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Europium substitution effects in superconducting $YBa_2Cu_4O_8$ synthesized under one atmosphere oxygen pressure

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$Y_{1-x}Eu_xBa_2Cu_4O_8$ powder samples, with $x = 0$, 0.25, 0.5, 0.75, and 1.0, were synthesized at ambient pressure using either an acetate-tartrate sol-gel method or a LiF flux process. The lattice parameters and purity of the samples were checked using x-ray diffraction. The superconducting transition was monitored by magnetic-susceptibility measurements. Replacing yttrium with europium increased the unit-cell volume, decreased the orthorhombicity (b/a) and the critical temperature. The hyperfine interactions at the europium site were studied by ^{151}Eu Mössbauer spectroscopy. The complete quadrupole Hamiltonian of the 21.5-keV γ transition of ^{151}Eu was successfully applied in the analyses of the Mössbauer spectra. The Mössbauer parameters obtained were found to resemble those measured for the $EuBa_2Cu_3O_{7-\delta}$ (1:2:3) system. It was demonstrated that magnetic alignment of the crystallites could not be obtained with an 11.7-T field, contrary to the 1:2:3 and other high-T_c systems.

I. INTRODUCTION

The $R_2Ba_4Cu_{6+n}O_{14+n}$ system (R = rare earth element; $n = 0,1,2$) offers wide possibilities for studying high-T_c superconductivity. The $YBa_2Cu_4O_8$ (1:2:4) phase[1] is the third ($n = 2$) member of this homologous series of compounds. In terms of applications the 1:2:4 phase has attracted much interest because of the high thermal stability of the oxygen content.[2] Its relatively low T_c of 80 K can be increased to 90 K by substituting yttrium partly by calcium.[3] From a theoretical point of view $YBa_2Cu_4O_8$ provides an additional model system for testing the general trends in the properties of high-T_c superconducting cuprates. The 1:2:4 phase differs from $YBa_2Cu_3O_{7-\delta}$ (1:2:3) in having a double, instead of single, Cu-O chain running parallel to the b axis.

The $YBa_2Cu_4O_8$ phase is thermodynamically favored at low temperatures and high oxygen pressures. Although it was first isolated under an oxygen pressure of 400 atm,[1] bulk synthesis in ambient conditions is possible as well.[4–6] Preparation of the 1:2:4 phase under normal pressure is, however, strongly limited by reaction kinetics. In the present study a sufficient reaction rate was achieved by using either homogeneous acetate-tartrate gels as precursors or LiF as a flux.[7,8] The similar chemistry of rare earth elements generally enables various mutual replacements in compounds containing these elements. This is also the case in the $YBa_2Cu_3O_{7-\delta}$ phase, in which yttrium may be substituted by most of the other rare earth elements from lanthanum to ytterbium without destroying the structure. In the $RBa_2Cu_4O_8$ phase the range of the R ionic radii tolerated by the structure seems to be narrower, since only Eu, Gd, Dy, Ho, and Er bulk 1:2:4 samples have been successfully synthesized under 1 atm oxygen pressure.[9–11] However, application of the high-pressure synthesis technique extends the upper and lower limits for the R radii to Sm and Tm, respectively.[12] Furthermore, the dependence of T_c on the lattice parameters is different in the 1:2:3 and 1:2:4 phases. The critical temperature is slightly increased with increasing volume of the 1:2:3 unit cell,[13,14] while in the 1:2:4 structure an opposite behavior has been observed.[9,12,15]

Room-temperature measurements of the magnetic susceptibility of several cuprate superconductors in single-crystal form have revealed a large anisotropy between the values obtained parallel to the c axis and perpendicular to it.[16,17] A crystallite put in a strong magnetic field will, due to the anisotropy of the susceptibility, be subjected to a torque striving to align the crystalline c axis either parallel or perpendicular to the field.[18] By using various R atoms in the lattice the magnitude and direction of the anisotropy can be altered, thus changing the preferred alignment direction of the crystallites.[17] This effect has been utilized in studies of the Bi- and 1:2:3-based cuprate systems.[19,20]

Several of the rare earth isotopes have γ transitions suitable for Mössbauer measurements. The most commonly used isotope for characterization of superconducting phases is ^{151}Eu.[19–21] Contrary to the 1:2:3 phase, only very few ^{151}Eu Mössbauer studies on the $Y_{1-x}Eu_xBa_2Cu_4O_8$ system have been published.[22] In the

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1:2:3 system a substantial electric field gradient (efg), with a negative-valued main component (V_{zz}) and a nonzero asymmetry parameter ($\eta = \frac{|V_{yy}|-|V_{xx}|}{|V_{zz}|}$) has been found. In the present study the volume of the 1:2:4 cell has been controlled by increasing the europium substitution level x gradually from 0.0 to 1.0. Local chemical and electrical interactions around the R lattice site have been examined. The complete electric quadrupole Hamiltonian of the excited $\frac{7}{2}$ and ground $\frac{5}{2}$ spin states was used when analyzing the Mössbauer spectra.[19] Along with Mössbauer spectroscopy the synthesis products have been characterized by x-ray diffraction for the phase purity, lattice constants, and texture effects in alignment experiments. Thermal analysis was used to study the oxygen stability and superconducting quantum interference device (SQUID) measurements to check the superconducting properties.

II. EXPERIMENTAL DETAILS

A series of $Y_{1-x}Eu_xBa_2Cu_4O_8$ samples with x= 0.0, 0.25, 0.50, 0.75, and 1.0 were prepared by an acetate-tartrate sol-gel method described in more detail in Ref. 7. Appropriate mixtures of Y_2O_3 and Eu_2O_3 (0.003 125 mol) were first dissolved in 100 ml of 0.2 M CH_3COOH. In each case a clear solution was obtained after stirring for 10 h at 55–60 °C in a beaker covered with a watch glass. Next, 50 ml of 0.5 M $Cu(CH_3COO)_2{\cdot}H_2O$, 25 ml of 0.5 M $Ba(CH_3COO)_2$, and 20 ml of 0.55 M aqueous tartaric acid solution were added to the rare earth acetate solutions with adequate intermediate stirrings. After concentrating for 8 h at 65 °C in an open beaker under stirring the above solutions turned into blue gels. The gels were first dried in air at 80 °C and then preheated (10 h) and sintered (30 h) at 780 °C in flowing oxygen. Additionally, in order to find out the possible effects of the synthesis technique on the material properties, another sample with x = 1.0 was prepared by a solid state reaction using stoichiometric amounts of $EuBa_2Cu_3O_{7-\delta}$ and CuO powders as starting materials and 2.5 wt. % of LiF as a reaction rate enhancer.[8] The mixture was heated in flowing oxygen at 785 °C in powder form for 15 h and as pelletized for 75 h with several intermediate grindings and repressings.

The thermal decomposition of the gel powders was studied by means of thermogravimetric (TG) analyses up to 1000 °C in a dynamic oxygen atmosphere (heating rate 2 °C/min; sample size 50–70 mg) using a Perkin-Elmer System 7 thermobalance. Also, the oxygen stability of the final products under oxygen and argon atmospheres was confirmed by TG measurements (heating and cooling rates 5 °C/min; sample size 25–40 mg).

The phase purity and the crystallinity of the products were studied by x-ray diffraction analyses using a Philips MPD 1880 diffractometer equipped with a graphite secondary monochromator and a Cu tube. The lattice parameters of the samples were obtained from the diffraction spectra by fitting the peaks of identified reflections using free intensities and one common line width [full width at half maximum (FWHM)]. Lorentzian-shaped lines were used.

The reported critical temperatures of superconductivity are onset temperatures of the diamagnetic signal determined by a SQUID magnetometer (Quantum Design $MPMS_2$).

For Mössbauer measurements powder-absorber thicknesses of 20 mg/cm^2 were used. Some of the samples were mixed in epoxy resin and exposed to an 11.7-T magnetic field while the mixture was hardening. The aim was to orient the crystallites in the direction of the field. These texture effects were first checked by x-ray diffraction.

Room-temperature ^{151}Eu Mössbauer spectra were recorded in transmission geometry. A standard 100-mCi $^{151}Sm{:}Sm_2O_3$ source was used. The 21.5-keV γ quanta were detected with a scintillation detector equipped with a 3-mm-thick NaI crystal. The linear periodic Doppler modulation used in the measurements had a maximum velocity of 4 mm/s. A maximum velocity of 20 mm/s was applied to check for the presence of Eu ions in the 2+ oxidation state.

III. RESULTS AND DISCUSSION

The 1:2:4 phase is formed in a flowing oxygen atmosphere above 750 °C as the annealing time is increased. The thermal decomposition of the (Y,Eu)-Ba-Cu acetate-tartrate precursor gels was followed up to 1000 °C by thermogravimetric measurements (Fig. 1). The weight loss below 200 °C is due to the evolvement of water and decomposition of the copper constituent part.[7] The final decomposition of the gels above 200 °C proceeds in several steps via various unidentified intermediate species

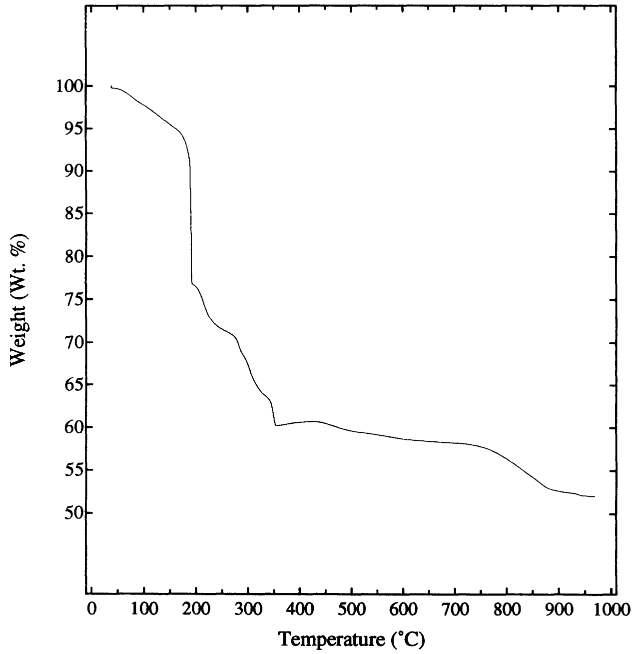

FIG. 1. Thermal decomposition of the dried Eu-Ba-Cu acetate-tartrate gel under a flowing oxygen atmosphere. The heating rate was 2 °C/min.

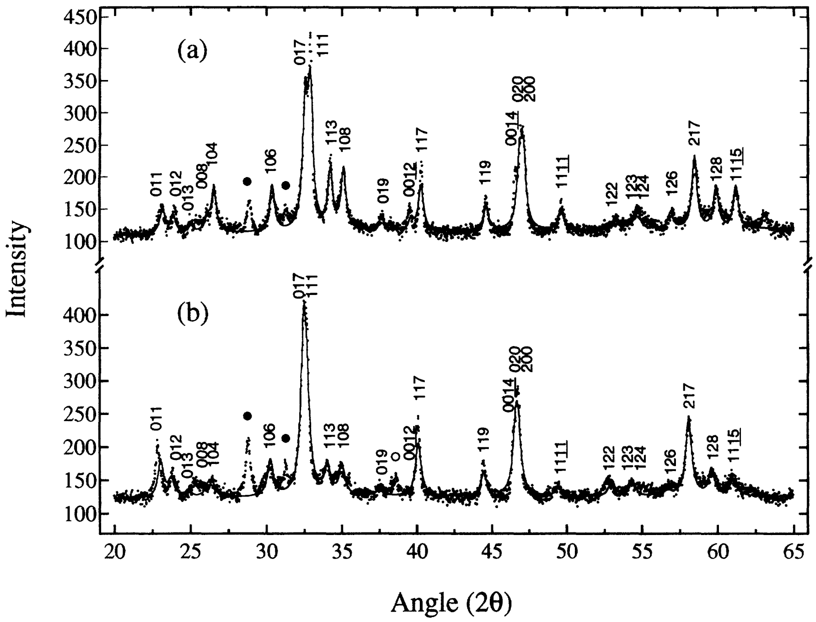

FIG. 2. Powder x-ray diffraction data (Cu $K\alpha$ radiation) for the (a) $YBa_2Cu_4O_8$ and the (b) $EuBa_2Cu_4O_8$ samples, synthesized by the acetate-tartrate sol-gel method. The obtained fit curves and the reflections of the 1:2:4 phase are shown. $BaCuO_2$ (●) and CuO (○) impurities are indicated as well.

and $BaCO_3$ (at around 750 °C). Essentially single-phase $Y_{1-x}Eu_xBa_2Cu_4O_8$ samples were obtained after annealing the dried gel powders at 780 °C for 40 h, as well as by the LiF-enhanced solid state reaction of $EuBa_2Cu_3O_{7-\delta}$ and CuO powders at 785 °C after a total heat treatment time of 90 h.

The x-ray diffraction spectra of the sol-gel-prepared $YBa_2Cu_4O_8$ and $EuBa_2Cu_4O_8$ are shown in Fig. 2. The reflections of the 1:2:4 phase are indicated; the unidentified peaks seen at the 2θ values of 29 ° and 31 ° are due to small amounts of $BaCuO_2$ impurities,[7] while the peak at 37.5 ° indicates the presence of CuO. The $BaCuO_2$ peaks are not observed in the sample synthesized by the LiF flux method, in which mainly traces of CuO and $Eu_2Ba_4Cu_7O_{15-\delta}$ (2:4:7) are found. Because of the structural similarities, the strongest peaks of the x-ray diffraction patterns of the 1:2:3 and 1:2:4 phases coincide, which makes it difficult to detect small amounts of 1:2:3 impurities. The single-phase character of all the $Y_{1-x}Eu_xBa_2Cu_4O_8$ samples was therefore checked by TG measurements. The 1:2:4 phase should be stable up to 670–900 °C depending on the atmosphere,[23] while the 1:2:3 phase starts to lose oxygen already around 330–400 °C. Figure 3 shows the TG curves of subsequent heating and cooling cycles under oxygen and argon atmospheres for the sol-gel-synthesized $EuBa_2Cu_4O_8$ sample. Even in an argon atmosphere no weight loss is seen below 680 °C and in an oxygen atmosphere the oxygen content is stable up to 840 °C. Finally, the SQUID measurements showed no indication of the characteristic 90-K transition of the 1:2:3 phase.

Throughout the whole substitutional range the line positions of the x-ray peaks indicated an orthorhombic lattice with no signs of superlattice effects. The results from lattice parameter fits of the spectra are given in Table I. As is seen the a and b parameters increase with increasing x, while the c parameter shows very little variation. The net effect is that the unit cell volume increases by 5.3(4) Å^3 as x is changed from 0.0 to 1.0. The increase is expected since europium has a larger ionic radius than yttrium. The orthorhombicity, here defined as b/a, decreases as the Eu portion is increased, which is, e.g., indicated by the decrease of the distance between the 020 and 200 reflections. In the fittings these two peaks were constrained to have equal intensities. The decrease in orthorhombicity is also expected since 1:2:4 samples based on R elements with larger ionic radii have smaller orthorhombicity according to Refs. 9 and 12.

The larger peak width for the x = 1.0 (LiF) sample could indicate the presence of a somewhat larger portion of the 2:4:7 phase, the peaks of which overlap with the 1:2:4 peaks. X-ray diffraction spectra measured from specimens subjected to the magnetic field merely repeated the patterns obtained for powder specimens. The magnetic field thus failed to change the random orientation of the crystallites.

The value for T_c was seen to decrease with increasing Eu content. The T_c value of 78 K was measured for the samples having 0% or 25% of yttrium replaced by europium. For the samples with x = 0.5, 0.75, and 1.0, T_c's of 77, 75, and 74 K were obtained, respectively. The trend of decreasing critical temperature with increasing

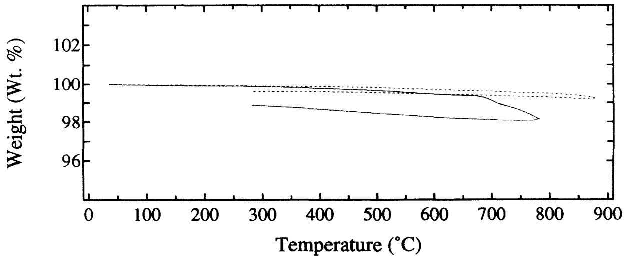

FIG. 3. Thermogravimetric heating and cooling curves for the $EuBa_2Cu_4O_8$ sample synthesized by the acetate-tartrate sol-gel method, showing sufficient thermal stability under flowing argon (solid line) and oxygen (dashed line) atmospheres. The heating and cooling rates were 5 °C/min.

TABLE I. Lattice characteristics obtained by lattice parameter fits of x-ray diffraction spectra of $Y_{1-x}Eu_xBa_2Cu_4O_8$ samples. The x-ray FWHM peak width (w) is also given for each spectrum.

x	a (Å)	b (Å)	c (Å)	Volume (Å^3)	b/a	w (deg)
0.0	3.8538(6)	3.8745(7)	27.267(6)	407.1(2)	1.0054(3)	0.195(4)
0.25	3.8648(8)	3.886(1)	27.290(8)	409.8(3)	1.0054(5)	0.205(4)
0.5	3.8743(2)	3.8930(4)	27.292(7)	411.6(2)	1.0048(2)	0.195(4)
0.75	3.8745(9)	3.892(1)	27.292(9)	411.5(4)	1.0044(6)	0.213(5)
1.0	3.8820(9)	3.895(1)	27.27(1)	412.4(4)	1.0034(6)	0.229(5)
1.0 LiF	3.880(1)	3.892(1)	27.25(1)	411.5(4)	1.0031(6)	0.275(7)

cell volume is consistent with the results observed for a series of 1:2:4 samples, having R atoms with ionic radii ranging from Tm to Sm.[9,12,15]

In Fig. 4 the ^{151}Eu Mössbauer spectrum measured for the $EuBa_2Cu_4O_8$ sample (sol-gel synthesis) is shown. Since no orientation effects could be observed in the x-ray spectra of samples exposed to a magnetic field, the Mössbauer spectra could be uniquely fitted with the following parameters: background level, total line intensity, line width Γ (in mm/s), center shift S (in mm/s), η, and the quadrupole coupling constant eQ_gV_{zz} (in mm/s). The latter two parameters fully determine the position and intensities of the 12 possible γ transitions. The values $Q_g = 1.14 \times 10^{-28}$ m^2 and $Q_e = 1.50 \times 10^{-28}$ m^2 for the quadrupole moments of the ground and excited states of ^{151}Eu were used.[24] The center shift gives a measure of the s electron density inside the nucleus and therefore also reflects the oxidation state of the atom. The values of the hyperfine parameters obtained for the R site resemble very much those observed for the 1:2:3 system. This is expected due to the similarity of the R sites in these two compounds. The value of $|eQ_gV_{zz}|$ is, however, smaller than for the 1:2:3 system, in which $|eQ_gV_{zz}| \simeq 5.5$ mm/s was observed.[19] In Table II the parameters obtained by fitting the Mössbauer spectra are given.

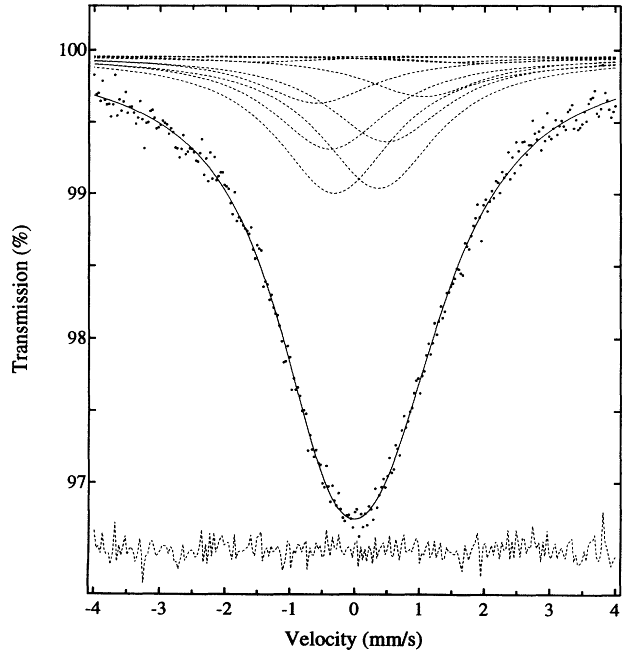

FIG. 4. ^{151}Eu Mössbauer spectrum measured from the $EuBa_2Cu_4O_8$ sample synthesized by the acetate-tartrate sol-gel method. The fit curve, its 12 Lorentzian-shaped components, and the difference between data and fit are shown.

All the Eu atoms are in a 3+ oxidation state since the relative line shift with respect to the Eu^{3+} atoms of the source is close to zero Doppler velocity. A tiny shift towards smaller Doppler velocities is, however, seen when the Eu portion is increased. This shift $\Delta S = -0.02(1)$ mm/s can be explained by the expansion of the crystal lattice, which lowers the s electron density by easing the pressure on the electron orbitals. A similar effect has been reported for the 1:2:3 system, in which the lattice expansion is caused by removal of oxygen.[19] With the aid of formulas (1) and (2) from Ref. 19 we may calculate the expected ΔS, taking the relative volume expansion $\frac{\Delta V}{V} = 0.006(1)$ between the samples $x = 0.25$ and $x = 1.0$, from the lattice parameter data (Table I). The result is $\delta S = -0.012(2)$ mm/s, which agrees with the measured value.

The slight decrease of η probably reflects the decrease of orthorhombicity, which makes the difference between the potential derivatives V_{xx} and V_{yy} smaller. In fact for a tetragonal sample η should be zero.

The larger linewidth and statistical errors for the $x = 1.0$ (LiF) sample could again indicate the presence of a somewhat larger amount of the 2:4:7 phase.

IV. CONCLUSIONS

Essentially single-phase Eu- and Y-based 1:2:4 samples can be synthesized under 1 atm oxygen pressure using sol-gel and LiF flux methods. Magnetic-susceptibility measurements showed only the 80-K transition of the 1:2:4 phase, with no signs of the 90-K transition. Thermogravimetric measurements also confirmed the purity of

TABLE II. Hyperfine parameters of the $Y_{1-x}Eu_xBa_2Cu_4O_8$ system.

x	eQ_gV_{zz} (mm/s)	η	S (mm/s)	Γ mm/s)
0.25	-4.2(5)	0.8(2)	0.08(1)	2.0(1)
0.5	-4.2(4)	0.8(1)	0.075(9)	2.1(1)
0.75	-5.0(1)	0.56(3)	0.082(5)	2.12(3)
1.0	-5.1(1)	0.66(4)	0.064(4)	2.19(3)
1.0 LiF	-5.1(3)	0.5(1)	0.056(7)	2.29(9)

the samples. Replacing yttrium with increasing amounts of europium (0–100%) decreases the orthorhombicity of the samples and lowers the T_c. The larger ionic radius of Eu^{3+} as compared to Y^{3+} also causes the unit cell to expand. The samples exhibit no orientational effects in an 11.7-T magnetic field, contrary to the 1:2:3 and related systems which orient readily.

In the Mössbauer spectra the expansion of the crystal lattice was detected as a change in the center shift. The value of the hyperfine parameters obtained resembled closely those obtained from the $EuBa_2Cu_3O_{7-\delta}$ system. The quadrupole coupling constant was somewhat smaller.

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