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SECURITY CLASSIFICATION OF THIS PAGE

(4)

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b RESTRICTIVE MARKINGS
DULE	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release Distribution Unlimited
AD-A198 988 BER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION Department of Chemistry University of North Carolina	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c ADDRESS (City, State, and ZIP Code) Chapel Hill, North Carolina 27514		7b ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, VA 22217	
8a NAME OF FUNDING/SPONSORING ORGANIZATION	8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0608	
8c ADDRESS (City, State, and ZIP Code)		10 SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO	PROJECT NO
			TASK NO NR 053-617
			WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification) UNCLASSIFIED: Synthesis and Characterization of BiCaSrCuO and BiSnCaSrCuO Superconduction Ceramics

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13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Technical Report	FROM _____ TO _____	1988 September 20	11

16 SUPPLEMENTARY NOTATION
Technical Report No. 32

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	magnetic susceptibility, resistance measurements, Rutherford backscattering, scanning electron microscopy, energy dispersive X-ray analyses.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

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DTIC ELECTE SEP 2 0 1988 S D

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code) / 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

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12. and William J. Riley

18. superconducting ceramics

OFFICE OF NAVAL RESEARCH

Contract N000014-86-K-0608

R&T Code 413a001-000-01

TECHNICAL REPORT NO. 32

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by

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Prepared for publication in
International Conference on the First Two Years of
High Temperature Superconductivity, Tuscaloosa, AL,
11-13 April 1988

SYNTHESIS AND CHARACTERIZATION OF BiCaSrCuO AND BiSnCaSrCuO SUPERCONDUCTING CERAMICS

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Abstract Magnetic susceptibility measurements, resistance measurements, Rutherford backscattering, scanning electron microscopy, and energy dispersive X-ray analyses were utilized in order to determine the effects of composition and firing conditions on the properties of the Bi-Ca-Sr-Cu-O superconducting ceramics.

INTRODUCTION

New high - temperature superconducting materials with T_c's in the range of 120K have recently been realized in both the Tl-Ca-Ba-Cu-O[1] and Bi-Ca-Sr-Cu-O[2] systems. These systems consist of at least two superconducting phases characterized by their superconducting transition temperatures of ~80K and ~120K. The transition temperature, critical current density, anisotropic properties, and volume fraction of the superconducting

material are inherently related to the microstructure of the ceramics. In this report, we have investigated the effects of starting composition, Sn doping, and annealing and sintering conditions on the magnetic and electrical properties, microstructure, surface stoichiometry, and multiphasic nature of the Bi-Ca-Sr-Cu-O system.

EXPERIMENTAL

Synthesis

Samples of the Bi-Ca-Sr-Cu-O ceramics were synthesized via intimate mixing of Bi_2O_3, CuO, $CaCO_3$, and $SrCO_3$ by thoroughly grinding the starting materials. This was followed by pressing into a pellet and sintering at 880°C (sample 1), doping with SNO and SNO_2, pressing into a pellet, sintering at 880°C, and annealing at 950°C for 15 minutes (sample 2), pressing into a pellet, and sintering at 820°C (samples 3 and 4). All materials were sintered and annealed in air in a muffle furnace. The ratios of the starting materials are given in Table 1.

TABLE I Molar ratios of starting materials

Sample	Bi-Sn-Ca-Sr-Cu molar ratios
1	2-0-1-2-2
2	2-1-1-2-2
3	1-0-1-1-2
4	2-0-1-2-2

SUPERCONDUCTING CERAMICS

Magnetic Measurements

Quantitative magnetic measurements were made using a vibrating sample magnetometer equipped with a continuous flow cryostat. The samples were cooled in zero field (ZFC) to 4.2K, and the diamagnetic shielding data was collected past the transition temperature in a field of 50 Oe. The sample was then field cooled (FC) through the transition temperature in order to monitor the Meissner effect. The density of the samples was measured and volume susceptibilities were determined. All data was corrected for demagnetization effects.

Resistance Measurements

Resistance measurements were made from 20-300K utilizing an in-line four-probe technique. Compensation for the Seebeck effect was made.

Surface Analysis

The surface, microstructure, and stoichiometry of the superconducting ceramics were determined by Rutherford backscattering (RBS) and scanning electron microscopy - energy dispersive X-ray analysis (SEM-EDX). A standardless semi-quantitative analysis program was used to determine the elemental analysis of the bulk material as well as that of the individual grains.

RESULTS AND DISCUSSION

Transition Temperature and Superconducting Volume Fractions

The magnetic data for the four samples studied show

relatively broad transitions, indicative of the multiphase nature of the samples. Sample 1 displayed the greatest volume fraction of superconducting material, with 8.4% bulk diamagnetism in the Meissner signal and 13.1% for the maximum diamagnetic shielding. The T_c for sample 1 was monitored by both resistance and magnetic measurements. The onset temperature of the decrease in resistance was 87K, with zero resistance being realized at 37K. The magnetic data determined the T_c to be 77.6K for the ZFC run and 79.5K for the FC data set. The anomolously low temperature necessary for zero resistance is most probably due to contact problems or the percolative nature of the superconductivity. The results of the critical temperatures and diamagnetic fractions are summarized in Table II.

Surface Analysis and Microstructure

RBS of samples 1 and 2 yielded valuable information concerning the constitution of the sample surface. The surface stoichiometries (Bi-Sn-Sr-Ca-Cu) were determined to be (1:0.0:0.7:1.0:1.5) and (1:0.53:1.27:0.93:1.33) respectively. This data indicates that the surface is rich in Ca and Cu, with the latter probably being present in the form of oxides.

An EDX elemental analysis of sample 1 yielded a stoichiometry of $Bi_{1.43}Sr_{1.62}Ca_{0.61}Cu_{2.00}$ and the SEM showed the material to be very porous with little or no melting. Analysis of single grains confirmed the multiphasic nature of the composite, however some grain of different morphology displayed very similar stoichiometries.

TABLE II Transition temperatures and percent bulk diamagnetism

Sample	T_c(ZFC)	T_c(FC)	T_c(onset)	T_c(zero)	%(ZFC)	%(FC)
1	77.6	79.5	87	37	13.1	9.4
2	72.3	76.9	88	61	8.2	1.6
3	69.5	72.7	--	--	5.6	4.1
4	73.5	73.5	--	--	1.0	0.7

The overall stoichiometry of sample 2 was $Bi_{0.61}Sn_{0.55}Sr_{1.28}Ca_{0.90}Cu_{2.00}$. Analysis of single grains showed large areas of Sr depletion. As in the case of sample 1, no melting was observed and the individual grains were of widely differing morphology and composition.

Sample 3 was very homogeneous and individual grains had stoichiometries similar to that of the bulk ($Bi_{1.50}Sr_{0.91}Ca_{1.07}Cu_{2.00}$). However, we did find areas heavily depleted in Bi, Sr, and Ca. In contrast to the previous ceramics, SEM showed some melting had occurred resulting in partial fusion of the grains in an annealed pellet. Analysis of some unannealed sintered powder yielded some lamellar grains of composition $Bi_{1.7}Sr_{1.4}Ca_{0.9}Cu_{2.0}$.

EDX of the final sample indicated severe Ca depletion. The sample was polycrystalline and very homogeneous (1μ dia.). As in the case of the first two ceramics, the pressed pellet was very porous.

CONCLUSIONS

The samples studied were generally multiphase in nature and very porous. The transition temperatures were found to be dependent on the molar ratios of the starting materials and firing conditions, but generally, the Tc's correspond to the 80K phase. More intimate mixing of the precursors must be obtained in order to increase the homogeneity of the fired material and increase the yield of the superconducting fraction. It may be that the best reaction conditions for the highest yields occur in a very narrow temperature range, requiring precise control of the firing temperature.

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ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Reasearch. J.H.M. acknowledges the receipt of an A.P. Sloan Research Fellowship, and R.J. Reynolds Faculty Development Award,and a grant from the U.N.C. Research Council.

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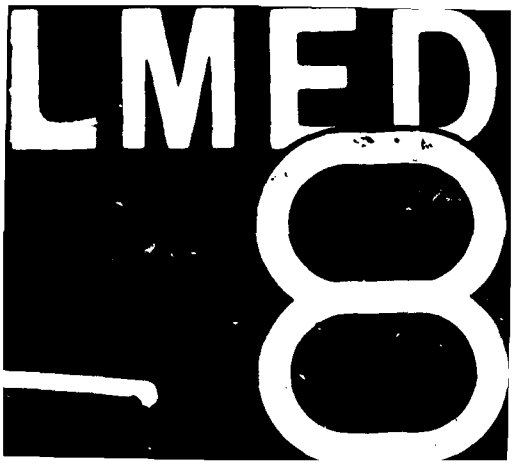
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