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Preparation of Bismuth- and Thallium-Based
Cuprate Superconductors

by

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13. ABSTRACT (Maximum 200 words) A review of the synthetic methods used to prepare the bismuth and thallium families of cuprate superconductors has been presented. An overview of our current knowledge of phase relationships in the bismuth systems is also given; such studies of the thallium-containing compounds are yet to be reported. The importance of and the difficulties posed by the preparation of phase-pure samples with reproducible structures and chemical compositions cannot be understated; the elucidation of structure-property relationships that correlate with the appearance of superconductivity begins with sample integrity. The synthetic challenge is particularly acute in the case of the superconducting oxides because of their apparently inherent "unstable" nature, a situation reminiscent of the difficult syntheses of metal-insulator type metal oxides. Neophytes are urged to be patient, diligent, and well-equipped with knowledge of the literature.				
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Cuprate Superconductors**

S.A. Sunshine and T.A. Vanderah

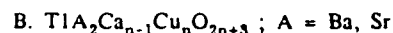
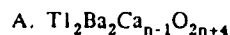
1.0 INTRODUCTION

Superconductivity in the Bi-Sr-Cu-O system at relatively low temperatures was first reported by Michel, et al. (1). Addition of Ca to this system led to the report of superconducting transitions between 80 and 110 K (2). These discoveries led to frantic attempts in a number of laboratories to prepare single-phase samples of the phases responsible for superconductivity. Study of single crystals revealed that these transitions are due to three different superconducting phases that are often represented by the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$; $n = 1, 2$, and 3. This represents an idealized formula for the phases involved and schematic drawings of the ideal structures are given in Figure 1.

Within weeks after superconductivity was observed above 77 K in the Bi-Sr-Ca-Cu-O system, Sheng and Hermann (3) reported a record-high T_c value of 120 K for a Tl-Ba-Ca-Cu-O phase. The results were quickly confirmed (4)-(9) and the existence of a large family of thallium-containing superconducting oxides was revealed (10).

A number of chemical reviews of cuprate superconductors have included the bismuth and thallium families (11)-(14). Reviews focussing on the structural chemistry of these two series are also available (15),(16). On the thallium cuprates, an overview of structural studies has appeared (17), and a detailed review of synthesis, structural chemistry, and electronic behavior will soon be available (18).

Two series of thallium-containing cuprate superconductors have been synthesized with the following ideal general formulas (10):



These structurally related series are intergrowths of oxygen-deficient perovskite layers (with "n" denoting the number of Cu-O layers per perovskite slab) and rock salt-type layers. These structures are cousins of the Aurivillius family of oxides (11) and are also related to the Ruddlesden-Popper-type phases (15). The compounds in Series A adopt the same ideal structures as those of the Bi family of superconductors which are depicted in Figure 1; the structures of the series B phases are shown in Figure 2. The two series differ in the thickness of the rock salt portion of the structure. In series A, the rock salt "slab" is three layers thick ($2\text{TlO} + \text{BaO}$); in series B, two layers thick ($\text{TlO} + \text{BaO}$). Series A is referred to as having "thallium bilayers"; series B, "thallium monolayers". The layer structures of these compounds lead to characteristic c-axis lengths of the unit cells. Although the unit cells all tend to be large and the X-ray powder patterns rather complex, the low-angle (002) or (001) reflections can often be used to sort out product phases; routine X-ray powder diffraction scans should therefore be started at 5 (or less) degrees two-theta in order to record this characteristic region (see Chapter 13).

It is common practice to refer to these compounds using numerical acronyms corresponding to the metal stoichiometries. The decoding scheme and T_c values are collected in the following table (13)(21)-(23); the lead-substituted phases are included but not generally referred to with acronyms.

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Table I Bismuth- and Thallium-Based Superconducting Cuprates ¹		
Acronym	Ideal Formula	T _c (K)
2201	Bi ₂ Sr ₂ CuO ₈	10
2212	Bi ₂ Sr ₂ CaCu ₂ O ₈	90
2223	Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₁₀	110
2234	Bi ₂ Sr ₂ Ca ₃ Cu ₄ O ₁₂	90
2201	Tl ₂ Ba ₂ CuO ₈	90
2212	Tl ₂ Ba ₂ CaCu ₂ O ₈	110
2223	Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	122
2234	Tl ₂ Ba ₂ Ca ₃ Cu ₄ O ₁₂	119
1201	TlBa ₂ CuO ₈	non-S C
1212	TlBa ₂ CaCu ₂ O ₇	80
1223	TlBa ₂ Ca ₂ Cu ₃ O ₉	110
1234	TlBa ₂ Ca ₃ Cu ₄ O ₁₁	122
1245	TlBa ₂ Ca ₄ Cu ₅ O ₁₃	110
	Tl _{0.6} Pb _{0.5} Sr ₂ CuO ₈	non-S C
	(Tl,Pb)Sr ₂ CaCu ₂ O ₇	90
	(Tl,Pb)Sr ₂ Ca ₂ Cu ₃ O ₉	122

¹ Recently, two analogous series of bismuth- and thallium-based uprate series have been reported with the formula Bi₂Sr₂(Ln_{1-x}Ce_x)₂Cu₂O_{10-y}; Ln = Sm, Eu, or Gd (19). In the thallium series Bi,Sr is replaced by Tl,Ba. The bismuth series is superconducting with T_c values below 30 K, while the thallium compounds were not superconductors. The structure is similar to the bilayer Aurivillius-like thallium and bismuth families, except that a fluorite-like layer (Ln_{1-x}Ce_x)O₂ separates the CuO₂ sheets instead of calcium ions. A very similar series with thallium monolayers instead of bilayers has also been found, but was not superconducting (20).

Some of the compounds in Table I have been prepared as single crystals and/or well-crystallized single-phase samples, while others have been obtained in multi-phase products with structural information provided by electron microscopy (13). Compounds that have been well-characterized in single-phase polycrystalline form and/or as single crystals include; the bismuth family, n=1,2,3 [2201, 2212, 2223] (13); the thallium bilayer phases, n=1,2,3 [2201, 2212, 2223] (13); the thallium monolayer phases, n=2,3 [1212, 1223] (13)(24); and the Pb-substituted thallium phases (25). The highest superconducting transition temperatures found to date, above 120K, are exhibited by the n=3 thallium bilayer phase (13), the n=4

thallium monolayer phase (20), and $(\text{Pb}_{0.6}\text{Tl}_{0.4})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ (25). It is now generally accepted that lower T_c values are found for phases with more than three or four Cu-O layers (21)(26).

The bismuth- and thallium-based cuprate superconductors differ in a number of aspects, most of which seem attributable to the chemical difference between trivalent bismuth and thallium: Bi^{3+} possesses a lone pair ($6s^2$) in its valence shell, in contrast to the noble gas configuration of Tl^{3+} . As can be seen in Figure 1 (see also Chapter 13), the ideal structures of the $n=1-3$ (Tl,Bi) bilayer phases are identical. However, the chemical nature of Tl^{3+} and Bi^{3+} result in different deviations from the ideal structures: Tl^{3+} behaves as if it were somewhat too small for its site, whereas Bi^{3+} possesses the lone pair that must be structurally accommodated (7). Figure 3 (7) depicts some of the differences between the average structures of the thallium and bismuth 2201 phases. Displacements within the Bi-O layers result in the formation of complex incommensurate superstructures which are discussed elsewhere. The formation of these superstructures, which involve the bonding between two adjacent Bi-O sheets, may be related to the failure to synthesize the bismuth monolayer analogs of the thallium compounds. On average, as can be seen in Figure 3, an unusually long Bi-O bond develops between the two Bi-O layers (3.2 Å), whereas the corresponding bond connecting the Tl-O sheets is much shorter (2.0 Å) (7). The weak Bi-O intersheet bonds likely cause the different morphologies of the bismuth and thallium compounds. The bismuth phases form extremely thin, micaceous platelets that tend to delaminate: cleavage between the Bi-O sheets yields charge neutral sections (7). The morphology of the thallium compounds is also platy, but not micaceous. The weak bonding along the c-axis of the bismuth compounds may also contribute to their stronger propensity to form intergrowth products, with sections of varying n-values in a single grain. The c-axis of the 2201 bismuth phase in Figure 3 is considerably longer than that of the thallium analog, despite very similar ionic radii of (Tl,Ba) and (Bi,Sr) (7). This could indicate that the thallium phases are also more tightly coupled electronically along the c-axis, thus leading to the higher T_c values observed for the thallium family.

The layer-type structures and chemical nature of the constituents of the bismuth and thallium-based cuprate superconductors - notably the lone-pair stereochemistry of Bi^{3+} , variable valence of copper, and considerable exchange among some of the cation sites - combine to make structural non-ideality, nonstoichiometry, and phase intergrowth the rule rather than the exception in these families of materials. These features, as well as the probable metastability of the phases (and possibly all high-temperature oxide superconductors), also contribute to the difficulties typically encountered in preparing single-phase samples with reproducible properties and compositions.

We are now acutely aware of the importance of the details of sample preparation; e.g., mixing, integrity of reactants, container, furnace design and sample placement therein, sample heating and cooling rates, actual vs. programmed temperatures, thermal gradients, and sample storage. Unfortunately, these details of sample preparation are not always known, and when known, are not always included in published reports - a situation that will hopefully self-correct in the future. Those attempting to repeat literature reports will most likely need to vary such details in their own particular experimental situation before success is attained. Hence, a considerable investment of time and effort should be expected.

This chapter presents an overview of our understanding of phase relationships and a summary of synthetic techniques for the synthesis of phase-pure superconducting samples in the bismuth- and thallium-based families of high T_c cuprate superconductors.

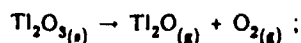
2.0 SYNTHETIC METHODS

Many of the high T_c ceramic superconductors can be prepared by similar solid state techniques. In the Bi-Sr-Ca-Cu-O system Bi_2O_3 , SrCO_3 , CaCO_3 or Ca(OH)_2 , and CuO are often used as the starting materials. These powders are combined in appropriate ratios, ground in an agate mortar, and heated in a high density alumina crucible at 810-820°C for 3-5 hours. It is important that this initial heat treatment is carried out below the melting point of Bi_2O_3 ($\approx 825^\circ\text{C}$) to allow for reaction of the Bi_2O_3 before melting. The samples are cooled to room temperature, ground, pressed into pellets, and heated at 830°C for 3-5 hours. This process is repeated, raising the temperature by 10-15°C, until no change is observed in the X-ray powder diffraction pattern. Typically, 4-6 heatings up to 900°C are required to reach equilibrium. While these latter reactions can be performed in high density alumina, the possible reaction of the samples with Al_2O_3 makes silver or gold a better container material.

Other starting materials such as SrO , CaO , $\text{Sr(NO}_3)_2$, and $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ can be used in place of the carbonates. However, the oxides readily react with CO_2 and H_2O from the air to form carbonates and hydroxides while $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ often contains an unreliable amount of water of hydration. These starting materials should be analyzed prior to use to determine the actual SrO or CaO content. This can be done by thermogravimetric analysis or by heating a known amount of material in air to 950°C and quickly weighing the cooled sample to determine the weight loss due to CO_2 , H_2O , and NO_2 evolution. Slow heating rates are necessary when the nitrates are used as starting materials since these compounds melt at low temperatures (550-600°C) and can splatter during NO_2 evolution.

The volatility of the reactants is a concern in some solid state syntheses. This may be a slight problem in bismuth cuprates synthesized at high temperatures because Bi_2O_3 has an appreciable vapor pressure at these temperatures (i.e. 900-950°C); however, chemical analyses of samples of bismuth-based superconductors before and after reactions at temperatures up to 900°C indicate no detectable loss of bismuth. This problem is much more severe in the case of thallium chemistry.

The primary difficulty in preparing the thallium-based cuprate superconductors lies in the toxicity and volatility of the reactant Tl_2O_3 and its decomposition products. Above 600°C, the following redox-vaporization process is well under way and would lead to substantial loss of reactant in an open system, although the magnitude of the partial pressure that would form in a closed system is not high enough to pose technical difficulties in containment (27):



small amounts of gaseous elemental Tl are also formed (27). Tl_2O_3 melts at 717°C and its conversion to Tl_2O is complete at 875°C in air (28). Reactions to prepare the complex oxides containing thallium should therefore be carried out in sealed containers that do not react with Tl_2O_3 . In addition to problems with volatility, soluble thallium compounds are particularly toxic because they are

absorbed through the skin. Federal regulations limit such exposure to 0.1 mg Tl per cubic meter of air per 8 hour time-weighted-average work period (29); early symptoms of thallium-poisoning include hair loss. Safety considerations in handling thallium compounds should include the following: 1) gloves should be worn at all times to avoid skin contact; 2) powders should be handled as much as possible in a well-ventilated hood to avoid dust inhalation; 3) use of Tl_2O , which is soluble, should be avoided in favor of the sesquioxide; 4) reactions should be carried out in sealed containers in furnaces placed in chemical fume hoods; and 5) chemical waste must be isolated and disposed of properly. In flow-through systems, volatile thallium constituents can be safely isolated by exiting the flow gases through traps containing basic peroxide solutions; insoluble Tl_2O_3 precipitates.

The following sections will outline specific methods for the synthesis of Bi- and Tl-based cuprate superconductors. Because the synthetic methods and historical evolution of the compounds are different, the bismuth and thallium families are described separately.

3.0 SYNTHESIS OF BI-BASED CUPRATE SUPERCONDUCTORS

3.1 Single Cu-O Layer Phase [2201], $T_c=10$ K

The most detailed studies to date have involved the $n=1$ system, i.e., the calcium-free system in which superconductivity was first detected near 20 K (1). This system can be described by a pseudo-ternary phase diagram. Equilibrium phase fields have been proposed by several groups (30)-(34). The equilibrium phase diagram for the Bi-Sr-Cu-O system as determined by Roth et al. is given in Figure 4 (30). The samples for this study were prepared from Bi_2O_3 , CuO , and SrCO_3 or $\text{Sr}(\text{NO}_3)_2$ using the heating sequence described in section 2.0 above. The surprising result of this study was the isolation of two distinct phases close to the ideal composition $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (Figure 5). Phase A has a composition very close to $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ although up to 10% Cu deficiency may occur (35). Phase B actually occupies a solid solution region described by the formula $\text{Bi}_{2-x}\text{Sr}_{2-y}\text{CuO}_{6\pm\delta}$. Importantly, Phase A is a semiconductor, although its composition is closest to the idealized $\text{Bi}_2\text{Sr}_2\text{CuO}_6$. Phase B shows signs of superconductivity between 6 and 10 K for samples at the Sr-rich end of this solid solution. The solid solution, as determined by Roth et al. (30), is bound by the compositions (a) $\text{Bi}_{2.17}\text{Sr}_{1.83}\text{CuO}_{6\pm\delta}$ (b) $\text{Bi}_{2.46}\text{Sr}_{1.76}\text{CuO}_{6\pm\delta}$, and (c) $\text{Bi}_{2.19}\text{Sr}_{1.39}\text{CuO}_{6\pm\delta}$ (Figure 5). The solid solution tolerates both Sr and Cu deficiencies although different limits of the solid solution have been reported by various groups (30)-(34). For example, Ikeda et al. (34) gives the limits as $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Cu}_{1+y}\text{O}_6$ with $0.1 < x < 0.6$ and $0 < y < x/2$, suggesting stability for excess Cu not Cu deficiency. The origin of these discrepancies is unclear. All researchers agree, however, that superconductivity is only observed in samples near the Sr-rich end of the solid solution. Furthermore, most groups report compositions for superconducting samples that are outside of some, if not all, of the solid solution ranges that have been reported. The superconducting fraction (as determined by Meissner measurements) is typically quite small which raises questions about the true nature and thermodynamic stability of the superconducting phase in the Bi-Sr-Cu-O system.

3.2 Cu-O Double Layers [2212], $T_c=80$ K

The idealized formula $\text{Bi}_2\text{Sr}_2\text{CaCuO}_{8\pm\delta}$ represents the next step in the "homologous series" of Bi-Sr-Ca-Cu-O superconductors. This phase has been reported to have a superconducting transition between 80 and 95 K. Because of the added complexity of the fourth element, Ca, no complete equilibrium phase diagram for the Bi-Sr-Ca-Cu-O system has been published. A myriad of partial phase diagrams and synthetic techniques for the preparation of this superconducting phase have been reported.

The synthesis of the $n=2$ phase is similar to that described above for the $n=1$ system. In general, stoichiometric portions of oxides and carbonates (or nitrates) are ground and reacted in a high density alumina crucible at temperatures between 800 and 820°C. The product is crushed and pressed into a pellet for further heat treatments at 840-870°C. The firing temperature must be raised incrementally to prevent melting of the sample.

Initial studies reported the existence of a solid solution $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{8\pm\delta}$ with $0.25 \leq x \leq 1.0$ (36)(37). These limits do not include the ideal formula $\text{Bi}_2\text{Sr}_2\text{CaCuO}_{8\pm\delta}$ as was noted early on (38). Recent work by Ono (39) indicates that the 80 K phase can be synthesized over a wider range of compositions described by the formula $\text{Bi}_2\text{Bi}_x(\text{Sr}_{2-y}\text{Ca}_{1+y})_{1-x}\text{Cu}_2\text{O}_y$ for $0.0 \leq x \leq 0.2$ and $0.0 \leq y \leq 0.5$ (Figure 6). Thus, this phase can be synthesized at a Ca/Sr ratio of 0.5 in the compound $\text{Bi}_{2.1}\text{Sr}_{1.93}\text{Ca}_{0.97}\text{Cu}_2\text{O}_y$. These results are consistent with the work in the $n=1$ system which suggests that Bi on the Sr site stabilizes the superconducting phase.

Alternate approaches to the standard synthetic methods described above have also been reported. Sastry et al. (40) report the synthesis of $\text{Bi}_2\text{Sr}_2\text{CaCuO}_{8\pm\delta}$ from a prereacted ceramic of " $\text{Sr}_2\text{CaCu}_2\text{O}_y$ " and Bi_2O_3 . The carbonates or oxides of Sr, Ca, and Cu are first reacted in appropriate ratios at 950°C to form a mixed-phase material. This is then combined with a stoichiometric amount of Bi_2O_3 , thoroughly mixed, heated to 927°C for 3-5 minutes, and cooled to room temperature. The resulting black powder is ground well, pressed into a pellet, and heated again for 3 minutes at 927°C. A final heat treatment at 852°C for 2 hours with furnace-cooling resulted in a single-phase sample.

A similar route to $\text{Bi}_2\text{Sr}_2\text{CaCuO}_{8\pm\delta}$ developed by Beltran et al. (41) involves the reaction of Bi_2CuO_4 , CaCO_3 , SrCO_3 , and CuO in appropriate ratios. These materials are well mixed and heated to 860°C in an alumina boat under flowing O_2 for 16 hours. The reacted powder is ground, compressed into pellets, and sintered at 880°C for 20 hours and furnace-cooled to room temperature. This technique reportedly also led to single-phase samples.

An alternate technique which eliminates the physical mixing necessary in the above reactions is the chemical mixing of salt solutions. One method involves the spray drying of nitrate solutions (36). Solutions of known molarity are prepared by dissolving the nitrates in dilute nitric acid (Bi, Ca, and Cu) or water (Sr). The desired compositions are mixed by volume and then sprayed through a quartz tube lining a furnace. The nitrates decompose on the walls of the quartz tube. This technique allows for the synthesis of a wide range of compositions in a relatively short time.

The nitrates can also be precipitated from solution in the form of the citrate salts (42). This also leads to intimate mixing and eliminates the need for a spray drying apparatus. For example, 8 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 4 mmol $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 8 mmol $\text{Sr}(\text{NO}_3)_2$, 8 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and 4.62 g of citric acid are dissolved in 40 ml distilled water. The pH of the solution is adjusted to 6.65 by the addition of concentrated NH_4OH solution and 3.5 ml ethylene glycol is added. This solution is stirred and

heated to 100-120°C for 1 hour to form a viscous mixture which is then pyrolyzed at 350°C for 1/2 hour to decompose the organic constituents and inorganic salts. At these temperatures, a vigorous exothermic reaction takes place and a spontaneous combustion is initiated by the nitrate salts. [CAUTION: This exothermic reaction can be explosive if not carefully controlled. Appropriate precautions should be in place before this reaction is attempted.]

The residue consists of homogeneous flakes. This residue is precalcined for 10 minutes at 500°C, ground, and then calcined for 8 hours at 800°C. This powder is then pressed into a pellet and sintered at 840°C for 4 hours. This method produces highly crystalline samples in spite of relatively low reaction temperatures and short reaction times.

3.3 Triple Cu-O Layers [2223], $T_c=110$ K

A phase in the Bi-Sr-Ca-Cu-O system with a superconducting transition temperature near 110 K was apparent in many early mixed-phase samples (2)(38). Superconducting onsets were often near 110 K although zero resistance was rarely achieved above 85 K. While chemical analysis, TEM, EDX, and single-crystal X-ray diffraction suggested a composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10\pm\delta}$ for the high- T_c component, attempts to synthesize a single-phase ceramic at this composition were unsuccessful. This led to further studies on the dependence of the fraction of the 110 K phase on starting composition, reaction temperatures, and annealing conditions. Several studies have reported the enhancement of this phase by heating samples very near the melting point (875-885°C) (2)(38). This method has proven successful in samples with nominal compositions $\text{Bi}_{2.8}\text{Sr}_2\text{Ca}_2\text{Cu}_4\text{O}_x$ (43) and $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_x$ (38). Still other work has suggested that low temperature anneals improve the fraction of the 110 K phase (44). To date, samples containing a 110 K superconductor in the Bi-Sr-Ca-Cu-O system are multiphase.

It was recognized early on that small amounts of Pb enhanced the formation of the 110 K phase (45). This has led to significant efforts to synthesize a Pb-stabilized 110 K superconductor. Partial phase diagram studies in air (46) and in reduced partial pressures of O_2 (47) have been reported. The work of Sasakura et al. (46) reports the partial phase diagram in air for samples prepared from Bi_2O_3 , PbO, CaCO_3 , and CuO. Powders in the appropriate ratios were mixed and heated at 795°C for 15 hours, reground, and pressed into pellets. These pellets were sintered in air at 858°C for 90 hours and reground. New pellets were pressed, sintered a second time at 858°C for 65 hours, then cooled at 1-2.5°C/min to room temperature. Samples of nominal stoichiometry $\text{Bi}_{1.68}\text{Pb}_v\text{Sr}_x\text{Ca}_y\text{Cu}_z\text{O}_w$ with $v = 0.28$ or 0.32 were prepared. Single-phase samples are formed over a fairly wide range of compositions as is depicted in Figure 7. For $\text{Bi}_{1.68}\text{Pb}_{0.32}\text{Sr}_{1.75}\text{Ca}_y\text{Cu}_z\text{O}_w$ single-phase samples are formed for $1.75 \leq y \leq 1.85$ and $2.65 \leq z \leq 2.85$. These samples show a transition to zero resistance above 105 K and exhibit a substantial Meissner fraction.

Synthesis from the nitrates at reduced partial pressure (1/13 atm O_2) leads to a slightly different phase diagram (47). Samples were prepared by dissolving Bi_2O_3 , PbO, $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and CuO in nitric acid to insure intimate mixing. This solution is stirred and heated until dry, resulting in a light blue solid. This material was decomposed at 800°C for 30 minutes. The resulting powder was pressed into a pellet and heated at 828-843°C for 36-130 hours in 1/13 atm O_2 pressure, cooled slowly to 750°C, and then cooled in pure O_2 to room temperature. Samples prepared with the general stoichiometry $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_x\text{Ca}_y$

Cu_xO_w were found to be single-phase in the region $1.87 \leq x \leq 2.05$, $1.95 \leq y \leq 2.1$, and $3.05 \leq z \leq 3.2$ (Figure 8). Again, zero resistance at $T > 105$ K was exhibited within this range of compositions.

It should be clear from the above sections that the idealized formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ with $n = 1, 2$, and 3 does not accurately describe the actual stoichiometry of single-phase ceramic samples. Substantial cation intersite substitution and/or vacancies probably occur in these materials. The role of these defects in the stabilization of the superconducting phases and their contribution to the superconducting properties is still being investigated.

4.0 SYNTHESIS OF THALLIUM-BASED CUPRATE SUPERCONDUCTORS

4.1 Preparations in Air or Lidded Containers

The earliest syntheses of the 2212 and 2223 thallium-based cuprate superconductors were carried out by reacting stoichiometric amounts of Tl_2O_3 , CaO , and a pre-reacted (920°C , 2 h) mixture of BaCO_3 and CuO (nominal composition BaCu_3O_4 or $\text{Ba}_2\text{Cu}_3\text{O}_6$) (3)-(5). The reaction mixtures were pressed into pellets, placed in hot furnaces at 880 - 950°C , heated for 2-5 min under flowing oxygen, and air-quenched. Since sealed containers were not used, product stoichiometries were not well controlled and the samples tended to be mixtures of the 2212 and 2223 phases with broad superconducting transitions. This group also reported a vapor-solid process that also produced mixtures of the 2212 and 2223 phases with broad transitions above 100 K (48): Pellets of different pre-reacted (925 - 950°C , 48 h) Ba-Ca-Cu-O mixtures were supported over platinum boats containing Tl_2O_3 . This combination was then placed into a hot furnace at 900 - 925°C and heated for 3 min in flowing oxygen followed by furnace-cooling.

In another procedure (49), the reactants (Tl_2O_3 , $\text{Ba}(\text{NO}_3)_2$, CaO , and CuO) were heated in two steps, the first in a lidded Pt crucible (1000°C , 15-25 min), and the second (as pellets wrapped in gold foil) in a sealed silica tube (865 - 905°C , 3-10 h) that had been flushed with oxygen. Products were multiphase, but a starting composition of $\text{Tl}_{0.5}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ yielded (apparently) sufficient 2223 phase to give a superconducting onset temperature of 123 K with zero resistance at 121 K.

Millimeter-sized crystals of several of the thallium-based superconductors have been grown using a "pseudo-flux growth" method in Pt crucibles with tight-fitting lids (24)(50). Dry powder-mixtures of Tl_2O_3 , BaO , CaO , and CuO of various starting metal ratios were placed in hot furnaces under flowing oxygen at 950°C , soaked 1 h, cooled to 700°C in 12.5 h and then to room temperature over 5-6 h; soak temperatures below 900°C did not produce crystals. In successful experiments, breakage of the reaction mass revealed "melt" pockets containing well-formed platelets 1-3 mm across and 0.01-0.20 mm thick. A starting $\text{Tl}:\text{Ba}:\text{Ca}:\text{Cu}$ ratio of 4:3:1:5 yielded predominantly 2223 crystals; in other experiments, starting metal ratios of 1:1:1:2, 2:2:2:3, 2:2:1:2, 1:1:2:2, 2:5:1:2, 2:1:3:2, and 2:1:1:2 all yielded mixtures of crystals, some intergrown, of the 2212, 2223, and 1212 superconductors. In general, the T_c values for the crystals were somewhat lower than those observed in ceramic phases, an effect attributed to microscopic inhomogeneity and cation site disorder/vacancy formation.

All of these procedures involve heating Tl_2O_3 in non-sealed systems, and all are typified by superconducting product stoichiometries far different from the starting compositions. Again, in addition to safety concerns, little control of superconducting-phase

composition and reproducibility of synthetic conditions is afforded by use of non-hermetically sealed reaction containers. The problem appears to be more complex than simply thallium reactant loss; factors related to reaction kinetics are most likely quite important for the preparation of these metastable phases.

4.2 Preparations in Hermetically Sealed Containers

Other researchers attempted improved control of product stoichiometry by wrapping reactant-mixture pellets (Ti_2O_3 , BaO , CaO , and CuO) in gold foil and then sealing them in silica ampoules that had been flushed with oxygen (8)(51). Multiphase samples, however, were still obtained. Nominal starting metal compositions of 1:1:3:3 and 2:2:2:3 (Ti:Ba:Ca:Cu) resulted in the largest amounts of 2223 and 2212 phases, respectively; the samples were heated at 880°C for 3 h, followed by furnace-cooling over a 4 h period (51). Sufficient amounts of the 2212 and 2223 phases were formed to confirm bulk superconductivity at 108 and 120 K, respectively, and to elucidate the basic structural features and unit cells by combining electron and X-ray powder diffraction methods. Using the same synthetic procedure with different starting compositions, this group also obtained multiphase samples containing the thallium monolayer 1201, 1212, and 1223 compounds (8); the basic structural features of the series were again elucidated by combining electron microscopy and X-ray powder diffraction methods.

Syntheses of X-ray-diffraction pure bulk samples of the 1223 (9), 2223 (52), and 1212 (53) phases with T_c values of 120, 125, and 50-65 K, respectively, were reported by another group. In all cases, intimate reaction mixtures of stoichiometric quantities of Ti_2O_3 , BaO_2 , CaO , and CuO were pressed into pellets that were supported in alumina crucibles which were then sealed in evacuated silica ampoules. Heating rates were not given; samples were cooled slowly to room temperature. The products, heating temperatures, and soak times follow: 1223: 750-830°C, 5 h; 2223: 750-900°C, 3-12 h; 1212: 780-820°C, 5-6 h. For the 1212 sample, a final anneal under Ar raised T_c from 50 to 65 K. Sample microstructure was studied by electron microscopy, and the basic structural features and unit cells of the phases were elucidated by combining electron microscopy and X-ray powder diffraction methods. Using the same synthetic method, this group also prepared a number of phases with various degrees of cation substitution on the thallium and alkaline earth sites (10)(20)(23)(54).

Considerable single-crystal X-ray diffraction and powder neutron diffraction structural studies have been reported on samples prepared in sealed gold tubes (6)(7)(25)(55)-(58). Fifteen-inch long pieces of 5/8-inch-diameter pure gold tubing are first cleaned thoroughly with soap and rinsed with acetone. The open tubes are supported on a ceramic tile or brick and, using a torch with a moderate flame (somewhat cooler than that required for working pure silica), are preheated by passing the torch over the length in one direction only. The "annealed" tubing is then cut into 4-5 inch lengths with metal shears, and one end is crimped very flat with flat pliers. The crimp should be inspected using an optical microscope; it should be very flat with no folding or holes. The crimp is then melted shut by passing a hot flame over it in one direction only; the torch should be fitted with a fairly small nozzle and the flame temperature should be high enough to work silica. The tubes are then loaded with reactant mixture and the open end is crimped flat in a like manner. The fused end of the tube is placed in a beaker of water while the final crimp is melted

shut with the torch flame. The tubing is not reused; the method reportedly works well with no leakage problems (59).

The gold tube containment procedure described above has been used in the following experiments to prepare a number of the thallium-based superconducting cuprates in single-crystal and pure or near-pure (according to X-ray powder diffraction) polycrystalline form from mixtures of Tl_2O_3 , BaO_2 , CaO_2 , and CuO .

1. In numerous initial experiments with various proportions of reactants heated at 850-915°C for 15 min to 3 h, most of the products were mixtures containing the 2212 and 2223 phases with superconductivity onset temperatures ranging from 100 to 127 K (6).
2. Essentially single-phase 2223 ($T_c = 125$ K with zero resistance at 122 K) was obtained by heating stoichiometric quantities of the reactants at 890°C for 1 h (6)(56); if this mixture was heated for more than 2 h or at temperatures above 900°C, a mixture resulted with 2212 as the major phase and 2223 as a minor component (56). The authors note that the temperature range in which the thallium-based superconductors can be formed without decomposition to barium cuprate phases is very narrow (6).
3. Single crystals of the 2212 phase were grown from a 2:1:1:3 (Tl:Ba:Ca:Cu) copper-rich melt that was heated to 900-920°C, held 1 h, and cooled at 2°C/min ($T_c = 110$ K, narrow transition) (6).
4. Single crystals of the 2223 phase were grown from a 2:2:3:4 (Tl:Ba:Ca:Cu) starting composition that was heated at 920°C for 3 h and cooled to 300°C at 5°C/min (56); according to magnetic measurements the T_c values varied from 127 to 116 K in different preparations, with 125 K as a typically observed onset temperature.
5. Polycrystalline 2201 phase formed as the major and sole superconducting component when stoichiometric amounts of reactants were heated at 875°C for several hours (7); transitions were broad with T_c onsets of 84 K. Reheating at 900°C caused partial melting and an increase in the T_c onset value to 90 K (with zero resistance at 83 K); increased amounts of second-phase BaCuO_2 were observed.
6. Single crystals of the 2201 phase were grown from a starting composition 2:2:2 (Tl:Ba:Cu) (7); presumably the mixture was heated to 900°C, soaked several h, and slow-cooled. Flux exclusion indicated a T_c onset of 90 K with zero resistance at 83 K.

* Prior to use, BaO_2 and CaO_2 reagents should be analyzed thermogravimetrically to determine actual weight per cent metal.

7. Single crystals of the 1223 thallium monolayer phase were grown from a copper-rich melt with molar composition 1:2:2:4 (Tl:Ba:Ca:Cu); the mixture was heated to 925°C, soaked 6 h, and cooled at 1°C/min (57). Magnetic flux exclusion experiments indicated a sharp T_c onset of 110 K.
8. A general summary of temperatures and heat-soak times that are favorable for the formation of the different thallium bilayer superconductors follows (59): 2201: 875°C, 3 h; 2212: 900°C, 6 h; 2223: 890°C, 1 h; 2234: 860°C, 3 h; 2245: 880°C, 6 h - the 2234 and 2245 phases were observed by electron diffraction only.

The lead-substituted compounds, $Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_2O_7$ and $Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_9$ were also synthesized in sealed gold tubing. Single-phase polycrystalline samples with somewhat broad superconducting transitions ($T_c = 80$ -90 and 120 K, respectively) were obtained by reacting Tl_2O_3 , PbO_2 , CaO_2 , SrO_2 , and CuO at 850-915°C for 3-12 h (25). Single crystals of $Tl_{0.5}Pb_{0.5}Sr_2Ca_2Cu_3O_9$ were grown from a mixture of the above reactants in a molar ratio 1:1:2:3:4 (Tl:Pb:Sr:Ca:Cu) that was heated at 910°C for 6 h and then cooled at 2°C/min (25); flux exclusion measurements indicated a sharp superconducting transition at 118 K.

4.3 Preparations under Flowing Oxygen

Bulk samples of the 2201, 2212, and 2223 thallium-based cuprates have been prepared by reacting Tl_2O_3 , $BaCuO_2$, dry CaO , and CuO in stoichiometric amounts (60). The mixed reactants were pelletized, wrapped in gold foil, and heated under flowing oxygen at 890°C for 5 min for 2201, 905°C for 7 min for 2212, and 910°C for 7 min for 2223, followed by cooling at 10°C/min. The products were single-phase according to X-ray powder diffraction and the Rietveld profile refinement technique was used to determine the structural parameters for the three phases. Interestingly, the 2201 phase was not superconducting; zero-resistance was observed at 98 and 114 K for the 2212 and 2223 samples, respectively. This group also reported the preparation of bulk 2234 phase (26) using the same synthetic procedure described above; the starting composition was off-stoichiometry - 1:2:2:3 (Tl:Ba:Ca:Cu) - and was heated at 895°C for 50 min, followed by slow cooling. The product was a mixture of 2234, $BaCO_3$, $BaCuO_2$, and CaO . The T_c onset was 112 K with zero resistance at 108 K. The unit cell and basic structural features of the superconducting phase were determined by combining electron microscopy and X-ray powder diffraction methods.

Mixtures containing as major components the thallium monolayer phases 1212, 1223, 1234, and 1245 have been prepared by heating the thallium bilayer 2212 and 2223 phases at 890°C in oxygen for various times ranging from 4 to 10 h (22). Sufficient quantities of each of the four superconducting phases were obtained in separate products so that reasonably sharp superconducting transitions were observed. T_c values for the phases were determined by resistivity and susceptibility measurements, and the basic structural properties were elucidated using x-ray powder diffraction and high resolution electron microscopy.

Syntheses of near-single phases of the lead-substituted thallium monolayer phases with up to 6 Cu-O layers; i.e., Pb-doped 1212, 1223, 1234, 1245, and 1256, have been recently reported (21). Reactant mixtures of various proportions of Tl_2O_3 ,

PbO, CaO, BaO₂, and CuO were pelletized, wrapped in gold foil, and sintered at 860-900°C under flowing oxygen for 10-30 h. The T_c value reached a maximum of 121 K for the 1234 compound and declined with further increase in the number of Cu-O layers. X-ray powder diffraction data for the different phases were refined using the Rietveld method and a consistent increase in the c-axis accompanied the increase in number of Cu-O layers.

The reports described above indicate that the thallium-containing cuprates can be prepared with reasonable degrees of purity under non-contained, flowing oxygen conditions. This somewhat surprising result is likely attributable to the relatively short heating times, the use of gold foil wrappings, and, possibly most importantly, a decrease in thallium volatility according to the principle of Le Chatelier (27). If the reactions are carried out in nonporous sleeves with exiting gases passed through multiple traps filled with basic peroxide solution, the method can be considered as adequately safe. (Furnaces should be placed in fume hoods).

5.0 CONCLUSION

A review of the synthetic methods used to prepare the bismuth and thallium families of cuprate superconductors has been presented. An overview of our current knowledge of phase relationships in the bismuth systems is also given; such studies of the thallium-containing compounds are yet to be reported. The importance of and the difficulties posed by the preparation of phase-pure samples with reproducible structures and chemical compositions cannot be understated; the elucidation of structure-property relationships that correlate with the appearance of superconductivity begins with sample integrity. The synthetic challenge is particularly acute in the case of the superconducting oxides because of their apparently inherent "unstable" nature, a situation reminiscent of the difficult syntheses of metal-insulator type metal oxides. Neophytes are urged to be patient, diligent, and well-equipped with knowledge of the literature.

While this chapter has focussed on synthesis of polycrystalline samples, other aspects of the bismuth and thallium cuprate superconductors are discussed elsewhere. An introduction to synthesis and crystal growth is given in Chapter 5, and a review of the crystal chemistry of the two families is presented in Chapter 2. The crystallographic data for these phases, including tables of calculated d-spacings and intensities for x-ray powder diffraction patterns, have been collected in Chapter 13. Characterization by electron microscopy, a particularly important technique because of the nature of the materials, is reviewed in Chapters 14 and 15.

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Figure 1: Schematic representation of the ideal structures of the homologous series of Bi- and Tl-based superconductors showing the coordination polyhedra about Bi or Tl (octahedra) and Cu (octahedra, square pyramids, or square planes).

Figure 2: Schematic representation of the ideal structures of the thallium monolayer cuprate superconductors.

Figure 3: Average structures of $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ as determined by single-crystal X-ray diffraction (7).

Figure 4: Equilibrium phase diagram for the Bi-Sr-Cu-O system in air at 875-925°C (30).

Figure 5: Portion of the Bi-Sr-Cu-O phase diagram near $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ (30).

Figure 6: Single-phase region (open circles) for the 80 K superconductor in the Bi-Sr-Ca-Cu-O system (39).

Figure 7: Composition diagrams for samples of nominal composition $\text{Bi}_{1.68}\text{Pb}_v\text{Sr}_x\text{Ca}_y\text{Cu}_z\text{O}_w$. In (A), $v=0.28$ and $x=1.73$, for (B) $v=0.32$ and $x=1.75$, and for (C) $v=0.32$ and $x=1.80$. The dashed area (marked A) indicates where single-phase 110 K superconductors are prepared (46). Regions marked B, C, and D contain 110 K phase + Ca_2CuO_3 , 110 K + 80 K + Ca_2CuO_3 , and 110 K + 80 K phase, respectively.

Figure 8: Partial phase diagram for phases of composition $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_x\text{Ca}_y\text{Cu}_z\text{O}_w$. The dashed area represents the single-phase region for samples of 110 K ($n=3$) material. The samples were prepared in 1/13 atmosphere O_2 (47).

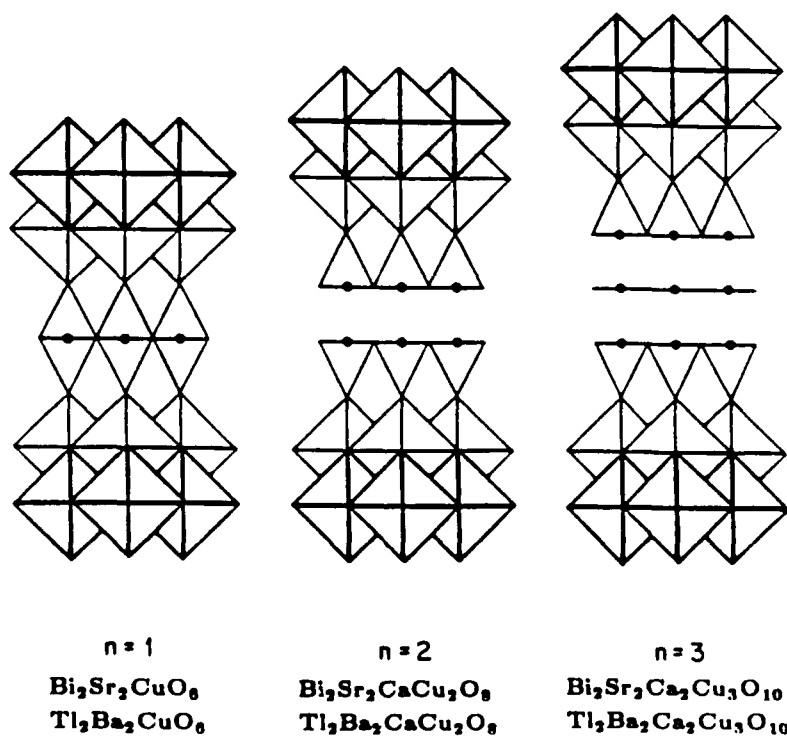


Fig 1

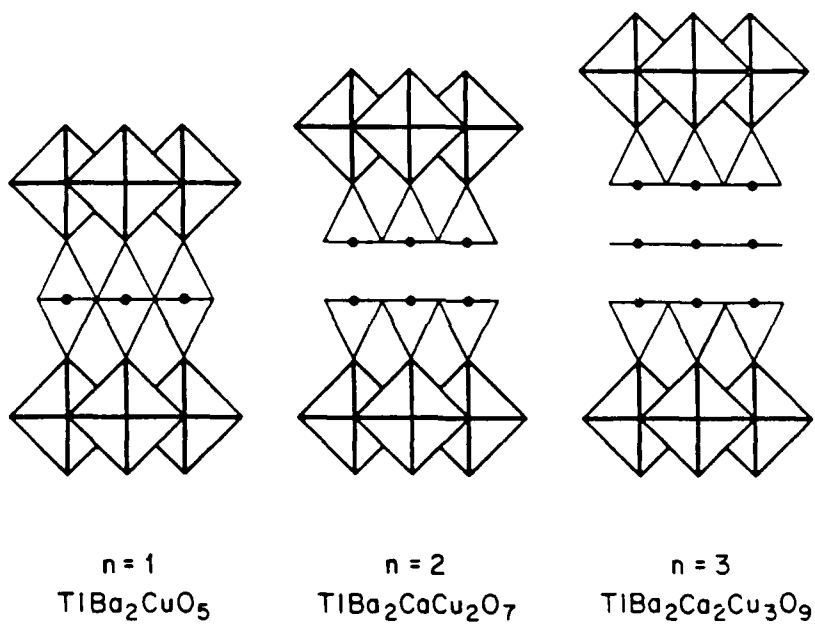


Fig 2

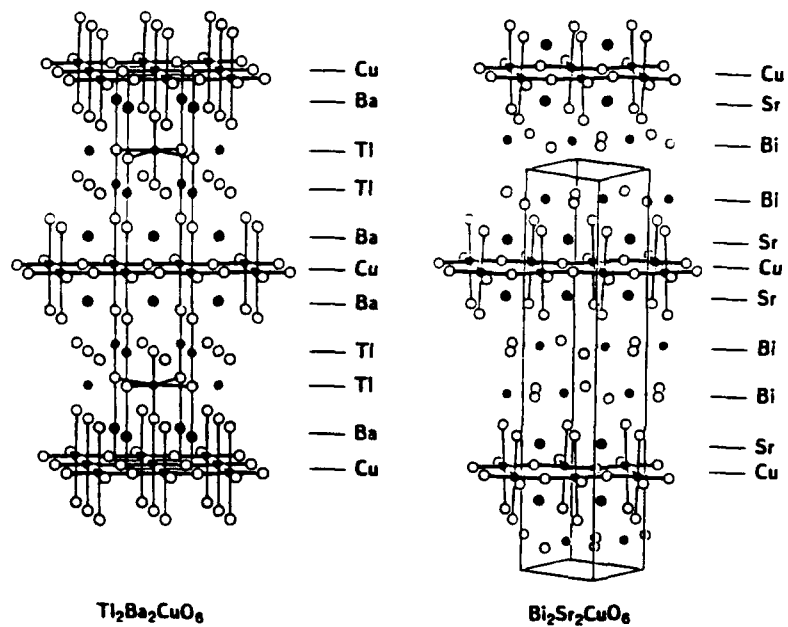


Fig 3

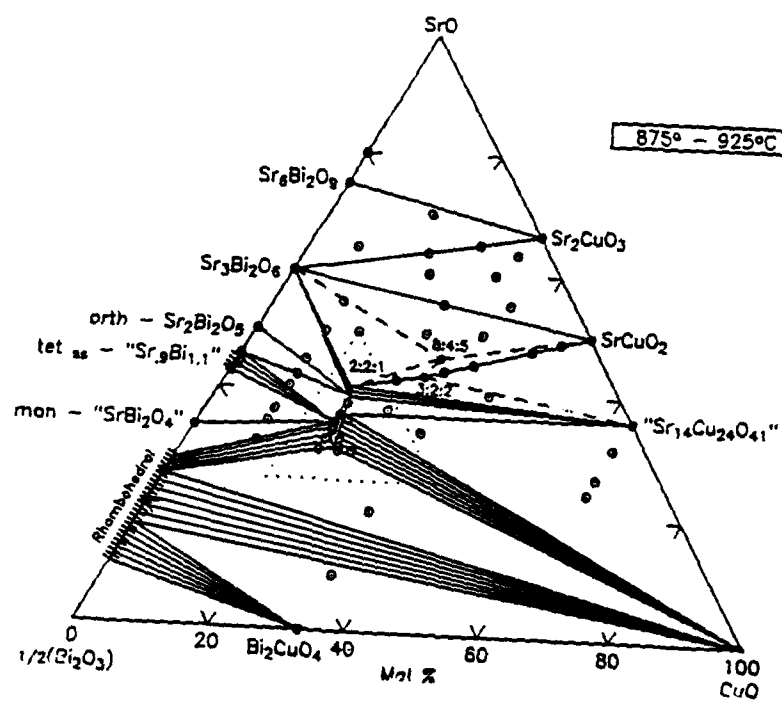


Fig 4

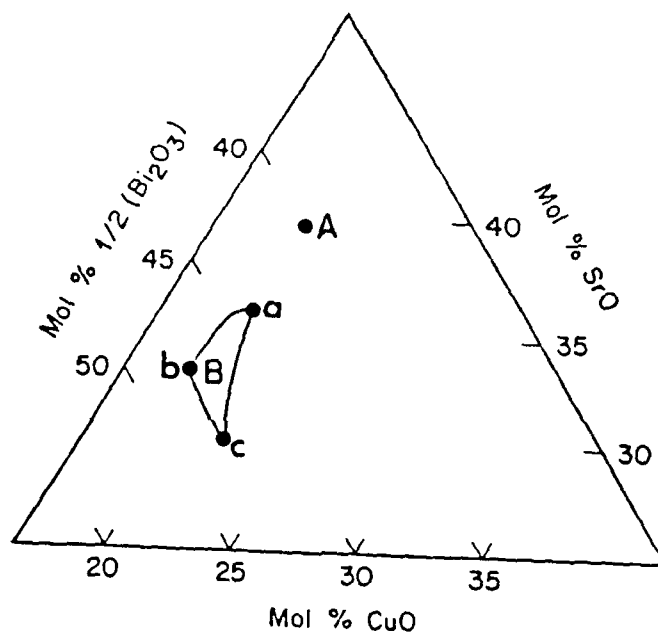


Fig 5

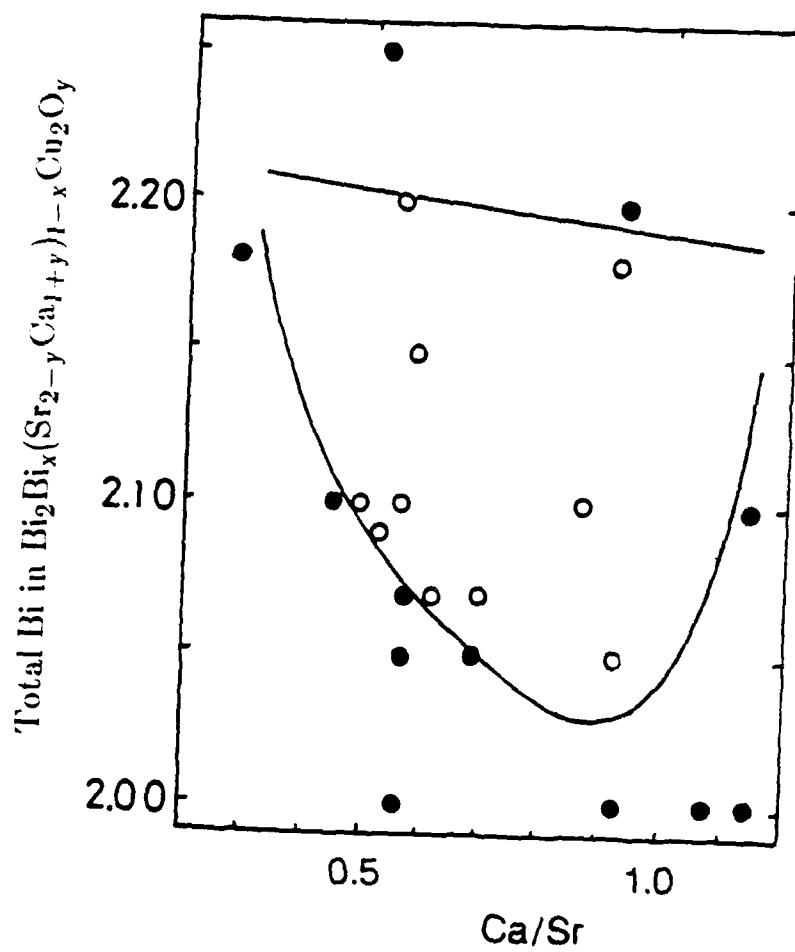


Fig 6

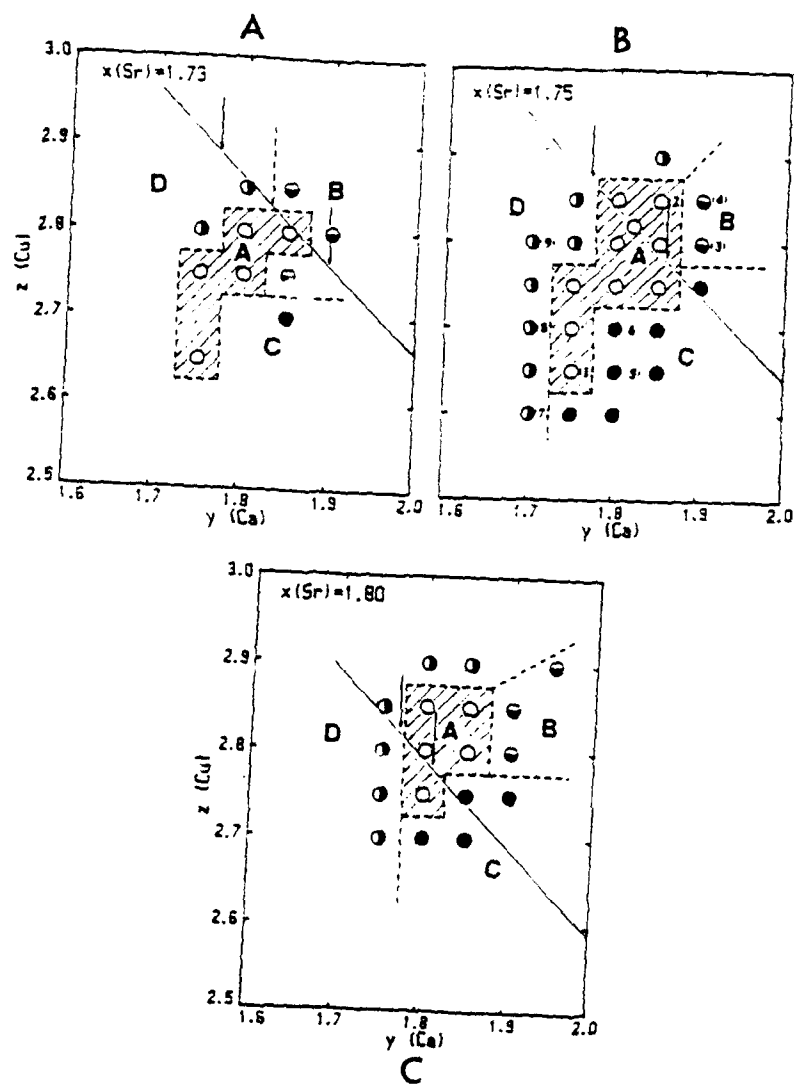


Fig 7

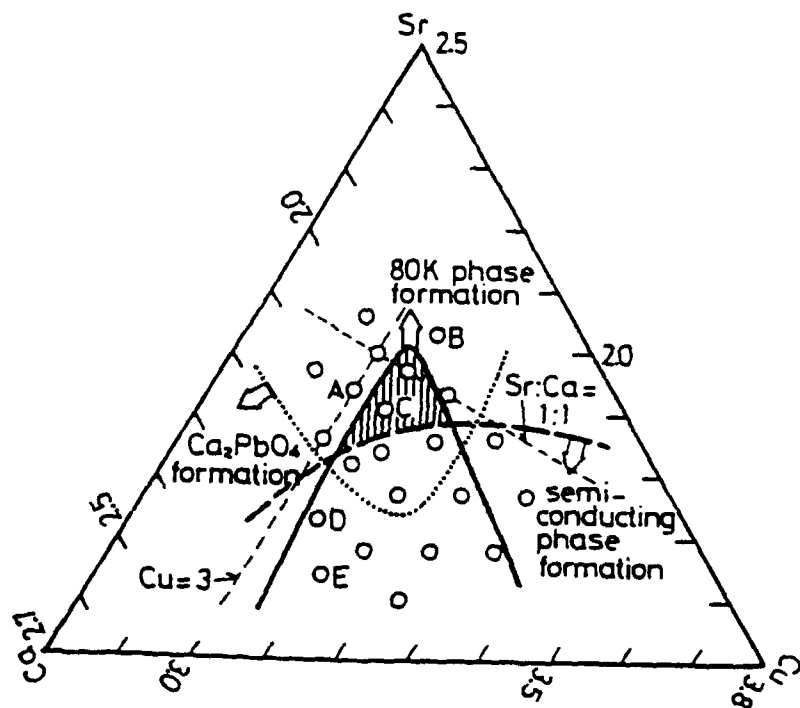


Fig 8