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Communications

Superconductivity in $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$

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Reports of high-temperature superconductivity in non-copper-containing $(\text{Ba},\text{K})\text{BiO}_3^1$ and $\text{Ba}(\text{Bi},\text{Pb})\text{O}_3^2$ and the new class of high- T_c thallium cuprates,³ as well as reports of low-temperature superconductivity (0.5 K) in $\text{Ba}(\text{Pb},\text{Tl})\text{O}_3^4$ suggest that oxide phases containing Tl, Bi, and Pb might well exhibit interesting superconducting properties, due to the close proximity in energy of the Tl, Bi, and Pb 6s energy levels to the oxygen 2p level.

Rather than examining a wide range of random combinations of the elements, we chose to limit the possibilities by recognizing that all of the recently discovered high- T_c superconductors have layered structures;⁵ we therefore used only stoichiometries that could possibly produce a centrosymmetric layered analogue of a cubic perovskite structure. This led us to consider materials of empirical formula $\text{Ba}_x\text{Bi}_a\text{Pb}_b\text{Tl}_c\text{O}_{3x}$, in which a , b , and c are whole numbers with $x = a + b + c$. The smallest value of x that could give rise to a centrosymmetric structure containing segregated planes of three species is four. Therefore, three

Table I. X-ray Powder Diffraction Data for $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$

h	k	l	rel int	d_{obs}	d_{calc}
1	0	1	3	4.9590	4.9549
0	0	2	8	4.2742	4.2790
0	2	0	100	3.0238	3.0294
2	2	0	4	2.1578	2.1453
0	0	4	10	2.1431	2.1395
1	1	4	8	1.9151	1.9147
2	0	4			1.7494
			31	1.7509	
3	1	2			1.7526
0	2	4			1.7476
			29	1.7473	
1	3	2			1.7491
2	2	4	6	1.5143	1.5149
0	4	0	13	1.5135	1.5147
3	3	0	3	1.4298	1.4302
1	1	6	11	1.3521	1.3535
4	0	4	4	1.2364	1.2387
0	4	4	4	1.2362	1.2362

samples were examined initially, corresponding to $\text{Ba}_4\text{-Bi}_2\text{PbTlO}_{12}$, $\text{Ba}_4\text{BiPbTl}_2\text{O}_{12}$, and $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12}$. The last of these constitutes a novel superconductor with $T_c = 10.7$ K.

In an attempt to determine if this new material was significantly different from the known phase $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$,² a series of materials of composition $\text{Ba}_4\text{BiPb}_x\text{Tl}_{3-x}\text{O}_{12-\delta}$ was prepared.⁶ The structures of the products were examined by X-ray powder diffraction;⁷ in

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(4) Subramanian, R.; Subramanian, M. A.; Sleight, A. W. *Mater. Res. Bull.* 1989, 24, 1413.

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(6) Samples were prepared in sintered Al_2O_3 crucibles or boats starting with 99.999% Bi_2O_3 , 99% PbO , 98% Tl_2O_3 , and 99.99% BaO , all supplied by Aldrich, using a modification of the procedure originally reported for $(\text{Ba},\text{K})\text{BiO}_3$.¹ Stoichiometric amounts of dry powders were ground in a wobble bug for 4 min; a 33% excess of Tl_2O_3 was used to compensate for loss during the reaction process. The mixtures were loaded into Al_2O_3 crucibles and placed in a quartz tube for 1 h under flowing argon (2–5 cm^3/min) at 850 °C and then quenched immediately by removal from the oven. Caution: Tl_2O is highly toxic and is volatile under the conditions used; the preparation should be performed in a good hood. The pre-reacted mixtures were then reground by hand and pressed into pellets (12.5 × 2 mm) that were loaded into boats for rapid (15 min) heating to 800 °C under flowing argon. After rapid cooling to 450 °C, the argon flow was replaced by oxygen with a flow rate of 2–5 cm^3/min . Subsequently, the temperature was reduced to 425 °C and maintained there for 1.25 h, followed by oven cooling to room temperature.

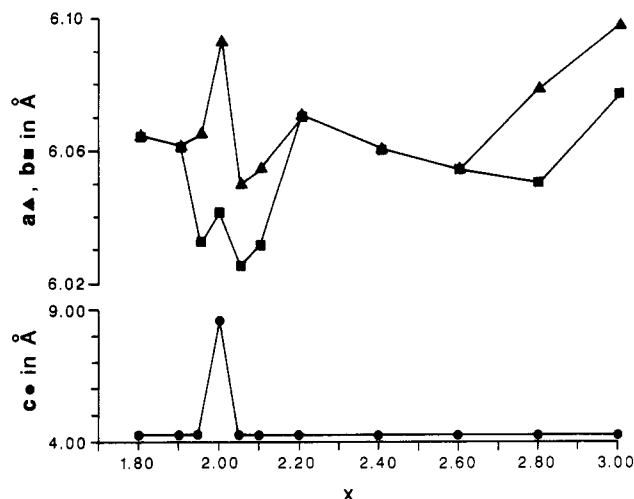


Figure 1. a , b , and c (in Å) vs x for $\text{Ba}_4\text{BiPb}_2\text{Tl}_{3-x}\text{O}_{12-\delta}$.

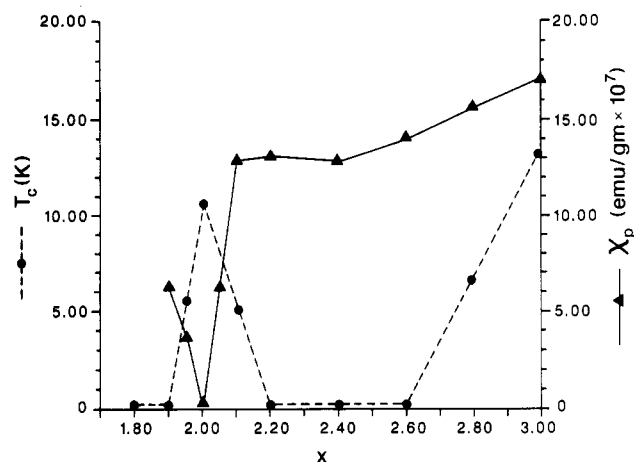


Figure 2. T_c (K) and χ Pauli in emu/gm vs x in $\text{Ba}_4\text{BiPb}_2\text{Tl}_{3-x}\text{O}_{12-\delta}$.

all cases, the powder patterns corresponded to the presence of a single phase. The X-ray powder patterns of the materials could be indexed by using a doubled cubic perovskite unit cell similar to that observed for BaBiO_3 .⁹ The indexed powder pattern for the $x = 2.00$ material (Table I) also shows the presence of a new (101) reflection at 4.959 Å, which is not observed in BaPbO_3 ,¹⁰ BaBiO_3 ,¹¹ or $\text{Ba}(\text{Bi,Pb})\text{O}_3$.² The stoichiometry of the $x = 2.00$ material was confirmed by chemical analysis for thallium, which is readily lost as volatile Tl_2O : calc 12.60%; found 12.87%. A structural transition from orthorhombic symmetry for the known $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$ to tetragonal symmetry for $x = 2.6$ (Figure 1) is accompanied by the loss of superconducting behavior above 4.2 K (Figure 2), as has been recently reported.¹² The return of orthorhombic symmetry for $1.95 \leq x \leq 2.10$ (Figure 1), as well as the reappearance of a superconducting transition (Figure 2), indicates that the $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$ material is both structurally and electronically different from $\text{BaBi}_{0.25}\text{Pb}_{0.75}\text{O}_3$.

(7) X-ray powder diffraction data were obtained on a Scintag powder diffractometer using $\text{Cu K}\alpha_1$ radiation (1.540 59 Å). Data were collected at 0.01° intervals over a 2θ range of 10 – 90° . Reflections were indexed and analyzed by a Fortran 4 X-ray fitting program.⁸

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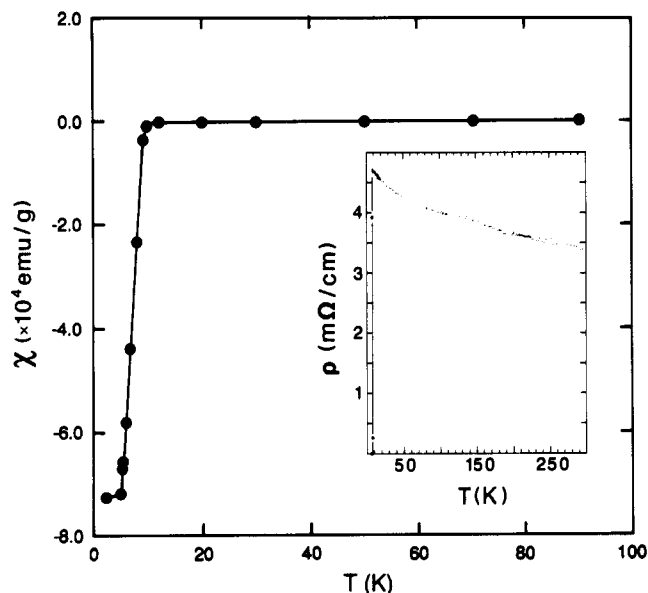


Figure 3. Susceptibility in emu/gm vs T (K) for $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$. Inset of resistivity in $\text{m}\Omega/\text{cm}$ vs T (K) for $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$.

A strong Meissner effect in a field of 5 G was observed,¹³ with the highest transition temperature of 10.7 K obtained for $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$. The magnetic susceptibility of this sample showed a sharp superconducting transition, as seen in Figure 3. The magnitude of the Meissner effect was ca. 90% of that of a lead standard, consistent with the presence of a homogeneous superconducting sample. Above T_c , the observed susceptibility was independent of temperature for all superconducting phases examined. Four-probe dc resistivity measurements (obtained on a pellet with a freshly prepared surface) confirmed the sharp superconducting transition (width ca. 0.5 K) in $\text{Ba}_4\text{BiPb}_2\text{TlO}_{12-\delta}$ (inset Figure 3). The room-temperature resistance was approximately 5 $\text{m}\Omega/\text{cm}$, and weak semiconducting behavior was observed at lower temperatures down to the T_c .

The high-temperature superconductors based upon cuprates possess a very low density of states at the Fermi surface, as opposed to that expected for a normal BCS superconductor;¹⁴ therefore, a study of the density of states of this new material was performed in an attempt to investigate the superconducting mechanism. Since the high-temperature susceptibility (χ Pauli) is directly proportional to the density of states at the Fermi surface for a metal,¹⁵ the gram susceptibility of all superconducting samples was measured to probe the dependence of T_c upon the carrier density. As shown in Figure 2, an inverse relationship between T_c and the high-temperature susceptibility was observed, indicating that the T_c of this material has the opposite dependence upon the density of states at the Fermi surface as predicted by BCS theory.¹⁵

This inverse relationship between the density of states and the T_c for the material indicates that a composition-dependent property of these materials is critically important for the observed superconducting properties. Since superconductivity in the BaMO_3 systems, $M = \text{Bi}$ or Pb , is considered to be dependent upon the overlap of the 6s

(13) All susceptibility data were collected on an S.H.E. SQUID magnetic susceptometer. Meissner effect data and χ Pauli data were collected in a field of 5.00 G.

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state with the oxygen 2p level,¹ the narrow range of composition that gives rise to superconductivity for this new material can be interpreted as indicating a very narrow range where the 6s state of the Tl, Bi, and Pb overlap sufficiently with the 2p level of oxygen. Although the 6s energy levels of Pb and Bi are nearly identical, that of Tl is considerably higher than that of Bi or Pb. Therefore, superconductivity in this system is not critically dependent upon the density of states of the Fermi surface as predicted by BCS theory, but rather upon the degree of overlap of the three different 6s states with that of the oxygen 2p level.

Band structure calculations for these materials may indicate why their electronic structure is so sensitive to slight variations in the thallium content and thereby help to elucidate the origin of the anomalous properties of these superconducting materials.

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2-(Pentacosa-10,12-diynylamino)-5-nitropyridine: A New Polymerizable Amphiphile for Nonlinear Optical Langmuir-Blodgett Films

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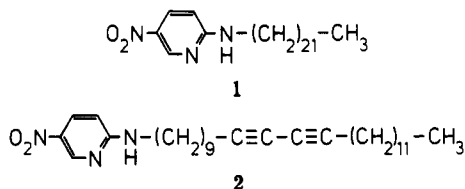
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Recently we have shown that long-chain-substituted 2-(alkylamino)-5-nitropyridines such as 1 are excellently



suited for optical second harmonic generation in Langmuir-Blodgett (LB) films.¹⁻³ Optical nonlinearities are due to the donor-acceptor-substituted pyridine headgroup and the noncentrosymmetric arrangement of the molecules in a polar Y-type (herringbone) structure (Figure 1).

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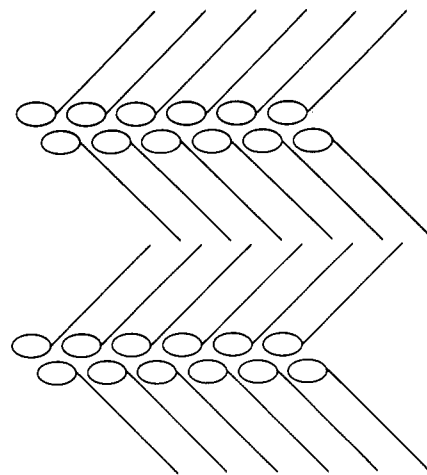


Figure 1. Structural model for polar Y-type structure (straight lines are alkyl chains, ovals represent chromophores).

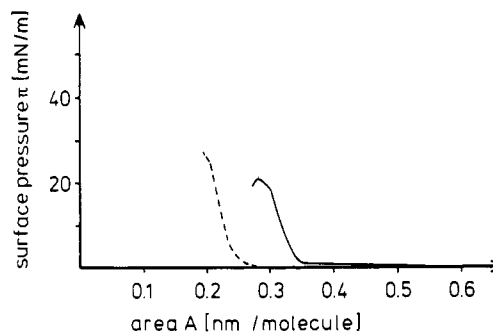


Figure 2. π/A isotherms of 2 (—, subphase, pure water, $T = 7.7$ °C) and a 1:1 mixture of 2 and 3 (---, subphase, 3×10^{-4} M CdCl_2 solution, pH 6.6, $T = 10$ °C).

Compounds such as 1 are superior to other donor-acceptor-substituted amphiphiles⁴⁻⁶ with regard to film-forming properties and ease of formation of the acentric structure.

The purpose of the present investigation was to further improve the stability of the LB films by using polymerizable amphiphiles. We therefore synthesized 2-(pentacosa-10,12-diynylamino)-5-nitropyridine (2) containing a diacetylene group in the alkyl chain. The diyne units can be polymerized in a solid-state 1,4-addition reaction upon UV or high-energy radiation.⁷ In the following, film-forming properties, polymerizability, and optical second harmonic generation from LB films based on 2 will be described.

2 (mp 55–57 °C) was prepared by nucleophilic substitution of 2-chloro-5-nitropyridine with 1-aminopentacosa-10,12-diyne⁸ in about 40% of the theoretical yield. The crude product was purified chromatographically (silica gel, hexane/ether 1:1) and recrystallized from ethanol. Spreading of 2 at the air-water interface (Lauda film balance equipped with a film lift FL-1; Milli-Q water) results in the formation of a monomolecular film with solid condensed behavior. As shown in Figure 2, the collapse

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(8) 1-Aminopentacosa-10,12-diyne was obtained from 3 via standard procedures including the formation of the acid amide and the reduction of the amide using lithium aluminum hydride.