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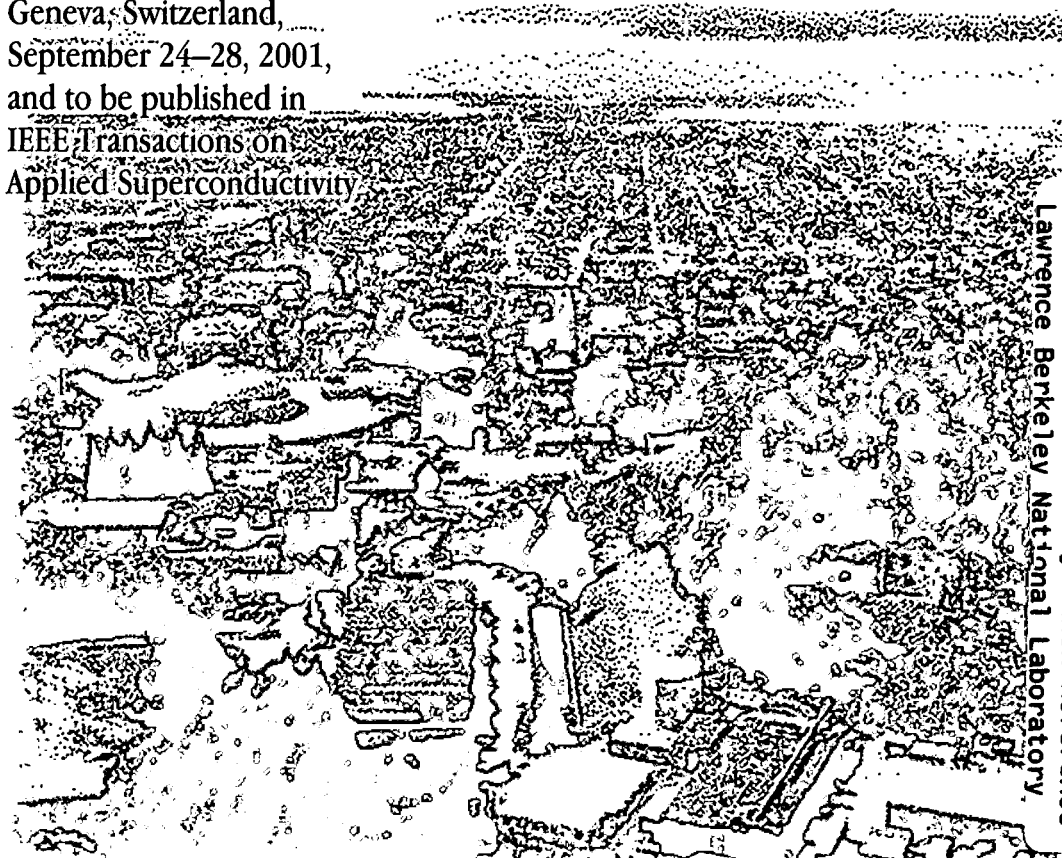
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N.M. Hamdan, P.V.P.S.S. Sastry, and J. Schwartz

Advanced Light Source Division

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**Magnetic Properties of Fluorinated Pb-Doped
Hg-1223 High T_c Superconductors**

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September 2001

Magnetic Properties of Fluorinated Pb-doped Hg-1223 High T_c Superconductors

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Abstract—Fluorination of Pb-doped $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (Hg-1223) system was investigated. Structural and magnetic measurements reveal that fluorine addition promotes the phase formation, optimize the charge carrier concentration, and enhance flux pinning. We report an increase in both the transition temperature and the critical current density through controlled fluorine incorporation. Even a possible change in the pinning mechanism in this technologically important system is suggested.

Index Terms—Fluorination, Hg-based, High T_c , Magnetic Properties

I. INTRODUCTION

Mercury based high temperature superconductors have the highest transition temperature (T_c) among all the high- T_c superconductors discovered so far. The T_c of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ (Hg-1223) is about 135 K at atmospheric pressure rising up to 164 K under high pressure. The critical current density values achieved so far, on the other hand are much less than that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ or Tl-1223, especially at temperatures close to T_c [1-3]. Several reports show that the critical current density and the phase formation of Hg-1223 can be improved through Re and Pb doping [4-6]. We have previously shown that the phase formation and superconducting properties of Re-doped Hg-1223 are enhanced through anion substitution [7]. Fluorine addition to this material is believed to have an effect on the charge carrier concentration in the CuO_2 planes, as fluorine is more electronegative than oxygen. Furthermore, because the ionic radius of fluorine is smaller than that of oxygen, the crystal anisotropy may also change due to replacement of oxygen by fluorine. Therefore, we have anticipated a change in both the material and superconducting properties of this system.

We reported significant improvements in the material and superconducting properties of the overdoped Tl-1223 system through fluorine addition[3]. We have found that fluorine mainly replaces the oxygen site in the CuO_2 planes causing a decrease in the hole concentration in the overdoped

Tl-1223, and hence improve its superconducting properties [8,9]. Unlike Tl-1223, Hg-1223 is underdoped. Therefore we expect the mechanism of fluorine incorporation to be different in the later. It is known that the oxygen site in the mercury plane is only partially occupied in Hg-based oxides including Hg-1223 phase to the Thallium based system in which the corresponding site occupancy of this site is close to unity[10]. Therefore we expect that fluorine would prefer to occupy this empty site in Hg-1223. This explains the positive effect fluorine would have in optimizing the charge carrier concentration in both the overdoped Tl-1223 and the underdoped Hg-1223.

Recently, there have also been several reports on the fluorination of Hg-based superconductors [10-13]. Peacock et al. [10] reported an increase in T_c for the first five congeners of the mercurocuprate family through post-synthetic incorporation of elemental fluorine as an interstitial anion. On the other hand, Putilin et al., Abakumov et al. and Lokshin et al., [11-13] found that the transition temperature T_c of Hg-1201 does not increase after fluorine incorporation, and increases slightly upon fluorination of Hg-1223. There are no detailed studies on the effect of fluorination of Hg-1223 on phase formation, magnetic properties and critical current density even though these properties are directly related to the pinning forces and charge carrier concentration in the CuO_2 planes. In this paper, we report the effect of fluorine incorporation on the transition temperature and magnetization hysteresis.

II. EXPERIMENTAL PROCEDURE

$\text{Hg}_{0.8}\text{Pb}_{0.2}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y/\text{F}_x$ (HgPb-1223) samples were prepared with nominal fluorine content (weight ratio of BaF_2), $x = 0.000, 0.050, 0.120, 0.185, 0.285$ and 0.50 identified as F0, F1, F2, F3, F4, and F5, respectively. Stoichiometric amounts of commercial $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$, ReO_2 or PbO , were mixed, pressed into pellets and placed in an alumina liner. CaHgO_2 and BaF_2 were placed in a separate alumina liner to act as the external sources for mercury and fluorine, respectively. Both the alumina liners were sealed in a quartz tube under vacuum. The heat treatment schedules followed were as reported earlier [7]. Samples were characterized by $\text{Cu-K}\alpha$ x-ray powder diffraction (XRD), and environmental scanning electron microscope (ESEM). Magnetization measurement as a function of temperature and magnetic field were carried out using a Quantum Design SQUID magnetometer up to 5.5 Tesla.

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The magnetization measurement as a function of temperature, were performed in 10 G applied magnetic field.

III. RESULTS AND DISCUSSION

The phase purity of the samples was investigated using XRD and ESEM techniques. XRD patterns of all the samples confirmed the samples are pure Hg1223. No noticeable changes were present between the XRD patterns of samples with varying F-contents. Figure 1 depicts XRD pattern of one of the samples indicating phase pure nature of the sample. The ESEM micrographs [7,14] show that fluorine addition promotes the growth of single Hg-1223 phase, with large platelet like grains ($\approx 50\mu\text{m}$) in both Re and Pb-doped Hg-1223 phase.

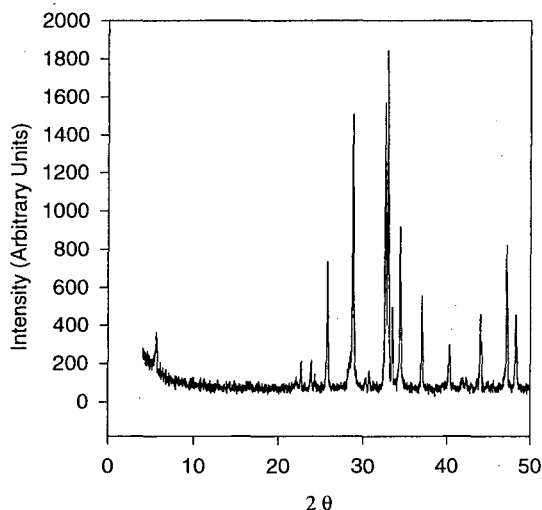
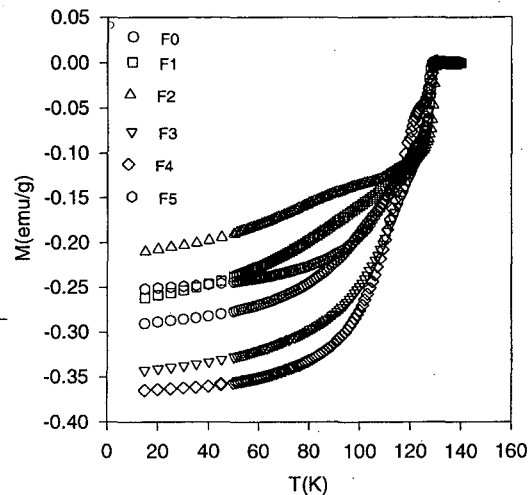


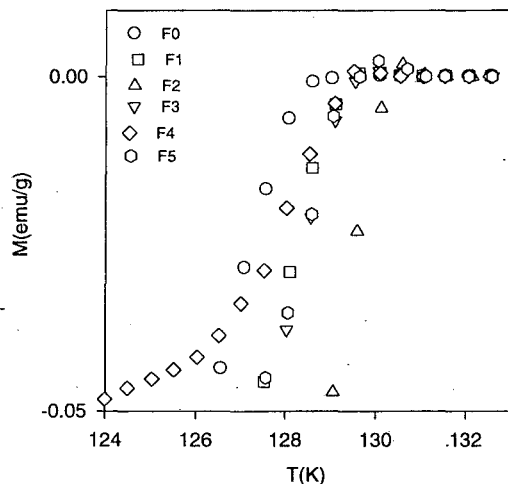
Fig. 1 Typical XRD Pattern for Pb-doped Hg-1223. The diffraction pattern shows the phase purity of the sample.

The transition temperature of the samples was determined from magnetization measurements as a function of temperature, as the samples were cooled in a 10 Oe applied magnetic field. Fig. 2a and Fig. 2b, show the variation of the magnetization of HgPb-1223 samples with temperature for samples with different fluorine content x .

The variation of the transition temperature with fluorine for HgPb-1223 system is shown in Fig. 3. It is clear from Fig 2 and Fig. 3 that the transition temperature of HgPb-1223 increases as fluorine is introduced up to a maximum value where it drops afterwards and saturates. As the transition temperature is directly related to the charge carrier concentration in the CuO_2 planes [3], we believe that fluorine incorporation in the under-doped HgPb-1223 material, optimizes the holes concentration in the CuO_2 planes. As fluorine favors to occupy an empty site, it would occupy the almost unoccupied oxygen site in the Hg-O plane discussed above.



(a)



(b)

Fig. 2: Magnetization as a function temperature for samples HgPb-1223 samples with different fluorine content.

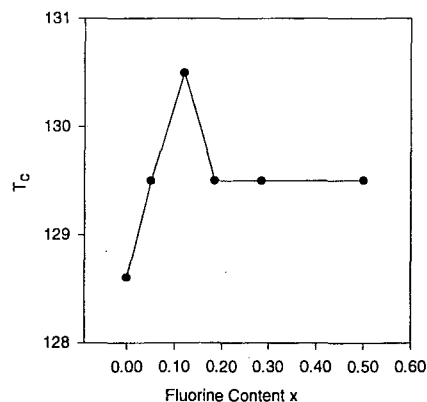


Fig. 3: variation of T_c with fluorine content x for the fluorinated HgPb-1223

Band structure calculations of Singh and Pickett suggest that because of Hg-O hybridization [15], each oxygen atom contributes only just over one hole into the CuO_2 planes. We believe that fluorine would show a lesser degree of hybridization with mercury due to its ionic nature, and therefore near one hole per fluorine atom in the Hg-O plane will be donated to the CuO_2 planes. This will result in increasing (optimizing) the hole concentration, and hence increase the transition temperature.

As more fluorine is introduced, all the unoccupied sites in the Hg-O planes will be filled. This will lead to more holes donated to the CuO_2 planes, and hence an overdoped state. Further increase of fluorine will not affect the charge carrier concentration in the CuO_2 planes, as there is no vacant state for fluorine to occupy. Its worth mentioning that we have shown that fluorine occupies the oxygen sites in CuO_2 planes in Tl-1223 [3,8-9]. In Tl-1223 system, fluorine was introduced internally in the form of CuF_2 , where it has the chance to compete with oxygen from the beginning of the reaction as other impurity phases were formed. But in the present work on Hg-based material, there are two major differences (i) the oxygen site in the Hg-O plane is almost vacant, while the corresponding site in Tl-O plane in Tl-based compounds is almost fully occupied, (ii) Fluorine is introduced as an external source in Hg-1223, while it was introduced internally with the reaction as CuF_2 in Tl-1223. We have reported earlier that transition temperature does not change upon fluorination of the Re-doped Hg-1223, following the same preparation technique [7]. As Re is believed to be in +4 valence state, while Pb is in +2 state, the unoccupied oxygen site in Hg-O of the un-doped Hg-1223, will be more occupied in the Re-doped case than that of the Pb-doped case.

Fig. 4 shows the variation of the magnetic hysteresis loops for samples with different fluorine contents cooled in zero field to 4.2 K. According to Bean's model, the critical current

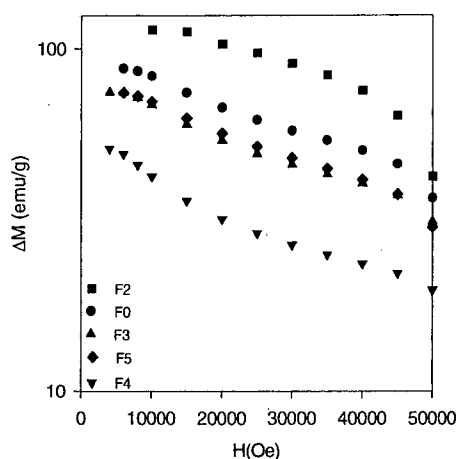


Fig. 4: Width of the isothermal hysteresis loops for samples Hg-Pb-1223 with different fluorine content at 4.2 K. ΔM is proportional to the critical current density.

density J_c is proportional to ΔM . The figure shows a considerable increase in J_c for the sample F2, which is the same sample that has a maximum transition temperature shown above. This also shows that variation in the charge carrier concentration not only affect the transition temperatures, but also changes the density of effective pinning centers that will affect the J_c and the irreversibility line position [16]. ΔM was doubled for the sample F2 compared to the fluorine free sample. fluorine free sample and the sample F2 is by a factor of 2. We also notice a change in the field dependency of J_c as fluorine is increased, also indicating a change in the pinning mechanism in this system[3].

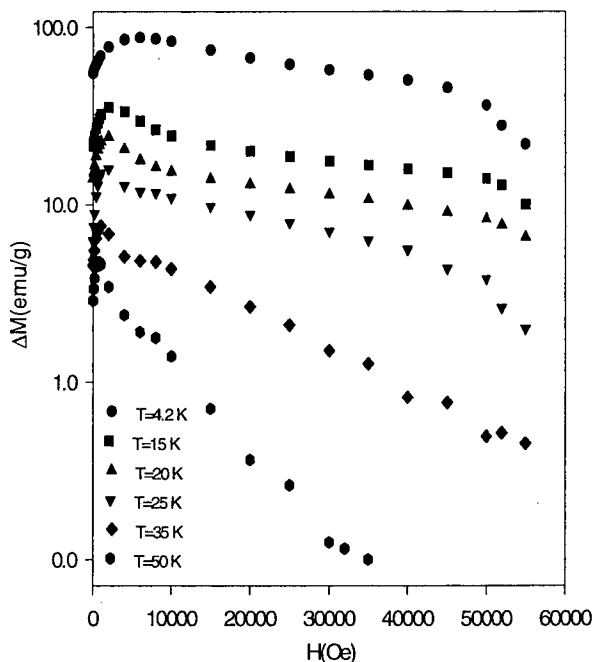


Fig. 5 Width of the isothermal hysteresis loops, up to 5.5 T, for the fluorine free Hg-Pb-1223 at various temperatures.

Fig. 5 and Fig. 6 show the variation of ΔM with field at various temperatures for fluorine free sample F0, and the sample F2 which has the highest transition temperature and the highest critical current density, respectively. The figures clearly show a considerable improvement in both the field and temperature dependence of ΔM for the sample F2. ΔM has a plateau-like behavior with field, both at low and high magnetic fields. This means that there has been a reduction of the weak links between the grains (low field). The high-field improvement of the variation of ΔM reflects that there have been improvements in the grain growth and enhancement of the pinning mechanisms within the grains [3]. This has also been confirmed by the formation of large grains (50-100 μm) for fluorinated samples were observed by ESEM [7,14].

Fig. 6: Width of the isothermal hysteresis loops, up to 5.5 T, for the F2 sample (the sample with highest T_c and highest J_c) at various temperatures.

The temperature dependence of ΔM has also significantly improved for the fluorinated samples. In fig. 6, ΔM decreases faster for $T=35$ K and 50 K, where it is still slowly decreases for the same temperatures in the sample F2. These improvements are particularly important for practical applications of this system.

IV. CONCLUSIONS

Fluorination of Hg-1223 system was performed by introducing fluorine as an external source in the reaction to avoid formation of impurity phases. Phase formation of the Hg-1223 phase was improved through fluorination as large grains were formed. The transition temperature of the samples increased with increasing fluorine content, up to a maximum value, then it drops and saturates for higher fluorine values. This shows that the hole concentration in the CuO₂ of this underdoped Hg-1223, increased to its optimum value for the sample F2, then it starts increasing to the overdoped region for higher fluorine contents. Fluorine addition also increased the pinning centers and changed the pinning mechanism between grain and within the grains. This is clear from the improvements in both the field and temperature dependence of the critical current density. These improvements could not be achieved through cation substitution as several groups already tried due to the fact that these cations may go to more than one place or the so called inherent doping will take place. These improvements are of great importance from both the basic understanding of the mechanism and the role of the charge carrier transfer in this system, and from the technological point of view.

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