Superconducting powders composed of 50:50 mixtures of yttrium and various rare-earth elements were analyzed by Rietveld analysis of x-ray diffraction data and magnetic susceptibility measurements. Crystallite size and micro-strain information obtained from the Rietveld analysis indicated that for mixtures containing Yb, Tm, and Er, crystallite sizes were significantly larger than for those containing larger rare-earths. Micro-strain minima were seen for the pure YBa$_2$Cu$_3$O$_{7-x}$ control sample, as well as Y$_{0.5}$Eu$_{0.5}$Ba$_2$Cu$_3$O$_{7-x}$ and Y$_{0.5}$Nd$_{0.5}$Ba$_2$Cu$_3$O$_{7-x}$. The minimum for the control sample is due to the lack of Y-R mixing on the Y-site. The minima observed for the Eu and Nd-containing samples are explained by cation exchange between the Y-R and Ba-sites. Magnetic susceptibility hysteresis loops indicate that the Eu-containing sample exhibits better magnetic flux-pinning properties than the YBa$_2$Cu$_3$O$_{7-x}$ control sample.

**INTRODUCTION**

In order for high temperature superconductors to be useful in power applications such as motors and generators, high superconducting current transport needs to be maintained in high magnetic fields. To maintain high critical currents in magnetic fields, it is necessary to pin the magnetic flux lines that penetrate the superconductor. Magnetic flux lines tend to be pinned by defects in the superconductor that may be present naturally, such as twin boundaries\(^1\), or by artificially-introduced defects such as fission tracks or ion beam tracks\(^2,3\). It has also been reported that novel flux-pinning stacking faults have been introduced into a superconductor of composition (Y$_{0.6}$Ho$_{0.4}$)Ba$_2$Cu$_3$O$_{7-x}$\(^4\), presumably as a result of the ionic size mismatch of the ions occupying the Y-Ho site. In this study we synthesized bulk superconductors of composition Y$_{0.5}$R$_{0.5}$Ba$_2$Cu$_3$O$_{7-x}$ using the rare-earth elements R=Yb, Tm, Er, Ho, Dy, Gd, Eu, Sm, and Nd, as well as a pure YBa$_2$Cu$_3$O$_{7-x}$ control sample. Magnetic susceptibility measurements were performed to investigate the effects of partial rare-earth element substitution for yttrium on the superconducting properties of these samples.

**ANALYSIS**

Diffraction patterns were collected from powdered samples using two separate Scintag instruments (XDS2000 and X5). Both instruments used a sealed-tube Cu k-alpha source and both were equipped with graphite monochrometers coupled with scintillation...
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detectors. A 1 mm divergence slit-2 mm antiscatter slit and a 0.3 mm detector slit-0.5 mm antiscatter slit combination was used with both instruments, and both instruments were set at a goniometer radius of 250 mm. Bragg peak broadening due to instrumental effects was determined by collecting data from a sample of LaB$_6$. The NIST standard LaB$_6$ (SRM660) was mounted on a quartz zero-background plate that had been lightly coated with silicone grease. The standard was run on each of the two machines in order to determine the extent of instrumental broadening. Data was collected on spinning samples using the following scheme:

1) 20-90° 2θ, 7 second count, 0.02° step
2) 70-139° 2θ, 14 second count, 0.04° step

Rietveld refinements were performed to obtain the “instrumental” values of the Gaussian and Lorentzian terms of the pseudo-Voigt function that was used in the analysis (GSAS$^5$ peak profile type no. 2$^6$). The values obtained for the two instruments were very similar.

The Y$_{0.5}$R$_{0.5}$Ba$_2$Cu$_3$O$_{7-x}$ samples were thoroughly ground and mounted on lightly-greased quartz zero-background plates, and diffraction data was collected from each sample in an identical manner to that done for the LaB$_6$ standard. Diffraction peak broadening was observed in these samples, indicating the presence of micro-strain and/or small (< 1 micron) crystallites in these samples. In order to quantify micro-strain and crystallite size contributions to the observed peak broadening, GSAS was used to perform Rietveld analysis on the data collected from these samples, with particular attention to variations in the Lorentzian terms in the pseudo-Voigt profile function for each sample.

For refinements of the Y$_{0.5}$R$_{0.5}$Ba$_2$Cu$_3$O$_{7-x}$ sample data, Gaussian parameters in the pseudo-Voigt function were assumed to represent instrumental effects only, and were therefore fixed at the values that were obtained from the LaB$_6$ refinements. The two Lorentzian terms were then refined, and it was assumed that the sample size and micro-strain effects were manifested in these variables. Three models were used in examining the micro-strain contribution to the observed peak broadening: 1) isotropic micro-strain, 2) anisotropic micro-strain about the c-axis, and 3) anisotropic micro-strain about the [103] direction (normal to the closest-packed plane in these samples). Attempts were made to refine peak broadening due to anisotropic crystallite size effects, but these generally resulted in unstable refinements; therefore an isotropic crystallite size model was used throughout the analysis.

Magnetic susceptibility hysteresis loops were measured at 10 K out to ±7 Tesla using a Quantum Designs squid magnetometer.

RESULTS AND DISCUSSION

The refined values of the crystallite size term in the peak profile were found to be relatively independent of the micro-strain model that was used in the refinement, so crystallite sizes were calculated from L$_x$ values obtained using the isotropic model.
Figure 1 shows the variation of $Y_{0.5}R_{0.5}Ba_2Cu_3O_{7-x}$ crystallite size as a function of the average Y-R-site cation radius\textsuperscript{8}. Most samples show crystallite sizes of 1500-3000 Å, which are on the order of the size of defects that are commonly observed in YBa$_2$Cu$_3$O$_{7-x}$, such as a-b twin domains and c-axis stacking faults and intergrowths. However, in the case of $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{7-x}$, $Y_{0.5}Tm_{0.5}Ba_2Cu_3O_{7-x}$, and $Y_{0.5}Er_{0.5}Ba_2Cu_3O_{7-x}$, calculated crystallite sizes approach 1 µm and greater, values which are essentially infinitely thick for this type of analysis. This suggests that the Y-R size contrast may be inhibiting the formation of defects in samples where Y is partially substituted for some of the smaller rare-earth elements. Also, the YBa$_2$Cu$_3$O$_{7-x}$ control sample shows a somewhat larger crystallite size than most of the other $Y_{0.5}R_{0.5}Ba_2Cu_3O_{7-x}$ samples; partial substitution of Ho, Dy, Gd and Eu for Y reduces the crystallite size in these samples by a factor of approximately 2/3, relative to the control sample.

Figure 2 shows the variation of micro-strain values that were obtained using the three different micro-strain models, plotted as a function of average radius of the Y-R-site cations. Minimum micro-strain is observed for the YBa$_2$Cu$_3$O$_{7-x}$ control sample, as well as a minimum at $Y_{0.5}Nd_{0.5}Ba_2Cu_3O_{7-x}$, and a local minimum at $Y_{0.5}Eu_{0.5}Ba_2Cu_3O_{7-x}$, regardless of what micro-strain model is used in the refinement. In the case of the two anisotropic models, it can be seen that in several cases there is significant separation between the values of the two micro-strain components for both the [001] and the [103] anisotropic micro-strain models, suggesting that an anisotropic model may be appropriate in these cases.

The micro-strain minimum observed for the YBa$_2$Cu$_3$O$_{7-x}$ control sample is an expected result, reflecting the lack of cation size-mismatch on the Y-R-site. The minimum at $Y_{0.5}Nd_{0.5}Ba_2Cu_3O_{7-x}$ is also not surprising; because the ionic radius of Nd$^{3+}$ (1.11 Å) is close to that of Ba$^{2+}$ (1.42 Å), it is likely that some Nd$^{3+}$ is occupying the Ba-site, serving as a micro-strain-relief mechanism. Site-disorder between Nd and Ba is well known in
NdBa$_2$Cu$_3$O$_{7-x}$; care must be taken to avoid Nd-Ba site-disorder in the synthesis of this compound. The local minimum at \( Y_{0.5}Eu_{0.5}Ba_2Cu_3O_{7-x} \) may also be a result of cation disorder. Of all the rare-earth cations, which are primarily trivalent, Eu shows the most divalent nature. The ionic radius of Eu$^{2+}$ (1.25 Å) is also close to that of Ba$^{2+}$ (1.42 Å), and Eu-Ba site-disorder may also serve as a micro-strain-relief mechanism for \( Y_{0.5}Eu_{0.5}Ba_2Cu_3O_{7-x} \).

![Fig. 2A. Isotropic model](image)

![Fig. 2B. [001] anisotropic axis](image)

![Fig. 2C. [103] anisotropic axis](image)

Although all three models are qualitatively the same with regard to maximum and minimum micro-strain values, it is still desirable to determine which model best explains the data. An inspection of the refinement agreement factor values (R values, reduced $\chi^2$) obtained using each model is one way to make this evaluation. The wRp (fitted) values associated with refinements using the three models are listed in Table II. It can be seen that there is very little model-dependence of the agreement factors, except in the case of the YBa$_2$Cu$_3$O$_{7-x}$ control sample, where a significant reduction in wRp indicates that the [001] anisotropic micro-strain axis is the best model. This is in keeping with other anisotropic properties of this material such as c-axis dependence on oxygen content and superconductivity properties.
Table I. Agreement factors (wRp) resulting from refinements using the three different micro-strain models.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isotropic wRp</th>
<th>// [001] wRp</th>
<th>// [103] wRp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb_{1/2}</td>
<td>0.0959</td>
<td>0.0959</td>
<td>0.0961</td>
</tr>
<tr>
<td>Tm_{1/2}</td>
<td>0.0754</td>
<td>0.0754</td>
<td>0.0754</td>
</tr>
<tr>
<td>Er_{1/2}</td>
<td>0.0916</td>
<td>0.0916</td>
<td>0.0917</td>
</tr>
<tr>
<td>Ho_{1/2}</td>
<td>0.0990</td>
<td>0.0990</td>
<td>0.0988</td>
</tr>
<tr>
<td>Y</td>
<td>0.0851</td>
<td>0.0840</td>
<td>0.0850</td>
</tr>
<tr>
<td>Dy_{1/2}</td>
<td>0.0819</td>
<td>0.0817</td>
<td>0.0819</td>
</tr>
<tr>
<td>Gd_{1/2}</td>
<td>0.0925</td>
<td>0.0924</td>
<td>0.0925</td>
</tr>
<tr>
<td>Eu_{1/2}</td>
<td>0.0940</td>
<td>0.0940</td>
<td>0.0940</td>
</tr>
<tr>
<td>Sm_{1/2}</td>
<td>0.1055</td>
<td>0.1054</td>
<td>0.1055</td>
</tr>
<tr>
<td>Nd_{1/2}</td>
<td>0.1071</td>
<td>0.1070</td>
<td>0.1071</td>
</tr>
</tbody>
</table>

However, agreement factors are not always sensitive to model differences. Correlations between refined variables can result in different refined-variable values with similar agreement factors, depending on which model is used. A second way to test for the best model is to examine ratios of the micro-strain parallel and perpendicular to the chosen anisotropic micro-strain axis. This ratio should be a maximum or a minimum for the best choice of axis. These ratios are plotted in figure 3 as a function of average Y-R-site cation radius. It can be seen that in most cases the ratios for the [001] anisotropic micro-strain model plot further from 1.0 than those for the [103] model, indicating that generally the [001] model is the best choice. An exception is Ho and possibly Tm, for which the [103] model seems to be the best choice. In the case of Dy and Eu, an isotropic model works the best. It should be noted, however, that for several samples the ratios obtained from both anisotropic models differ significantly from 1.0. In these cases, a uniaxial anisotropic model is probably not appropriate; the true situation may involve a mixture two and possibly more anisotropic axes.

Figure 4 is a plot that compares magnetic susceptibility hysteresis data obtained from the Eu-containing sample to that obtained from the control sample. At 6.5 Tesla the hysteretic gap is 0.48 normalized units for the Y_{0.5}Eu_{0.5}Ba_{2}Cu_{3}O_{7-x} sample compared to 0.41 for the control sample. The increase in the hysteretic gap at high magnetic field observed for the Eu-containing sample is evidence of improved magnetic flux pinning in this sample.

CONCLUSIONS

The crystallite size results indicate that partial substitution of rare-earth elements for yttrium in Y_{0.5}R_{0.5}Ba_{2}Cu_{3}O_{7-x} may affect microstructure. Results indicate that micro-strain in the YBa_{2}Cu_{3}O_{7-x} control sample is highly anisotropic, with less anisotropy
Correct axis choice: \( r_1/r_2 = \min \mathrm{or} \max \)  
Incorrect axis choice: \( r_1/r_2 \sim 1 \)

Fig. 3. Ratio of micro-strain parallel:perpendicular to anisotropic micro-strain axis.

[001] anisotropic axis \( \bullet \)  [103] anisotropic axis \( \bigcirc \)

Fig. 4. Magnetic susceptibility hysteresis loops for \( \text{Y}_{0.5}\text{Eu}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-x} \) compared to the \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) control sample.
evident in the $\text{Y}_{0.5}\text{R}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ samples. The [001] anisotropic axis model seems to be the best model for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ control sample and most of the other $\text{Y}_{0.5}\text{R}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ samples. Exceptions to this are $\text{Y}_{0.5}\text{Ho}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ and possibly $\text{Y}_{0.5}\text{Tm}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$, where the [103] anisotropic axis model seems to work best. In some cases a simple uniaxial micro-strain model may be inadequate. Improved flux pinning was seen in the $\text{Y}_{0.5}\text{Eu}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ sample.

REFERENCES


