chemical stability against water corrosion and its durability improves.[5] Such possibilities of properties alterations depend upon how fluorine interacts with the superconducting phase in the resulting structural product. In this study, we will determine how fluorine structurally interacts within the final resulting products from two types of fluoridation processes using both Raman spectroscopic and x-ray powder diffraction data. We will investigate F-containing products that were prepared either by initially doping appropriate fluorides into the starting mixtures to be fired, or by NF_3 treatment of the pure superconducting oxide material.

EXPERIMENTAL PROCEDURES

As mentioned earlier, two types of chemical processes were used in this investigation in order to attempt to replace O by F in the superconducting material. The molar content (X) of fluorine in the investigated materials was on the basis of the compositional formula ($YBa_2Cu_3O_{7-y}F_X$). The first fluoridation process involved mixing together the appropriate amounts of Y_2O_3, $BaCO_3$ and CuO with appropriate amounts of either YF_3, BaF_2 or CuF_2 in order to prepare $YBa_2Cu_3O_{7-y}F_X$ materials containing various controlled amounts of fluorine. The doping with CuF_2 was carried out in a dry box with flowing dry nitrogen in order to minimize reaction with the water in the atmosphere. The mixtures were ground in dry alcohol. These materials were heated slowly in aluminum crucibles to ca. 920°C and held for 12-15 hrs within an air atmosphere. The samples were then cooled, reground and refired under the same conditions. This cycle was repeated three times. The second fluoridation process involved annealing pure $YBa_2Cu_3O_7$ materials in gaseous NF_3. The powders were heated at 250°C (in a tube furnace) under an NF_3 atmosphere for 5-10 minutes. The soaking was followed by cooling the sample in a dry nitrogen atmosphere.[4,5] The fluorine contents of the samples were calculated from their weight gains during treatment.

X-ray powder diffraction data were measured with a Siemens diffractometer using Cu K_α radiation. The investigated powdered samples were mounted on either a zero-background quartz plate that was cut perpendicular to the c-axis or a side-loaded drift holder. A silicon or a copper and fluorophlogophite internal standard were used for the least-squares refinement of the pattern calibration for instrumental deviations.

Raman spectra were measured for powdered samples using an Instruments SA spectrometer with an Innova 90 argon ion laser. The spectra were excited with both the green (514 nm) and the blue (488 nm) line of the laser using 90° optics. Investigated powder samples were ground and then were pressed into pellets under a pressure of 20,000 psi in an evacuated die. Each pressed pellet was placed on a rotating cell, and then spun during spectral measurement.

The low-temperature inductances were measured for investigated materials using an impedance bridge at an oscillator voltage of 0.1 V (60 mA) and a frequency of 500 KHz. Each investigated sample was placed in a pyrex glass vial in the area crossing the magnetic flux. When the sample was cooled, there could be a large decrease in the magnetic permeability of the material if it passed into the superconducting state. Therefore, a superconducting phase used as the core of a solenoid would show a drop in inductance at T_c. The change in inductance at T_c would correspond to the precentage of superconducting phase in the material.[6]

RESULTS AND DISCUSSION

The investigated F-containing $YBa_2Cu_3O_{7-y}$ samples were formed by annealing the pure ceramic superconducting materials in NF_3 using same procedures as samples that were characterized in an earlier study by LaGraff et al.[4] As noted earlier, these materials showed no degradation of superconductivity upon the treatment of the oxides with NF_3. As a matter of fact, several of the superconductivity-related properties improved. For instance, plots of Meissner state magnetization (M_m) and the diamagnetic shielding magnetization (M_d) versus fluorine content indicated substantial increases in both the flux exclusion and expulsion with increasing fluoride content. Also, the percent Meissner effect (M_m/M_d) at 4.5 K showed the same tendency. However, there was no significant change in the critical temperature (T_c) with fluorine addition. Also, the chemical stability of the superconducting material to water corrosion improved with the fluorine addition.[5] In contrast, the superconductivity degraded significantly for F-containing $YBa_2Cu_3O_{7-y}$ materials that were prepared with the metal fluoride additives with respect to that of the related pure ceramic oxide superconductor. For instance, this effect on superconductivity is illustrated in Fig. 1 where change in inductance at T_c versus fluorine content is plotted for the various metal fluoride additives. The drop in apparent diamagnetic response with added fluoride content involving the three different additives clearly indicates a drop in the percent of superconducting phase that is present with increasing fluoride content. Also, these latter treated materials were less stable to

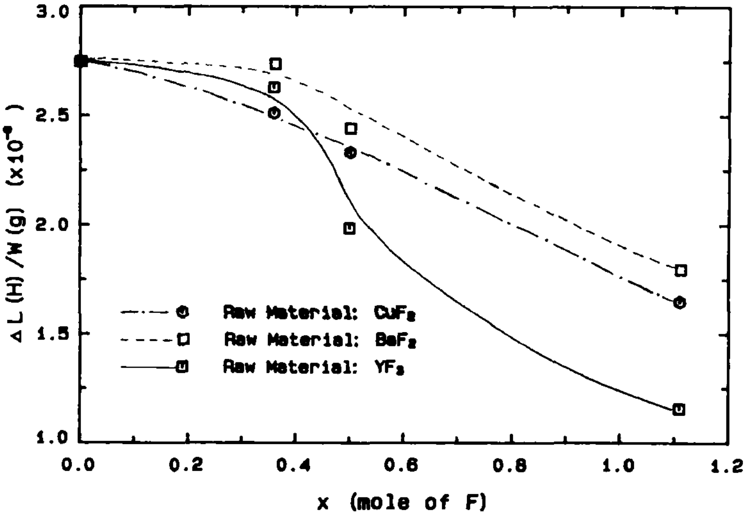

Figure 1: Impedance data for 1:2:3 materials containing various molar amounts of fluorine (X) from the different additives.

water corrosion than samples prepared by annealing in NF_3. Such differences in physical and chemical properties must relate to structural differences in the different treated materials.

The x-ray powder diffraction patterns that are associated with the investigated F-containing superconducting materials prepared by the NF_3 annealing process were discussed earlier by LaGraff et al.[4] Comparison of the diffraction patterns for the related nonfluoridated and fluoridated 1:2:3 samples indicated that with increasing fluorine content, the a-axis expanded while the b- and c-axes contracted, producing a systematic decrease in orthorhombic distortion. No growth of secondary crystalline phases with increased fluoride content was noted. Also, no broad amorphous humps were detected in the x-ray diffraction patterns of the samples with the illustrated fluorine contents, indicating the presence of an amorphous phase. The interpretation of the neutron diffraction patterns for the fluoridated materials was consistent with the interpretation of the x-ray diffraction data.[4] Interpretation of diffraction data indicated fluoride atoms occupying oxygen sites in the superconducting oxide phase.

Figures 2-4 illustrate the x-ray powder diffraction patterns which were measured for the materials containing different amounts of fluorine that were prepared by solid-state reactions involving additives of YF_3, BaF_2 and CuF_2, respectively. Pure materials containing only the fluorine-containing superconducting phase could not be produced by these reaction techniques. X-ray peaks associated with the 1:2:3: phase along with those of phases such as BaF_2, Y_2BaCuO_5, CuO and barium cuprate were detected in all of their diffraction patterns. The resulting relative concentrations of the latter phases were dependent upon the type and amount of metal fluoride additive that were used in the particular reaction process.

Fig. 5 illustrates the atomic arrangement within the unit cell of $YBa_2Cu_3O_7$. This illustration defines the locations of Cu (1) and Cu (2) along with those of O (1), O (2), O (3) and O (4) within the unit cell. Certain vibrational bands in the Raman spectra will be discussed in terms of vibrational modes involving some of these atoms in the unit cell of the superconducting 1:2:3 phase.

Figs. 6-8 illustrate the Raman spectra of fluorine-containing materials prepared by the additive solid-state reaction process for samples containing various added amounts of YF_3, BaF_2 and CuF_2, respectively. Earlier, we noted that the analysis of the x-ray powder diffraction patterns indicated

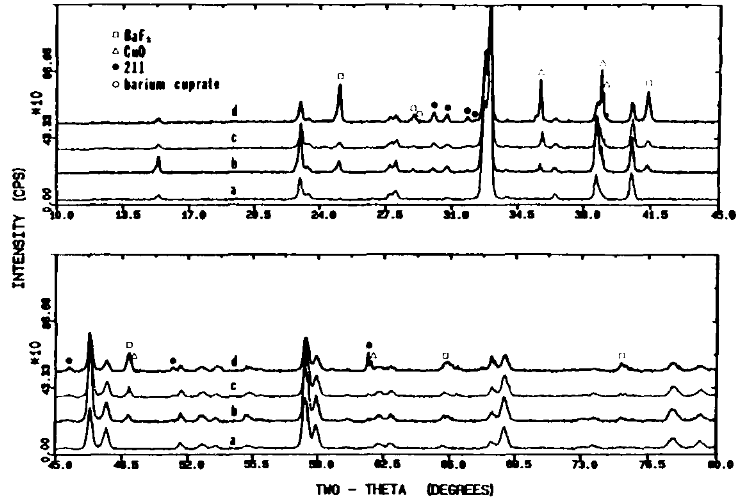

Figure 2: X-ray powder diffraction patterns of 1:2:3 materials containing various molar amounts of fluorine (X) from the addition of YF_3: a) x=0.00, b) x=0.36, c) x=0.50 and d) x=1.11.

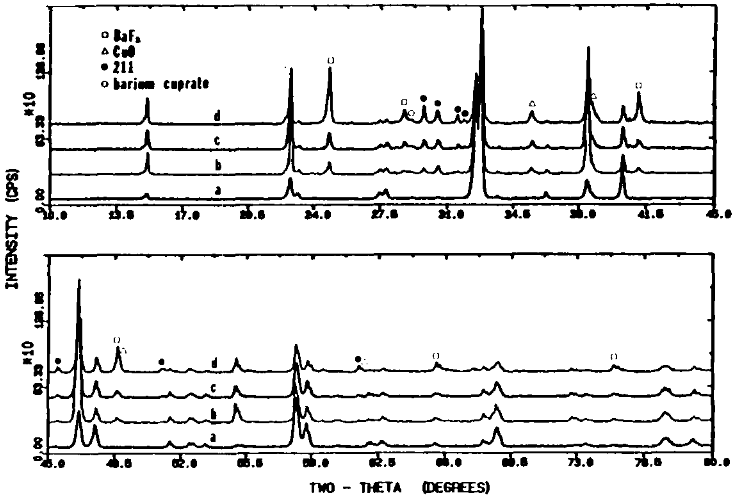

Figure 3: X-ray powder diffraction patterns of 1:2:3 Materials containing various molar amounts of fluorine (X) from the addition of BaF_2: a) x=0.00, b) x=0.36, c) x=0.50 and d) x=1.11.

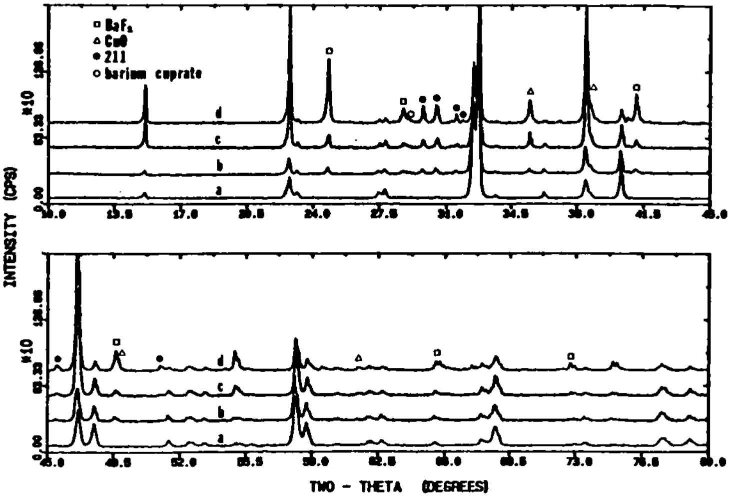

Figure 4: X-ray powder diffraction patterns of 1:2:3 materials containing various molar amounts of fluorine (X) from the addition of CuF_2: a) x=0.00, b) x=0.36, c) x=0.50 and d) x=1.11.

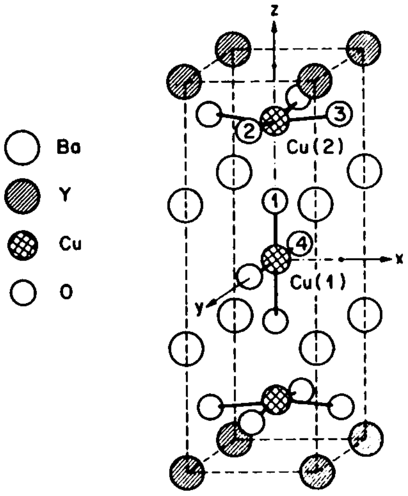

Figure 5: Atomic arrangement in unit cell of $YBa_2Cu_3O_7$.

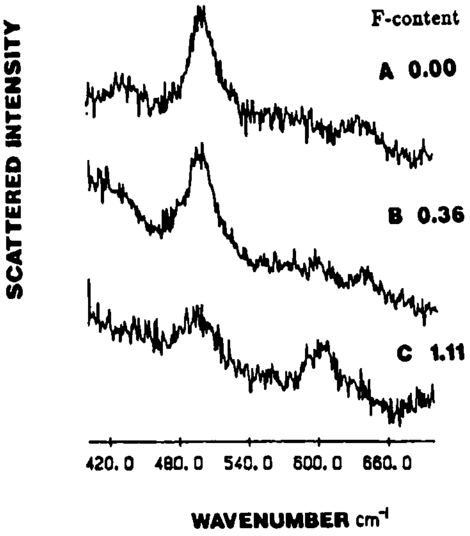

Figure 6: Raman spectra of 1:2:3 materials containing various molar amounts of fluorine (X) from the addition of YF_3.

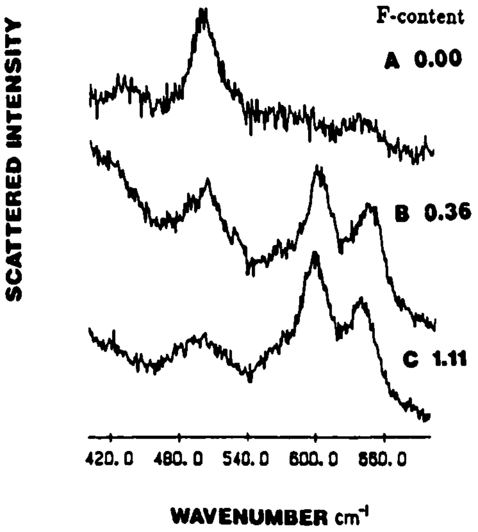

Figure 7: Raman spectra of 1:2:3 materials containing various molar amounts of fluorine (X) from the addition of BaF_2.

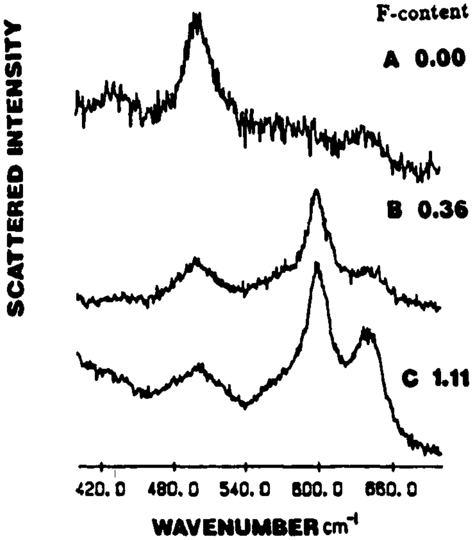

Figure 8: Raman spectra of 1:2:3 materials containing various molar amounts of fluorine (X) from the addition of CuF_2.

the presence of varying amounts of crystalline phases such as the 1:2:3 superconducting phase as well as BaF_2, Y_2BaCuO_5, CuO and barium cuprate. BaF_2 and CuO were not detected in the illustrated region of the Raman spectra for all of the materials that were prepared by solid-state reactions because these phases do not possess strong first order Raman bands in this region. The band at ca. 500 cm^{-1} that occurs for 1:2:3 phases is observed in the Raman spectra of all prepared samples. The spectra for samples prepared by using BaF_2 or CuF_3 as an additive possess a band at ca. 640 cm^{-1} along with other bands indicating the presence of a barium cuprate phase.[7] One may note that the relative intensity of the above-mentioned Raman band at ca. 640 cm^{-1} is quite strong compared to the band at ca. 500

cm^{-1} for the 1:2:3 phase even though x-ray diffraction indicates that the concentration of the cuprate phase is much lower than that of the latter phase. This observation indicates that Raman spectra is a more sensitive tool for detecting barium cuprate in these type of treated materials. This Raman band was not detected for samples prepared with YF_3, indicating that barium cuprate was not formed at comparable relative concentrations during its reaction process. A band appears at ca. 600 cm^{-1} in the Raman spectra of all material that were prepared by using either of the three additives. This Raman band can be related to a strong Raman band at this spectral location which can be assigned to Y_2BaCuO_5. However, this band can be overlapped in the case of two of the preparations by a weaker Raman band which appears in this region for barium cuprate along with the much stronger earlier-mentioned Raman band at ca. 640 cm^{-1}.[7] The intensity of the band at ca 600 cm^{-1} increases with respect to the band at ca. 500 cm^{-1} for the 1:2:3 phase with increasing fluorine content, indicating that the concentration of Y_2BaCuO_5 increases relative to the concentration of the 1:2:3 phase. A band at ca. 590 cm^{-1} which could possibly give us information concerning fluorine substitution can not be resolved off the wing of the band at ca 600 cm^{-1}. The latter band is stronger and sufficiently broad to convolute the former weaker band within itself. The nature of the band at 590 cm^{-1} will be discussed below.

Fig. 9 illustrates the Raman spectra of NF_3 treated materials containing various amounts of fluorine. The characteristic band at ca. 500 cm^{-1} for the superconducting phase appears in the illustrated region of the spectra for all of the investigated materials, indicating that a superconducting phase is present in all of these materials. One may also note that a Raman band is not observed in the 570-595 cm^{-1} region for the untreated oxide

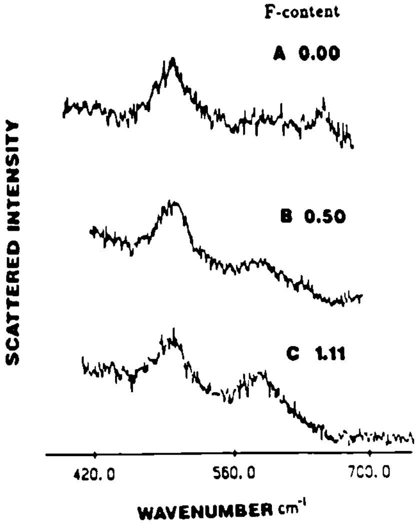

Figure 9: Raman spectra of 1:2:3 phase prepared by NF_3 annealing containing various molar amounts (X) of fluorine.

material which is consistent with the expectation of a pure polycrystalline material containing only $YBa_2Cu_3O_7$ with no significant nonstoichiometry.[7] This Raman band is forbidden for the expected crystalline phase if nonstoichiometry does not exist. However, one may observe that a Raman band does appear at ca. 590 cm^{-1}, and increases its intensity with increasing fluorine content. Earlier investigators observed bands in this region when the materials either possessed oxygen vacancies or involved metal substitution for copper. According to lattice dynamical calculations and inelastic neutron scattering, vibrational modes can occur in this wavenumber region for $YBa_2Cu_3O_7$.[8] An asymmetric stretching mode involving O (4) atoms occurs in this region which is forbidden as a first order mode in the Raman spectra but is allowed in the infrared spectra.[6] This mode can become Raman active by O (4) vacancy disorder, by substitution of other metal ions on the Cu (1) or by substitution of F ions on the O sites around Cu (1), causing a change in the local symmetries involving the Cu (1)-O (4) bonds. It appears that the Raman band which occurs at ca. 590 cm^{-1} for the fluorine-containing materials is due to replacement of F ions for O ions on O sites around the Cu (1) ion sites, causing the vibrational band to become Raman-active. This interpretation is consistent with the interpretation by LaGraff et al. for the x-ray and neutron diffraction data.[4] They suggested models in which either the fluorines occupy O (5) sites or the fluorines substitute into O (4) or O (1) sites with displaced oxygens moving into O (5) sites. The strongest effect in terms of intensity change would involve substitution of fluorines on the O (4) sites. For the investigated fluorine contents, there are no indications in the diffraction data with respect to amorphous humps, or in the electron microscopic data of an amorphous phase present in the investigated materials prepared by NF_3 annealing. This latter result is in sharp contrast to the results for annealing the 1:2:3 phase in an F_2 atmosphere.[9] The spectral data for NF_3 treated materials indicate that fluorine substitutes or adds directly into the network structure of the superconducting phase.

CONCLUSIONS

The following conclusions can be drawn on the basis of this investigation:

1. The structural interpretation of the Raman spectra for all of the investigated series of fluorine-containing materials is consistent with the interpretation of x-ray and neutron difraction data along with other properties of the materials.

2. Analysis of the Raman spectra for the fluorine-containing materials prepared by the solid-state reaction processes using either of the three metal fluoride additives indicated multi-phase compositions containing the 1:2:3 phase, Y_2BaCuO_5 and barium cuprate, whose relative concentrations were dependent upon process conditions. The inductance measurements for the various series of materials are consistent with the interpretation of increased non-superconductor phase development with increasing fluorine content.

3. Raman spectroscopy is more sensitive for detection of barium cuprate in fluorine-containing 1:2:3 materials than x-ray diffraction analysis.

4. Consistent with the earlier interpretation of x-ray and neutron diffraction data, analysis of the Raman spectra indicates that fluorine enters the crystal structure of the 1:2:3 phase. The fluorines either occupy O (5) sites or they replace oxygens at either O (1) or O (4) sites with displaced oxygens moving to O (5) sites. The largest intensity increases for the band at ca. 590 cm^{-1} should occur with fluorines occupying O (4) sites.

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