

refractive index is indicative of the atomic composition and structural density. The AES studies have shown that the atomic composition of the silicon carbonitride films does not depend on temperature. Therefore, the temperature dependence of the refractive index must be attributed to the increase in the structural density. We postulate that as temperature increases, the rupture of the cyclic structure of the methylsilazane compound is enhanced, which leads to a denser packing of the film network structure.

In conclusion, we have demonstrated the ability to deposit silicon carbonitride films using a gas mixture of methylsilazane and hydrogen in the relatively low temperature range 873-1073 K. The apparent activation energy for the film deposition is 105 kJ/mol, far lower than the dissociation energies of individual bonds in the methylsilazane compound. While the change in temperature causes no change in the composition of the film, it has a significant effect on the structural density of the film. The increase in the structural density with temperature may be attributed to the enhanced rupture of the cyclic structure of the methylsilazane compound, which results in a denser packing of the silicon carbonitride network structure.

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**Registry No.** Silicon carbonitride, 64477-28-7.

### Effect of Oxygen Stoichiometry on the Superconductivity of $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$

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The new superconducting system  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  has recently been investigated.<sup>1-3</sup> In order to ascertain whether the observed properties are optimized with respect to the oxygen content, we have systematically varied  $\delta$  and characterized the following superconducting properties: critical temperature ( $T_c$ ), flux exclusion (diamagnetism), and flux expulsion (Meissner effect). In addition, for one sample, with  $x = 0.4$  and  $\delta = 0.22$ , the critical current density ( $J_c$ ), as determined by magnetic measurements, was obtained as a function of temperature.

Ceramic samples of  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  with  $x = 0, 0.2$ , and  $0.4$  were prepared by sintering at 900 °C, annealing at 860 °C, and cooling in a low oxygen atmosphere to preserve the orthorhombic phase and  $\delta \approx 0$ . Subsequently, the samples were reheated in a thermobalance in an oxygen atmosphere so that  $\delta$  increased to various values between  $\delta = 0$  and 1.5. Each sample was then quenched to preserve its value of  $\delta$ . Quenched samples were examined by X-ray diffraction (XRD) to ascertain the phase content and by magnetic measurements to determine  $T_c$  and qualitatively

Table I. Summary of Magnetic Measurements

$x^a$	$\delta^b$	$T_c$ , K	fraction	
			diamagnetic (5 K)	Meissner (5 K)
0.4	0.22	67	0.71	0.16
	0.06	78	0.84	0.25
	0.22	77	0.74	0.18
	0.39	77	0.58	0.15
	0.64	75	0.44	0.11
0.2	0.16	61	0.35	0.08
	0.08	71	0.80	0.18
	0.31	66	0.27	0.06

<sup>a</sup> $x$  is the Ca content per formula unit. <sup>b</sup> $\delta$  is the O excess over 8 per formula unit.

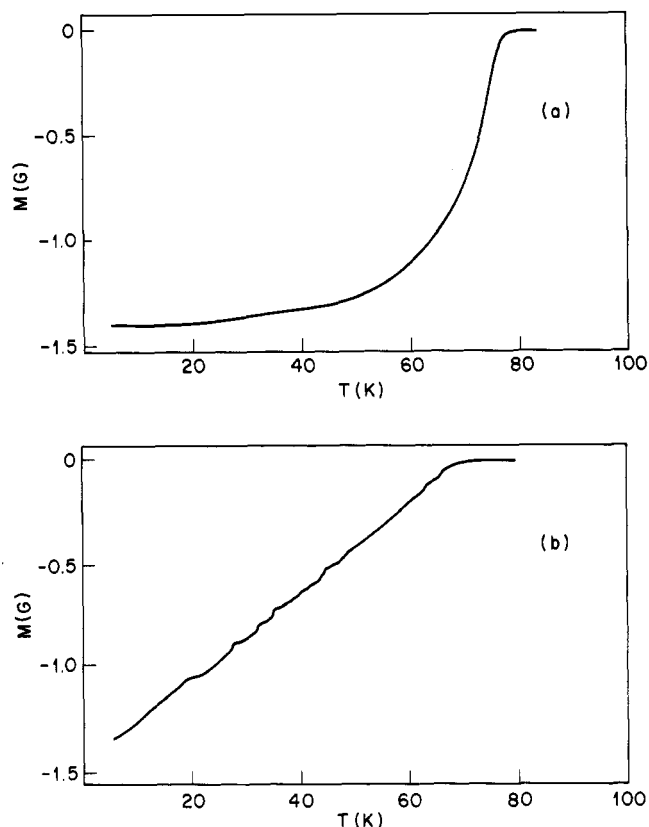


Figure 1. Magnetic moment as a function of temperature for samples cooled in zero field ( $H < 0.1$  G) and then measured in a field of 20 G as the temperature is increased. (a)  $x = 0.4$ ;  $\delta = 0.06$ ; (b)  $x = 0.2$ ,  $\delta = 0.08$ .

the percentage of the superconducting phase present. The XRD indicated each sample was essentially single phase. However, this examination does not directly confirm that the oxygen content is uniform throughout the sample since previous work has shown that single phase exists over a wide range of oxygen content.<sup>3</sup>

The magnetic measurements were carried out by using a vibrating sample magnetometer, VSM. Samples nominally  $2 \times 2 \times 10$  mm<sup>3</sup> were cut from 1/4-in. pellets. The field was applied along the long axis. The magnetic results are summarized in Table I where we give  $T_c$ , the diamagnetic fraction, and the Meissner fraction as a function of  $x$  (the Ca content) and  $\delta$  (the oxygen excess over eight oxygen atoms per formula unit).

To obtain the diamagnetic fraction, the sample is cooled to 5 K in zero field ( $< 0.1$  G). Then the applied field is increased to 20 G, and the effective magnetization is obtained as a function of increasing temperature. The Meissner fraction is measured by decreasing the temperature from above  $T_c$  in the field of 20 G. It is interesting

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to note that the diamagnetic magnetization,  $M$ , measured for all the samples with  $x = 0.4$  has the usual behavior as a function of temperature. That is,  $M$  is essentially flat until the temperature is within 10–20 K of  $T_c$ , where it then rises rapidly to zero at  $T_c$  (Figure 1a). In contrast, for the samples with  $x = 0.2$ ,  $M$  increases nearly linearly from 5 K to 0 at  $T_c$  (Figure 1b). We have no explanation for this observation, and a detailed study would require samples known to be homogeneous. However, the data in Table I do show that a  $T_c$  substantially above 77 K cannot be obtained in  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$  by varying the oxygen content.

From Table I, it may be seen that for the samples with 0.4 Ca per formula unit there is a broad peak in the superconducting quality around  $\delta = 0.06$ . A similar peak for  $x = 0.2$  is seen at  $\delta = 0.08$ . It should be stressed, however, that the quoted values of  $T_c$  are at best accurate to only  $\pm 1$  K. In addition, the fraction of a ceramic sample that appears diamagnetic is not a definitive measure of the volume fraction of the sample that is superconducting. Any number of effects, such as a spongelike superconducting phase, can lead to an overestimate of the fraction actually superconducting. In this case, the nonsuperconducting phase filling the holes in the superconducting sponge is shielded from the applied field and thus contributes to the diamagnetic fraction.

The critical current density,  $J_c$ , for  $\delta = 0.22$  and  $x = 0.4$  was determined from magnetic measurements using the Bean model<sup>4</sup> and the usual assumption for these materials that all the shielding currents are intragranular.<sup>5</sup> At 15 K,  $J_c = 3 \times 10^5$  A/cm<sup>2</sup>, which is about a factor of 5 smaller than that obtained from representative  $\text{Ba}_2\text{YCu}_3\text{O}_7$  samples.  $J_c$  falls rapidly with increasing temperature to  $10^4$  A/cm<sup>2</sup> at 54 K.

**Acknowledgment.** We thank W. W. Rhodes for the sample preparation.

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## Aryl-Bridged Polysilsesquioxanes—New Microporous Materials

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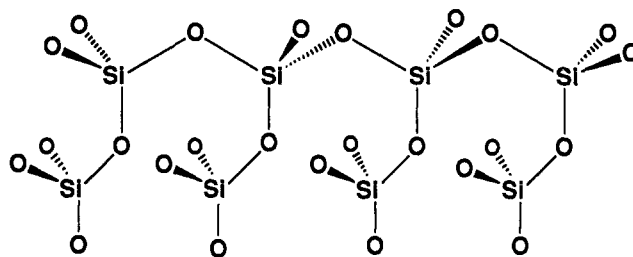
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The silicate framework of alternating silicon and oxygen atoms (1) comprises the earth's most abundant mineral form.<sup>1</sup> A remarkable diversity of silicate morphology exists within this simple pattern of connectivity.

Synthetic silicates, prepared by sol-gel processing of alkoxy silanes (eq 1), allow for the preparation of amor-

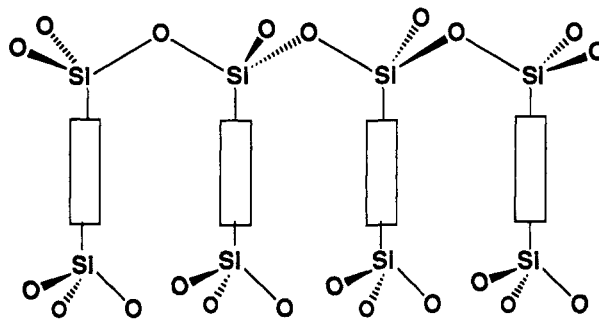


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phous materials (xerogels) that are precursors for high-purity glasses, ceramics, coatings, and fibers.<sup>2</sup> Sol-gel processing also provides for the preparation of organolithic macromolecular materials by co-condensing tetraethoxysilane (TEOS) with hydroxy-terminated poly(dialkylsiloxanes)<sup>3</sup> or by replacing an alkoxy substituent on TEOS with an alkyl or aryl group to produce aryl- or alkyl-substituted polysiloxanes (T resins).<sup>4</sup>

In principle, sol-gel technology provides an opportunity to produce an almost infinite variety of silicate-like structures by the introduction of organic spacers at regular intervals in the silicate framework (2). We report the



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preparation of aryl bridged polysilsesquioxanes that are produced by the sol-gel processing of bis(triethoxysilyl) and bis(trichlorosilyl)aryl monomers 3–5. The phenyl, biphenyl, and terphenyl groups separating the silicon atoms are rigid-rod spacers with Si-aryl-Si distances of 0.67, 0.87 and 1.08 nm, respectively. The bis(triethoxysilyl) and bis(trichlorosilyl)aryl monomers can be represented by two silicon tetrahedra elongated by an aryl spacer. The monomers can condense at three vertices of each tetrahedra to produce an extended network (2b) without an opportunity for close packing. When highly condensed, such materials are expected to possess microporosity. The organic portion provides an opportunity for engineering mechanical, bulk dielectric, and optical properties of the material. In addition, the aryl groups may permit molecular level control over the aryl-bridged polysilsesquioxane microstructure, influencing properties such as microporosity. Such an effect has been proposed in layered metal aryl-bisphosphonates<sup>5</sup> and was anticipated but, as

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