

Figure 1. (a) Changes in the electronic spectrum of $[\text{Mn}(\text{O}_2\text{CO}_2)\text{TPP}]^-$ (**2(TPP)**) in toluene resulting from an increase in temperature from -70 to -35 °C. (b) Changes in the electronic spectrum of $[\text{Mn}^{\text{III}}\text{Cl}(\text{TPP})]$ upon reaction in THF at -70 °C with potassium peroxycarbonate prepared in DMF.

or phenoxathiine hexachloroantimonate led to species having spectral properties that are identical with (TPP) or similar to (TPFPP, $\text{TP}_{\text{piv}}\text{P}$) those reported for manganese(V)-oxo-porphyrin species;^{5,9-11} (d) the X-band EPR spectra of these species, run at -150 °C in frozen DMF-THF solution present a strong signal at $g \approx 2$ (**3(TPP)**, 2.050; **3(TPFPP)**, 2.056 (Figure 2); **3(TP_{piv}P)**, 2.048) and a weaker signal at $g \approx 4.4$ (**3(TPP)**, 4.331; **3(TPFPP)**, 4.407 (Figure 2); **3(TP_{piv}P)**, 4.390). It is known that the nature and complexity of frozen-solution d^3 ion EPR spectra depend on the zero-field splitting parameters. When the axial parameter D is small ($2D \ll 0.31 \text{ cm}^{-1}$), the dominating signal lies at $g \approx 2$ attended by one or more broad and weak signals at low fields (1000–1500 G).^{15,16} The spectra observed for **3** present these characteristics. Thus, they are consistent with the presence of high-spin $S = 3/2$ manganese(IV)¹³ porphyrin derivatives. The spectra of different samples of **3(TPFPP)** presented several times an additional weak signal at $g = 6.20$ that showed at 20 K a well-resolved ⁵⁵Mn six-line hyperfine structure with $A = 85 \text{ G}$. This high-field signal is probably not due to an $S = 3/2$ manganese(IV) system^{17,18} and corresponds most probably to a small amount of a decomposition product that has, so far, not been identified.

Moreover, solutions of **3** react instantaneously in THF at -70 °C with trimethylsilyl azide to yield the corresponding manganese(IV)-diazide species **4**¹⁹ (**4(TP_{piv}P)** $\lambda_{\text{max}} = 422, 523 \text{ nm}$) and with trimethylsilylisocyanate to form the manganese(IV) diisocyanate derivatives¹⁹ **5** (**5(TP_{piv}P)** $\lambda_{\text{max}} = 421, 525 \text{ nm}$). They

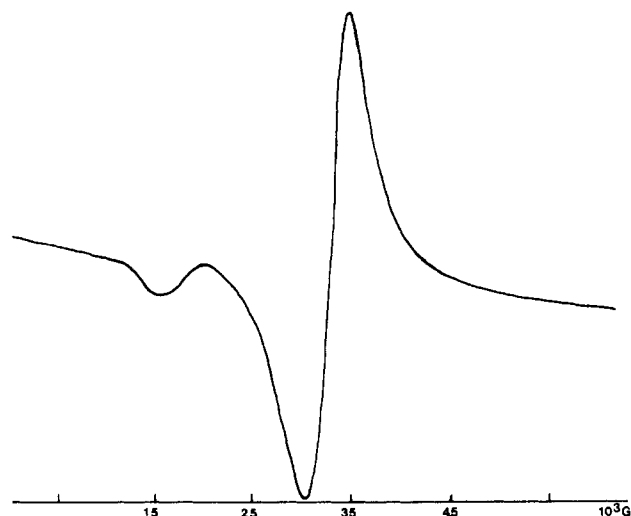


Figure 2. EPR spectrum of $[\text{Mn}^{\text{IV}}(=\text{O})(\text{TPFPP})]$ (**3(TPFPP)**, 10 mmol) in frozen THF-DMF solution ($t = -160$ °C; $\nu = 9.497 \text{ MHz}$).

react also with (trimethylsilyl)imidazole to yield probably the manganese(IV)-diimidazolate complexes **6**²⁰ (**6(TP_{piv}P)** $\lambda_{\text{max}} = 420, 522 \text{ nm}$). Furthermore, **3(TPFPP)** reacts with cyclohexene to give a manganese(II) species and a mixture of cyclohexene oxide (relative yield 40%), cyclohexen-1-ol (30%), and cyclohexen-1-one (30%), identified by GLC.

- (20) The precise nature of these species **6** is presently under study. The EPR spectrum of **6(TP_{piv}P)** indicates the presence of a high-spin $S = 3/2$ manganese(IV) derivative.
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Synthesis, Structure, and Superconductivity of Single Crystals of High- T_c $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

Sir:

Record high onset superconducting transition temperatures (T_c) of ~ 30 – 36 K (at ambient pressure),¹⁻⁴ and ~ 40.2 ^{5a} to 52.5 K ^{5b} (at pressures to $\sim 12 \text{ kbar}$), have very recently been reported for the La-Ba-Cu-O (LBCO) system. Superconducting T_c 's as high as 70 K have been reported in some metastable LBCO samples.⁹

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Table I. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ^a

	x	y	z	$10^4 U_{\text{eq}}, \text{\AA}^2$
La(Sr)	0.0000	0.0000	0.36094 (2)	74 (1)
Cu	0.0000	0.0000	0.0000	40 (1)
O(1)	0.0000	0.5000	0.0000	125 (9)
O(2)	0.0000	0.0000	0.1825 (3)	235 (9)

^aThe complete temperature factors are $\exp(-8\pi^2 U_{\text{eq}}(\sin^2 \theta)/\lambda^2)$, where $U_{\text{eq}} = 1/3 \sum_{ij} U_{ij} a_i^* a_j^* a_i a_j$.

These T_c 's are well above the previous maximum of 23.7 K established⁶ more than a decade ago in Nb_3Ge . The synthesis of LSCO materials requires high-temperature oxidizing conditions, and only polycrystalline samples, sometimes with mixed phases, have been available to date. The nominal composition of the highest T_c materials appear to be $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ ($x \approx 0.1-0.3$, Ba can be replaced by Sr, and y is undetermined). In this communication we report the synthesis, X-ray structural characterization, and superconducting properties of the first single crystals of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$.

Synthesis. Black polycrystalline powders of the title compound, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (LSCO), were prepared by the following procedure. An aqueous solution containing 2.5 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10.3 mmol), 8.29 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (19.1 mmol), and 0.334 g of $\text{Sr}(\text{NO}_3)_2$ (1.58 mmol) was neutralized to pH 7-8 by slow addition of a KOH (0.98 g in 15 mL of H_2O) solution. The hydroxy carbonates of La/Sr/Cu were precipitated by mixing with a K_2CO_3 (6.89 g, 50 mmol) solution and were washed thoroughly with distilled water until the filtrate gave a pH around 8. The blue powders obtained were dried at 140 °C overnight and further calcined at 900 °C for 3 h to give 4.16 g of black powder (quantitative yield). After the product was sintered at 1100 °C for 2 h, chemical analysis by use of inductively coupled plasma/atomic emission spectroscopy gave the following results. Anal. Calcd (found): La, 64.63 (64.4); Sr, 3.31 (2.99); Cu, 15.97 (15.35). The ratio La:Sr:Cu is 1.85:0.14:0.96 (errors approximately 5%). A tube furnace equipped with a chromel/alumel thermocouple was set in vertical position in a hood for the high-temperature flux growth. Initial attempts at crystal growth by mixing the LSCO compound (after 900 °C calcination) with PbF_2 as flux, after heating at 950 °C for 15 h, yielded LaF_3 as the major product (established by powder X-ray diffraction analysis). Subsequent trials in which PbO was used as flux were successful. Thus, a platinum crucible charged with 66 mg of the LSCO compound and 210 mg of a lead oxide and lead dioxide mixture (200 mg:10 mg) was heated at 1050 °C in air. Approximately 77 mg of product and remaining flux were obtained after 65 h. Many black shiny platelet crystals on the order of $0.14 \times 0.14 \times 0.009 \text{ mm}^3$ were found imbedded in the small amount of remaining melt.

Structure. Powder X-ray diffraction studies of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system have been reported.⁷ Uchida et al.² and Takagi et al.³ identified the structure of the superconducting phase as being of the K_2NiF_4 layered-perovskite type (tetragonal, space group $I4/mmm$), but neither crystal structure lattice parameters nor coordinates were reported. Subsequently, by use of powder neutron diffraction data, Jorgensen et al.⁸ confirmed the structure of $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ (~95% purity, $T_c \sim 35 \text{ K}$) suggested by Uchida et al.² and Takagi et al.³ and gave the first report of the tetragonal structural parameters [$a = 3.7873$ (1) \AA , $c = 13.2883$ (3) \AA ; for La, 0, 0, $z = 0.36063$ (9); for Cu, 0, 0, 0; for O(1), 0, $1/2$, 0; for O(2), 0, 0, $z = 0.1828$ (2)] with $Z = 2$ formula units per unit cell at 295 K. The refined site occupancies of the oxygen atoms (O(1) and O(2)) suggested a limit on the oxygen atom vacancies in this system of 1% or less, which is within the limits

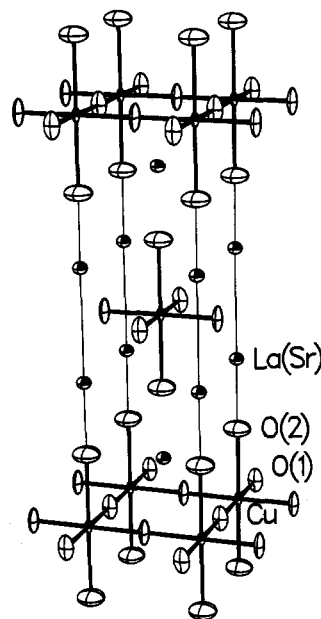


Figure 1. Crystal structure of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. The thermal ellipsoids are drawn at the 90% probability level. Layers are formed by corner-sharing, tetragonally elongated CuO_6 octahedra. There are two layers per unit cell, related by the I -centering operation.

of accuracy of the neutron powder diffraction measurement.

The single-crystal analysis¹⁰ confirms that $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ is of the K_2NiF_4 type (space group $I4/mmm$;¹¹ see Figure 1), in agreement with the powder diffraction data. Final coordinates and thermal parameters are given in Table I. The atomic positions are in good agreement with those obtained for the barium-doped analogue derived from powder neutron diffraction data,⁸ thus establishing that $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ are isostructural. The coordination geometry around the copper atoms is a tetragonally elongated octahedron (D_{4h} symmetry; $d[\text{Cu}-\text{O}(1)] = 1.898$ (1) \AA , $d[\text{Cu}-\text{O}(2)] = 2.406$ (4) \AA). The lanthanum (and strontium) sites have a coordination number of 9 (C_{4v} symmetry) with bond distances $d[\text{La}-\text{O}(2)]$ (1 bond) = 2.354 (4) \AA , $d[\text{La}-\text{O}(1)]$ (4 bonds) = 2.639 (1) \AA , and $d[\text{La}-\text{O}(2)]$ (4 bonds) = 2.745 (1) \AA . As seen in Figure 1, the structure contains layers of corner-sharing elongated octahedra. The lanthanum ions occupy cavities formed primarily by the terminal oxygen atoms, O(2).

We have attempted to verify the strontium doping level in our crystals ($x = 0.15$) derived from chemical analyses from our starting materials. However, although extensive multiple X-ray data were collected, the data are not sensitive enough to allow us to refine the Sr mole fraction. The crystallographic agreement factors are essentially the same for Sr levels of $x = 0.05$ and $x = 0.15$, with minor changes in the La(Sr) thermal parameters.

Superconductivity. The individual crystals were too small to attach leads for a four-probe conductivity measurement or for

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(10) X-ray diffraction data were collected on a Nicolet P3/F diffractometer, and the tetragonal unit cell parameters (space group $I4/mmm$, $Z = 2$) are as follows (296 K): $a = 3.7966$ (7) \AA , $c = 13.186$ (4) \AA , $V = 190.1$ (1) \AA^3 , $\rho_{\text{calcd}} = 6.945 \text{ g/cm}^3$. Diffraction data ($\theta-2\theta$ scans, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.7107 \text{ \AA}$) were collected in the range $4^\circ < 2\theta < 70^\circ$, and 1753 data from all octants were corrected for absorption ($\mu = 280 \text{ cm}^{-1}$, $T_{\text{min}} = 0.074$, $T_{\text{max}} = 0.782$) and averaged ($R_{\text{int}}(F) = 0.025$) to yield 160 unique reflections. The intensities of three standard reflections, measured every 93 reflections, deviated randomly by less than 2% from their mean values. Full-matrix least-squares refinement with anisotropic temperature factors and isotropic extinction correction (13 variables) yielded $R(F_o) = 0.016$, $R_w(F_o) = 0.022$, and $\text{GOF} = 0.79$. A superposition of La and Sr scattering factors in the proper proportions was employed for the La(Sr) site. Computer programs by: Strouse, C. "UCLA Crystallographic Program Package", 1986.

(11) The space group was confirmed from systematic absences and the successful least-squares refinement. Neither the angle settings of carefully centered high- θ reflections nor the intensities obtained from the 16 forms of all general reflections (within the accuracy of the absorption correction) indicate any deviation from tetragonal symmetry.

inductive measurements on a single-crystal specimen. However, superconductivity was detected by rf penetration depth measurements at 500 kHz in a 1.5-mg sample consisting of many crystal specimens. This sample gave an onset temperature for superconductivity (T_c) of 8.5–9.0 K, a broad transition, and a low signal response (increase in resonant frequency). These properties indicate that only a small fraction of the sample had bulk superconductivity and that the crystals possessed a range of T_c values. Resistivity measurements would likely give a much higher (average) T_c , as evidenced by a comparison between published resistivity and magnetic studies of the polycrystalline samples. We plan to investigate the doping levels, oxygen deficiencies, and conductivity in our crystals as larger amounts of material become available.

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Note Added in Proof. It has been reported¹² that the Sr content and T_c in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are reflected in the c/a ratio of the lattice constants. In our study we find $c/a = 3.47$, thus giving the formula $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ and $T_c \approx 8$ K, which is consistent with our single-crystal results. Since Pb-doped La_2CuO_4 is not superconducting,¹³ we believe that very little, if any, lead has been incorporated into our crystals.

Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and anisotropic thermal parameters (Table X2) (2 pages). Ordering information is given on any current masthead page.

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Occurrence of Superoxide Radical Ion in Crystalline $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ Prepared via Solid-State Reactions

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Superoxide radical ion O_2^- is an active species of oxygen and is known to play important roles in many chemical reactions involving O_2 . The formation of O_2^- on or in solid oxides is usually achieved with the aid of energetic photons such as UV, X-ray, or γ -ray radiation. It has been found that O_2^- occurs in the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ crystal prepared by the solid-state reaction between CaCO_3 and Al_2O_3 or $\text{Al}(\text{OH})_3$ powder without any accompanying irradiation; the concentration of O_2^- goes up to ca. 4×10^{18} units/g. From the change in the line shape with temperature, the O_2^- is concluded to be included in the structural cavity inherent in the crystal lattice. A drastic reduction in the concentration of O_2^- on anion substitution and on heating under an oxygen-free atmosphere strongly suggests that the occurrence of O_2^- is closely related with "free oxygen", which is a unique characteristic of the $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ crystal. Such characteristics found for $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ are analogous to those for ultramarine, $\text{Na}_8[\text{Si}_6\text{Al}_6\text{O}_{24}]_2\text{S}_2$.

Introduction

The superoxide radical ion O_2^- is of importance as an active species of oxygen in the oxidation reactions of inorganic molecules as well as hydrocarbons.¹ Curiosity about the role of oxygen at surfaces led to extensive studies on O_2^- adsorbed on oxide surfaces being carried out as summarized in two thorough reviews.^{1,2} In these studies, O_2^- formation is induced by irradiation of solid oxides in an atmosphere containing oxygen with energetic photons such as X- or γ -rays except for a few cases.^{3,4}

In this paper the authors report that high concentration (4×10^{18} units/g) of O_2^- occurs as a guest of inherent structural cavity in crystalline $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ prepared without the aid of irradiation by such energetic photons. A compound $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$,

one of the crystalline phases in the system of CaO and Al_2O_3 , is a major constituent in aluminous cements. It has attracted much attention from cement chemists and crystallographers because of its atmosphere-sensitive properties and structural characteristics.⁵⁻⁹

The physical properties such as density, refractive index, or unit cell volume vary with atmosphere in the preparation or in heat treatment. Because of reversible absorption of water over a wide temperature range without a major change of structure, $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ is termed a zeolitic phase. The crystallographical

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