Magnetic alignment in 2212 Bi-based superconducting system: Part I. Magnetic orientation of $Bi_2Sr_2Ca_{1-x}(RE)_xCu_2O_{8-y}$ [(RE) = Gd, Dy, Ho, Er] powder dispersed in epoxy resin at room temperature[a]

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The magnetic anisotropy of rare-earth substituted 2212 materials ($Bi_2Sr_2Ca_{0.8}RE_{0.2}Cu_2O_x$ with RE = Gd, Dy, Ho, Er) is put into evidence. Superconducting powder dispersed in epoxy resin is oriented under an external magnetic field (4 T) in a direction that depends on the nature of the rare-earth used in the substitution. Both directions of observation (parallel or perpendicular to the field) were investigated. Splitting of (00*l*) peaks is neatly observed and discussed.

I. INTRODUCTION

A major problem encountered in unoriented polycrystalline materials is the very low value of the critical current density which characterizes them, as compared to textured materials such as thin films or oriented ceramics. It is a direct consequence of the shortness and the anisotropy of the coherence length in such type II superconductors. The existence of grain boundary current barriers seems thus to be responsible for these low J_c values. It is thus necessary to texture the materials in order to enhance their transport properties by decreasing the unfavorable grain boundaries.

Several techniques have been put forward in order to achieve texturation: uniaxial pressing at room temperature,[1] hot forging,[2] melt texturing growth,[3] and magnetic field orientation in resin[4] or metallic matrix,[5] or a combination of the latter two techniques.[6,7]

These methods have been extensively applied to texture YBCO-based systems and in particular to melt texturing growth in magnetic field.[8,9] This is not the case for bismuth-based materials for which very few approaches, in particular the uniaxial pressing, have been reported.[10] The present work deals with the possibility to align Bi-based cuprates containing rare-earth (RE) elements under a magnetic field.

Chen *et al.* in a conference report already reported some investigation of $Bi_2Sr_2CaCu_2O_y$ samples where Ca is replaced by a RE ion.[11] Even though it can be understood from their report that much more work than that presented was performed, a systematic investigation is lacking. For example, only one x-ray spectrum and two x-ray spectra for RE = Ho and Er with $x = 0.5$ can be seen in Ref. 11, and only for the face of observation perpendicular to the magnetic field. The field value was not precisely given either (it is between 1 and 15 T), and the fine peak structure seems nonexistent, although nowadays one expects some peak splitting due to the possible appearance of various (so called N and D) phases[12] in such 2212 substituted compounds. An interesting point in the Chen *et al.* report is the observation that the RE induced grain alignment can

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be different for YBCO and BSCCO compounds, in particular when RE = Gd. Otherwise, Chen *et al.* found that light RE (before and included Ho) align with the *c*-axis parallel to the field, but perpendicular for Er and heavier RE.

Therefore, we investigated more systematically the RE substitution at fixed concentration and for a known field. Different observation directions were used.

In this report we consider RE = Gd, Dy, Ho, and Er for a fixed $x = 0.2$, and concentrate our attention to wide band x-ray spectra in order to indicate and discriminate between alignment effects on different peaks. We observed that alignment quantification formulae from x-ray data were, however, quite unreliable. Therefore we simply compare visually the data. It should be noticed that alignment occurs because of an enhanced magnetic anisotropy of the crystals due to RE-substitution. In nonsubstituted materials, the anisotropy is only caused by the superconducting CuO_2 layers, and the grains always orient with their *c*-axis parallel to the applied magnetic field. In rare-earth substituted materials, the grains align with their *c*-axis parallel or perpendicular to the field direction, as a function of the nature of the rare-earth ion. The often very large value of the rare-earth magnetic moments thus allows good alignment in substantially low fields.

Splitting of $(00l)$ peaks in x-ray patterns was observed and is discussed through a binary phase coexistence model.

II. EXPERIMENTAL DETAILS

The $Bi_2Sr_2Ca_{0.8}(RE)_{0.2}Cu_2O_{8-y}$ powder synthesis starts by mixing stoichiometric amounts of Bi_2O_3, $SrCO_3$, $CaCO_3$, $(RE)_2O_3$ [(RE) = Gd, Dy, Ho, Er] and $CuCO_3 \cdot Cu(OH)_2$. The mixture is treated at 820 °C for 48 h, including two intermediate grindings. Energy dispersive x-ray (EDX) analysis shows that the RE ions are well and homogeneously incorporated into the grains. Ca is missing with respect to that concentration found in pure 2212 synthesized by the same method.

The resulting powder (~1 g) is then mixed with an epoxy resin (~7 ml). Disk-shaped samples on some plastic support were then held in a horizontal magnetic induction of 4 T at room temperature for a few hours until the epoxy resin solidifies (Fig. 1). A zero field run was performed in each case for comparison.

III. RESULTS

The degree of alignment was checked by means of x-ray diffraction analysis using Cu K_α monochromatized radiation ($\lambda = 1.5406$ Å) with a Siemens D5000 diffractometer. X-ray powder diffraction patterns were recorded for the cross sections with planes parallel or perpendicular to the applied magnetic induction. Intensities
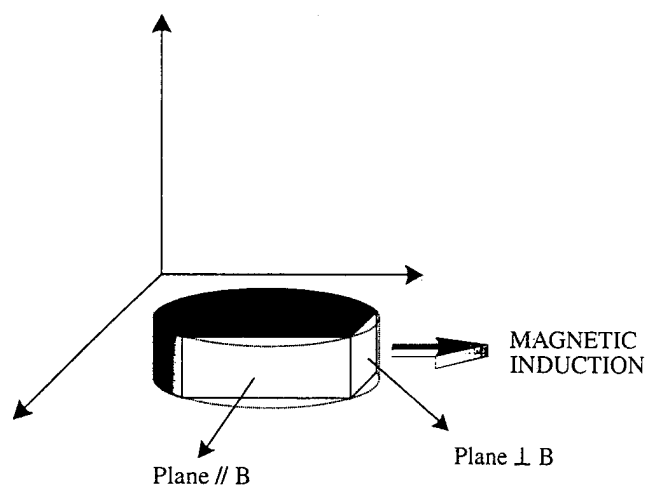

FIG. 1. Sketch of the experimental setup for the preparation of magnetically oriented 2212 powder dispersed in epoxy resin.

are given in arbitrary units. However, the same relative scale is used for a given compound. We consider that the bulk of the sample is probed since the disk-shaped sample has been cut in order to provide a parallel and a perpendicular plane to the magnetic induction (Fig. 1). The observed results are thus representative of the whole material and not only of a surface effect.

As depicted in Fig. 2(a) for the $Bi_2Sr_2Ca_{0.8}Gd_{0.2}Cu_2O_{8-y}$ compound, the x-ray diffraction spectra of the starting powder shows usual peaks of unoriented grains.[13] For the oriented sample with the observation plane parallel to B, the $(hk0)$ are the major peaks [Fig. 2(b)]; (110) and (200) reflection peaks are very much enhanced in the so-called oriented sample for the observation plane parallel to the magnetic field [Fig. 2(b)], when compared to the same unoriented
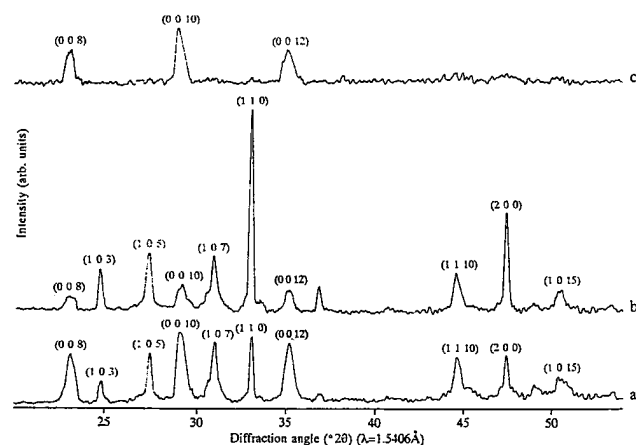

FIG. 2. X-ray diffraction patterns of $Bi_2Sr_2Ca_{0.8}Gd_{0.2}Cu_2O_{8-y}$ samples: (a) unoriented specimen; (b) oriented sample, observation plane parallel to the applied magnetic induction; and (c) oriented sample, observation plane perpendicular to the applied magnetic induction.

specimen [Fig. 2(a)]. This is in marked contrast with the observation plane perpendicular to the magnetic induction where only the (00*l*) reflection peaks, i.e., 008, 00$\underline{10}$, and 00$\underline{12}$ are seen. One should note that Gd is thus a "parallel" aligner, as mentioned by Chen *et al.*, but the diffractogram is here free of (*hk*0) and (*hkl*) peaks. It means that such samples in which calcium is partially substituted by gadolinium are oriented with their *c*-axis parallel to the applied magnetic induction. There is still some freedom left for orienting the (*hk*0) planes.

The same behavior is observed for the Dy (Fig. 3) and Ho (Fig. 4) substituted samples. They can be considered as *c* parallel to *B* aligners. In Fig. 3(c), we can already see a fine peak structure in the (00*l*) peaks when Ca is partly substituted by Dy. *A posteriori*, we can guess the presence of such a structure in the Gd spectrum. The (00*l*) peak splitting is very much manifested for the holmium case [Fig. 4(c)], and those (00*l*) peaks are the only ones visible when the observation plane is perpendicular to the applied magnetic induction. This is a much better result than that of Chen *et al.* who still observed "many" (*hk*0) and (*hkl*) peaks for the same experiment and who did not observe the peak splitting due to the partial substitution of Ca by a rare-earth.

The opposite behavior to that described above is observed in the Er-case: (*hk*0) reflection peaks are visible only in the observation plane perpendicular to the magnetic induction [Fig. 5(c)]. For this type of samples, measurements in the plane parallel to the applied induction [Fig. 5(b)] show that the (00*l*) peaks are proportionally much more intense than in the nonaligned material. Erbium can thus be considered as a *c* perpendicular to *B* aligner. Some splitting is seen in (00*l*)
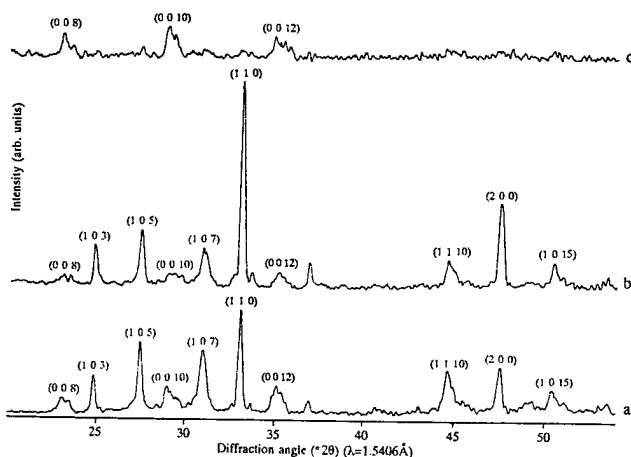
FIG. 4. X-ray diffraction patterns of $Bi_2Sr_2Ca_{0.8}Ho_{0.2}Cu_2O_{8-y}$ samples: (a) unoriented specimen, (b) oriented sample, observation plane parallel to the applied magnetic induction; and (c) oriented sample, observation plane perpendicular to the applied magnetic induction.
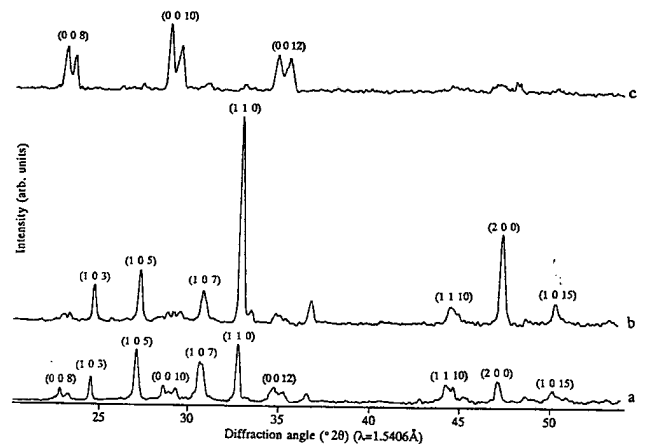
peaks when the direction of observation is parallel to *B* [Fig. 5(b)].

IV. DISCUSSION

An explanation of the (00*l*) peak splitting can be found in a recent paper of Zhang *et al.*[12] The authors identified two phases in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ single crystals with different Y content: the so-called "N-phase" which is the "normal" Ca-substituted 2212 phase with Y^{3+} at the Ca sites, and the so-called "D-phase" with Y substituting both Ca and Sr sites. The latter phase forms only when sufficient Y is present. Both phases have slightly different *c*-axis parameters that vary as
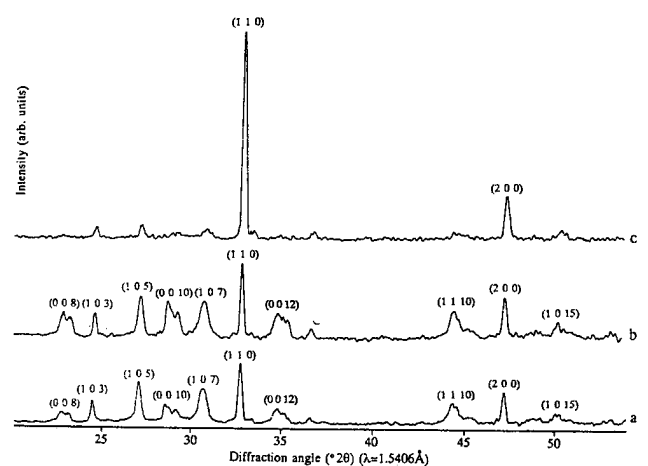
FIG. 3. X-ray diffraction patterns of $Bi_2Sr_2Ca_{0.8}Dy_{0.2}Cu_2O_{8-y}$ samples: (a) unoriented specimen; (b) oriented sample, observation plane parallel to the applied magnetic induction; and (c) oriented sample, observation plane perpendicular to the applied magnetic induction.

FIG. 5. X-ray diffraction patterns of $Bi_2Sr_2Ca_{0.8}Er_{0.2}Cu_2O_{8-y}$ samples: (a) unoriented specimen; (b) oriented sample, observation plane parallel to the applied magnetic induction; and (c) oriented sample, observation plane perpendicular to the applied magnetic induction.

a function of the Y content. From the observed peak splitting, it can be concluded that the same behavior and mechanism is thus likely to occur in our RE-substituted materials.

The formation mechanism of the N and D phases can be described as follows.[12] Stoichiometry pure 2212 phase is likely to nucleate first. During the growth, Ca, which is deficient due to nominal composition, is replaced by some Y^{3+} (or other RE) at Ca sites. This causes a decrease of the c-parameter since Y^{3+} substitutes a $2+$ ion. At this stage, the N phase is formed. Then, in order to prevent large change of the c-parameter, Y^{3+} diffuses toward the SrO planes. In fact, Ca and Sr easily interchange and Y can thus be found at the Sr sites by replacing Ca. This results in a balance between two opposite effects; c decreases when Y substitutes Ca but increases when it replaces Sr. The resulting c-parameter is thus very close to that of the Y-free 2212 material, and the D phase is formed with a random distribution of Y (or other RE) at Sr or Ca sites.

V. CONCLUSIONS

The above set of experiments is thus of great interest in order to understand the mechanism responsible for the crystal magnetic anisotropy from which good alignment results in an external magnetic field. These experiments confirm that RE substituted BSCCO systems can be well oriented in a magnetic field just like REBCO.[8,9] Therefore, magnetic texturing growth (Mag TG) of these Bi (Tl, Hg, ...) systems should be envisaged for improving electric percolation paths. Inelastic neutron diffraction analysis of such materials could be useful in order to quantify the magnetic anisotropy of the crystals (and also to observe magnetic phases at low temperatures).

Another important implication of the hereby orientation dependence as a function of the nature of the RE ions is the "indirect" but real proof of RE ion incorporation into the 2212 crystal structure.

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