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^{151}Eu Mössbauer spectroscopy and x-ray-diffraction studies on the $\text{Pb}_2\text{Ba}_2\text{EuCu}_3\text{O}_{8+\delta}$ system

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Simultaneous replacement of Sr by Ba and Y by Eu in the Pb-2213 system was found to yield single-phase $\text{Pb}_2\text{Ba}_2\text{EuCu}_3\text{O}_{8+\delta}$ samples, suitable for ^{151}Eu Mössbauer measurements. The samples were synthesized by a solid-state reaction of metal oxides and carbonates under an inert atmosphere. An oxygen-rich sample corresponding to $\delta = 1.79$ was obtained by annealing the as-synthesized material ($\delta = 0.16$) in oxygen. The oxygen annealing increased the size of the lattice constants and led to an orthorhombic-to-tetragonal phase transition of the structure. The samples were also oriented in an 11.7-T magnetic field. The x-ray-diffraction spectra showed that the c axes tended to orient perpendicular to the applied field. The measured Mössbauer spectra exhibited an electric quadrupole interaction typical of the Eu site in high- T_c cuprates. The average orientation angles obtained from fittings of the Mössbauer spectra were in accordance with the results from the x-ray-diffraction measurements.

I. INTRODUCTION

$RCuO_2$ -type ($R =$ rare earth) oxygen-deficient perovskite-type building blocks are found in several of the high- T_c superconducting phases. The next neighbor atoms of the (Y,Ca) site in the $\text{Pb}_2\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_3\text{O}_{8+\delta}$ system are also configured in this structure. The hyperfine interactions around the (Y,Ca) site can easily be studied by Mössbauer spectroscopy using one of the existing Mössbauer isotopes from the lanthanide family. The ^{151}Eu isotope is the most widely used due to the high recoilless fraction of its 21.532-keV γ transition.

The $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta}$ structure (Pb-2213) provides a host lattice which is suitable for various substitution studies.¹ As in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, yttrium can be replaced by most rare-earth elements or by calcium and the oxygen content may vary within a wide concentration range. On the other hand, strontium has been successfully substituted by barium in the Y-based Pb-2213 system.²

In this work, the parent $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta}$ phase has been modified by simultaneously replacing Y by Eu and Sr by Ba. Results from ^{151}Eu Mössbauer measurements of as-synthesized ($\delta = 0.16$) and oxygen-rich ($\delta = 1.79$) samples are reported. The observed resonance line is broadened due to an electric quadrupole interaction, lifting the degeneracy of 12 transitions under the action of a nonzero electric field gradient (EFG). In the principal axis coordinate system, the EFG can be uniquely described with two parameters: the main component V_{zz} and the asymmetry parameter defined as $\eta = \frac{|V_{yy}| - |V_{xx}|}{|V_{zz}|}$. The values of V_{zz} and η obtained by fitting the spectra were typical of Eu in perovskite systems.³⁻⁶

The crystallites of high- T_c cuprates, with their layered structure, exhibit a very anisotropic magnetic susceptibility. This enables the creation of orientational effects in specimens subjected to strong magnetic fields. The results from such studies are reported as well.

II. EXPERIMENTAL DETAILS

Two $\text{Pb}_2\text{Ba}_2\text{EuCu}_3\text{O}_{8+\delta}$ samples with different oxygen contents were synthesized by a solid-state reaction of analytical grade PbO , BaCO_3 , Eu_2O_3 , and CuO . Stoichiometric mixtures of the starting materials were first calcined in air at 700 °C for 50 h and then sintered in a flowing argon atmosphere at 750 °C for 50 h. The oxygen content of the as-synthesized sample (cooled down to room temperature in argon) was determined by a Coulometric titration technique.^{7,8} In order to prepare an oxygen-rich sample, part of the furnace-cooled sample was further annealed in a flowing oxygen atmosphere. The annealing was performed in a Perkin-Elmer System 7 thermobalance in three batches (100–150 mg) using the following temperature program: heating up to 450 °C with a rate of 1 °C/min, annealing at 450 °C for 100 min, and cooling down to 200 °C with a rate of 1 °C/min. The oxygen content of the oxygen-rich sample was determined by monitoring thermogravimetrically (TG) the weight gain during the annealings.

The purity of the samples was checked by copper $K\alpha$ x-ray powder diffraction using a Philips MPD 1880 facility. The orthorhombic lattice constants were obtained by fitting the recognized peaks with Lorentzian lines. One common linewidth and free peak intensities were used. To check for possible superconducting properties a super-

conducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS₂) was used.

In order to orient the powder samples flat cylindrical containers ($r = 1$ cm, $h = 0.4$ cm) filled with epoxy-soaked crystallites were subjected to a magnetic field of 11.7 T. The magnetic field was applied either perpendicular or parallel to the cylindrical axis. X-ray-diffraction spectra were recorded from hardened samples after first removing the containers. Analysis of the texture effects followed the scheme presented in Ref. 5. In brief, diffraction peak intensities were obtained by separately fitting each diffraction peak, with a Lorentzian line. The intensity ratios of the diffraction peaks of the oriented sample and the random crystallite sample were plotted as a function of the angle θ between the c axis and the surface normal. The data were fitted with the following function:

$$I(\theta) = I_0 e^{-\left(\frac{\theta-\theta_0}{w}\right)^2} + C, \quad (1)$$

where C is the background level, representing the unoriented crystallites, I_0 gives the amplitude of the distribution, θ_0 ($= 0, \frac{\pi}{4},$ or $\frac{\pi}{2}$) is the direction into which the crystallites orient, and w is the width of the distribution.

In room-temperature ¹⁵¹Eu Mössbauer measurements both powder absorbers (random orientation) and magnetically oriented samples were used. The thickness of the samples was 1.5 mg/cm² of ¹⁵¹Eu. The spectra corresponding to the same sample material, oriented in various directions, were fitted simultaneously using the same values of the hyperfine parameters:⁵ quadrupole coupling constant ($eQ_g V_{zz}$), asymmetry parameter (η), isomer shift (S), and linewidth (Γ). The following fit parameters were separately specified for each spectrum: total intensity, background level, and the angle ($\bar{\theta}$) measured between the quantization axis and the direction of the Mössbauer γ beam. The quantization axis is the z axis of the EFG expressed in the principle axis coordinate system. The z axis coincides with the crystal c axis. The $\bar{\theta}$ angle obtained in the fit corresponds to the average of the Mössbauer intensity factors ($\frac{1}{2} \sin^2 \theta$ or $\frac{1}{4} + \frac{1}{4} \cos^2 \theta$) calculated over the c axis distribution in the sample.^{4,5} For a randomly orientated sample $\bar{\theta}$ can immediately be fixed to its average value (magic angle) $\bar{\theta} = 54.74^\circ$.

III. RESULTS AND DISCUSSION

Synthesis of the Pb-2213 phase with the simultaneous replacements of Sr and Y by Ba and Eu, respectively, was found to yield essentially single-phase samples. The x-ray-diffraction spectra measured from the samples could be readily indexed using reflections of the known orthorhombic symmetry. The observed small impurity peaks at 20.8°, 29.6°, and 42.4° were identified as the 100, 110, and 200 reflections of Cu₂O (Fig. 1). The fourth impurity peak at 38.8° is possibly due to a Ba-based oxide. The following structure parameters were obtained for the as-synthesized sample: $a = 5.4977(6)$ Å, $b = 5.5316(6)$ Å, $c = 16.202(1)$ Å, $b/a = 1.0062$, and $V = 492.7(2)$ Å³, while the oxygen-rich sample yielded $a = 5.5564(1)$ Å, $b = 5.5589(1)$ Å, $c = 16.278(3)$ Å, $b/a = 1.0004$, and $V = 502.8(1)$ Å³. The former val-

ues are, with respect to all lattice parameters, slightly larger than those reported for a powder Pb₂Sr₂EuCu₃O₈ sample.⁹ On the other hand, with increasing oxygen content the Pb₂Ba₂EuCu₃O_{8+ δ} lattice is expanded in all three directions and becomes tetragonal as was observed in the Pb₂Sr₂YCu₃O_{8+ δ} system as well.¹⁰

According to Coulometric titrations the oxygen content of the as-synthesized sample is 8.16(2). The TG data of the oxygen annealings reveal a δ value of 1.79(3) for the oxygen-rich sample.¹¹ No signs of superconductivity above 4 K were observed for any of the samples. This was expected, since superconductivity is found only in Pb-2213 powder samples having a part of the trivalent rare earth substituted by divalent Ca.¹

In Fig. 1, the x-ray-diffraction spectra of the oxygen-deficient samples are shown. The diffraction pattern of the unoriented powder sample is shown in Fig. 1(a). The pattern in Fig. 1(b) was obtained from a sample oriented with the magnetic field parallel to the cylindrical axis and a pattern from a sample oriented with the magnetic field perpendicular to the cylindrical axis is shown in Fig. 1(c). The amorphous background in the two latter spectra is due to the epoxy. The texture effects are seen as an enhancement of the $hk0$ reflections in Fig. 1(b). This means that the c axes tend to orient perpendicular to the applied magnetic field, and furthermore that $\theta_0 = \frac{\pi}{2}$ in Eq. (1). A certain portion of the crystallites, however, remains unaffected by the magnetic field. The x-ray-diffraction spectrum in Fig. 1(c) shows very little texture effects, since in this case the distribution of the c axes is close to random orientation, due to the fact that all hkl peaks are allowed.

The intensity ratios calculated for the pattern in Fig. 1(b) and the Gaussian fit are shown in Fig. 2. The average angle $\bar{\theta}$ can be calculated with the expression

$$\frac{1}{2} \sin^2 \bar{\theta} = \frac{\int_0^{\frac{\pi}{2}} I(\theta) \frac{1}{2} \sin^2 \theta \sin \theta d\theta}{\int_0^{\frac{\pi}{2}} I(\theta) \sin \theta d\theta}, \quad (2)$$

for which the following analytical expression can be derived if the lower boundary of the Gaussian integral can be extended to $-\infty$ (w is sufficiently small) and $\theta_0 = \frac{\pi}{2}$:

$$\frac{1}{2} \sin^2 \bar{\theta} = \frac{\frac{C}{3} + \frac{I_0 w \sqrt{\pi}}{16} (3e^{-w^2/4} + e^{-9w^2/4})}{C + \frac{I_0 w \sqrt{\pi}}{2} e^{-w^2/4}}. \quad (3)$$

Using the values obtained from the fit, $I_0 = 0.926$, $w = 35.17^\circ$, and $C = 0.6284$, we get $\bar{\theta} = 60.10^\circ$. For the oxygen-rich sample $\bar{\theta} = 61.60^\circ$.

The Mössbauer spectra of the unoriented and oriented specimens of the oxygen-deficient sample are shown in Fig. 3. The average angle $\bar{\theta} = 58(2)^\circ$ was obtained from the spectrum of a sample where the orienting field was parallel to the cylindrical axis [Fig. 3(b)]. This agrees with the value obtained from the texture analysis, confirming that the quantization axis is parallel to the crystal c axis, as assumed. A value of $\bar{\theta} = 54(2)^\circ$ was obtained, when the aligning field was perpendicular to the cylindrical axis [Fig. 3(c)]. This corresponds to an essentially randomly oriented sample, in agreement with the x-ray-diffraction results. The spectrum of the oxygen-rich sam-

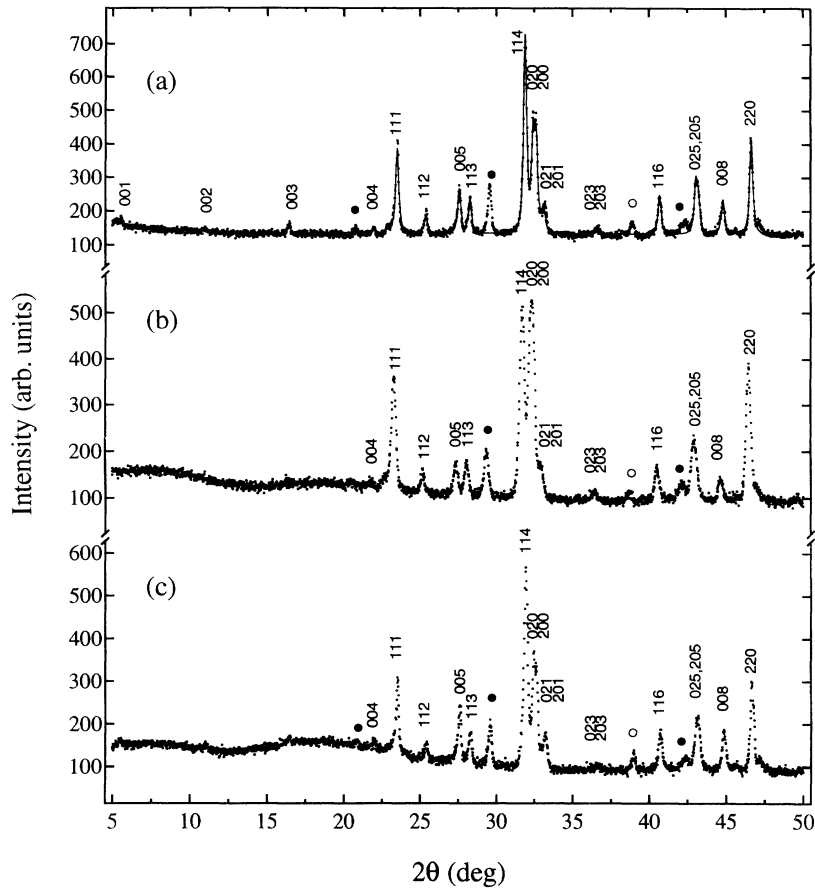


FIG. 1. X-ray-diffraction spectra of $\text{Pb}_2\text{Ba}_2\text{EuCu}_3\text{O}_{8.16}$ crystallites in (a) powder form, (b) oriented with $\vec{B} \parallel$ cylindrical axis, and (c) oriented with $\vec{B} \perp$ cylindrical axis. The lattice parameter fit of the (a) spectrum is also shown. The impurity peaks are due to Cu_2O (●) and a Ba-based oxide (○).

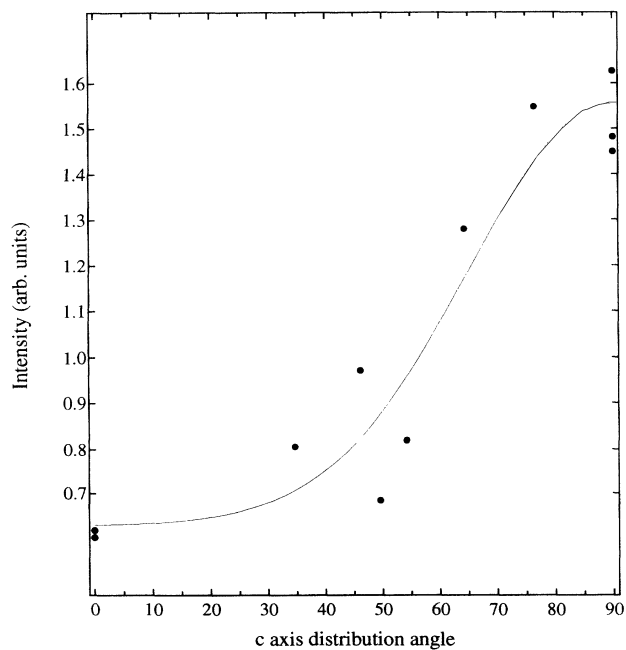


FIG. 2. The c axis distribution obtained from the diffraction peak intensity ratios between an oriented [Fig. 1(b)] and a random [Fig. 1(a)] sample. The fit curve consisting of a Gaussian distribution is also shown.

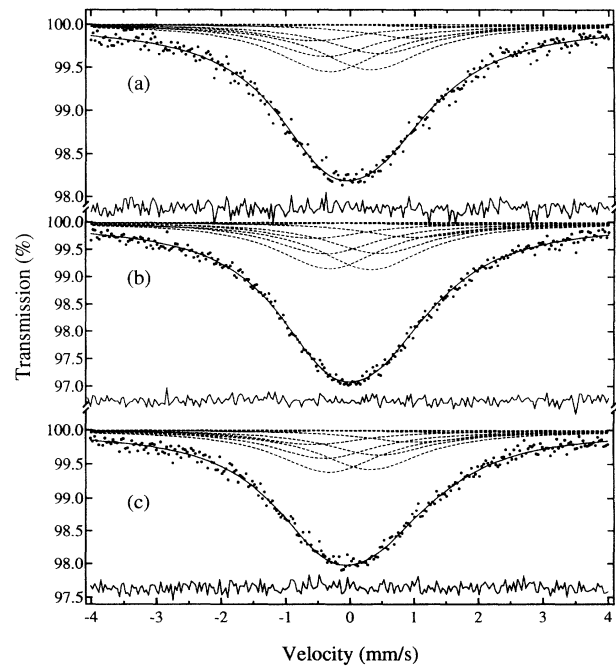


FIG. 3. Simultaneously fitted Mössbauer spectra of $\text{Pb}_2\text{Ba}_2\text{EuCu}_3\text{O}_{8.16}$ absorbers in (a) powder form, (b) oriented with $\vec{B} \parallel$ cylindrical axis, and (c) oriented with $\vec{B} \perp$ cylindrical axis. The differences between the data and fits are also shown.

ple, oriented with $\vec{B}||$ cylindrical axis, yielded $\bar{\theta} = 57(1)^\circ$. Orientation with $\vec{B} \perp$ cylindrical axis was not performed.

The hyperfine parameters received the following values: $eQ_g V_{zz} = -4.9(2)$ mm/s, $\eta = 0.63(7)$, and $S = 0.045(9)$ mm/s (as-synthesized sample) and $eQ_g V_{zz} = -4.5(2)$ mm/s, $\eta = 0.94(5)$, and $S = 0.007(6)$ mm/s (oxygen-rich sample). Negative-valued quadrupole coupling constants and nonzero asymmetry parameters have been observed for the other Eu-based cuprates as well.³⁻⁶ The large expansion of the unit cell [$\Delta V = 10.1(2)$ Å³] is directly reflected in the values of the isomer shifts.⁴ A theoretical value for the difference in isomer shifts can be calculated with Eqs. (1) and (2) in Ref. 4 and the value of $\frac{\Delta V}{V} = 0.0201(5)$ for the relative unit cell expansion. The theoretically predicted isomer shift difference of $\Delta S = -0.0371(8)$ mm/s is in excellent agreement with the experimental value of $\Delta S = -0.038(1)$ mm/s. Both the values of the isomer shifts are, however, typical of trivalent Eu. No traces of divalent Eu were found in measurements performed using higher Doppler velocities.

IV. CONCLUSIONS

Lead-2213 samples with europium at the rare-earth site and barium at the alkaline-earth site were successfully synthesized in single-phase form. Loading the as-synthesized sample with oxygen could be easily performed. This increased the size of the unit cell and decreased the orthorhombicity. The lattice expansion was directly seen in the difference between the Mössbauer isomer shifts of the oxygen-rich and oxygen-deficient samples. The values of the Mössbauer parameters are typical of the Eu site in high- T_c cuprates. The asymmetry parameter of the oxygen-rich sample is, however, surprisingly large considering that the sample is tetragonal. Possibly the extra oxygen entering the lattice gives rise

to a distribution of various EFG's seen by the Eu nuclei. This could in some cases force η to attain a value close to 1.⁵ The absence of large difference between the two values of the quadrupole coupling constant confirms that the charge transfer to the vicinity of the rare-earth site is small when the samples are loaded with oxygen.¹⁰

The direction into which the crystal c axes orient is typical of Eu-based cuprates.^{4,5} The portion of the powders that remains unoriented seems to vary from one cuprate to another and to depend on the method used to synthesize the compound. This could be related to the size of the obtained crystallites, because the torque exerted on the crystallites is proportional to the volume, while the friction in the epoxy is proportional to the surface area. In the $R-124$ system, orientation effects of both 0% and 100% have been observed.^{6,12} Low-temperature sol-gel synthesis, yielding very small crystallites, was used in a former work and no orientation was observed.⁶ Samples prepared by a high-pressure and high-temperature solid-state reaction yielded crystallites, orienting readily in an applied magnetic field.¹² In the present work, the crystallites clearly have a size distribution and thus only a part of the crystallites is affected by the magnetic field.

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