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**High Tc Superconductivity in the Triple-Perovskite  
La-Rare Earth or Alkali Metal-Ba-Ca-Mg or  
Cd-Cu-Oxide System**

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**ARL-TR-1131**

**March 1997**

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# REPORT DOCUMENTATION PAGE

Form Approved  
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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate of any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0 188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 1997	3. REPORT TYPE AND DATES COVERED Technical Report: Jan 96 to Dec 96	
4. TITLE AND SUBTITLE High $T_c$ Superconductivity In The Triple-Perovskite La-Rare Earth or Alkali Metal-Ba-Ca-Mg or Cd-Cu-Oxide System			5. FUNDING NUMBERS  PR: 611102 PE: H94	
6. AUTHOR(S) Arthur Tauber*, Steven C. Tidrow, Daniel Pierce, and Donald W. Eckart				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory (ARL) Sensors and Electron Devices Directorate (SEDD) ATTN: AMSRL-SE-EI Fort Monmouth, NJ 07703-5601			8. PERFORMING ORGANIZATION REPORT NUMBER  ARL-TR-1131	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  *Arthur Tauber is with Geo-Centers, Inc., 615 Hope Road, Eatontown, NJ 07703.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Bulk targets of compounds in the system $La_{3-2}Me_2Ba_3Ca_{1-v}Nc_vCu_7O_{16+v}$ where Me=rare earth or Na and Nc=Mg or Cd were prepared by solid state reactions. They were employed to deposit by pulse laser deposition thin films of the superconductor on single crystal substrates of $LaAlO_3$ , LSAT, and GGG. Phase relationships and orientation relationships were obtained from diffractometer scans. All compounds exhibited a (00 $\bar{2}$ ) relationship with all substrates. Lattice parameters, transition temperatures and widths are reported for each superconducting compound. All substituted compounds were superconducting but no increase in $T_c$ was observed for any. All thin films heated to 750 deg C desorbed little oxygen compared to YBCO.				
14. SUBJECT TERMS High temperature superconductivity; thin films; perovskite; oxygen transition temperature			15. NUMBER OF PAGES 10	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

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# HIGH $T_c$ SUPERCONDUCTIVITY IN THE TRIPLE-PEROVSKITE La-RARE EARTH OR ALKALI METAL-Ba-Ca-Mg OR Cd-Cu-Oxide SYSTEM

## INTRODUCTION

The high  $T_c$  superconducting system  $\text{La}_{3-z}\text{Me}_z\text{Ba}_3\text{Ca}_{1-v}\text{Nc}_v\text{Cu}_7\text{O}_{16+x}$  is attractive for device applications because it is stable with regard to oxygen compared to  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  and undergoes no phase transition between the sintering temperature and room temperature [1]. Thermal cycling demonstrated reversible oxygen losses of less than 1% up to 1000 °C in bulk samples [2]. One useful consequence should be more easily prepared multilayered structures and such multilayered devices as Josephson junctions, broadband impedance transformers, and flux flow and field effect transistors. One objective of this investigation has been the preparation and characterization of thin films of  $\text{La}_3\text{Ba}_3\text{CaCu}_7\text{O}_{16+x}$ . A second objective has been an investigation of the effect of substitutions for La and Ca with the hope of increasing  $T_c$ .

A superconducting bulk compound in the system  $\text{La}_{3-z}\text{Me}_z\text{Ba}_3\text{Ca}_{1-v}\text{Nc}_v\text{Cu}_7\text{O}_{16+x}$  where  $z=0$  and  $v=0$ , namely  $\text{La}_3\text{Ba}_3\text{CaCu}_7\text{O}_{16+x}$  (La3317), was first prepared by Engelsberg [3]. The material was found to be a superconductor with a  $T_c = 80.2$  K and to have a triple perovskite structure. It is tetragonal with  $c=3a$  ( $c=11.61$ ,  $a=3.87$ ). In an earlier study [4], carried out on a composition close to La3317, it was deduced that most of the Ca atoms occupy the central position of the unit cell that is occupied by Y atoms in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (YBCO). Recently Kao et al. [5] reported that about half of the Ca enter the Y sites and the remainder are on Ba sites. Similar results have been obtained in studies of other La-Ba-Ca-Cu-oxides [4,6] where much of the La is found on the Ba sites.

The substitution of Mg and Sc for Ca was already investigated by Engelsberg [3]. He found a slight increase in lattice parameter when Mg is substituted,  $c=11.71\text{\AA}$  and  $a=3.91\text{\AA}$ ; and superconductivity was observed below 30 K. Sc substitution led to a multiphase material and no superconductivity was observed. Wu et al. [7] have investigated rare earth substitution for La in bulk samples.

## EXPERIMENT

Bulk samples and targets, in the system  $\text{La}_{3-z}\text{Me}_z\text{Ba}_3\text{Ca}_{1-v}\text{Nc}_v\text{Cu}_7\text{O}_{16+x}$  where  $\text{Me}=\text{Nd}$ ,  $\text{Yb}$ ,  $\text{Y}$  and  $\text{Nc}=\text{Mg}$  or  $\text{Cd}$ , were prepared for pulsed laser deposition (PLD) by mixing precursor powders of  $\text{La}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{MgO}$ , and  $\text{CdCO}_3$  in a BC mortar until homogeneous. The powder was pressed into 2.54 cm discs and heated in air at 3 °C/min to 975 °C and held for 10 hours, cooled at 3 °C/min and removed from the furnace. Subsequently, the disc was reground to a powder of <100  $\mu\text{m}$  particle size and pressed into 2.54 cm diameter discs and re-pressed isostatically at 344 MPa. The discs were then heated at 3 °C/min to 1000 °C, held for 24 hours, in flowing oxygen gas. Lattice parameters were obtained from powder diffractometer scans taken between 15-155° 2 $\theta$  using  $\text{CuK}\alpha$  radiation ( $\lambda=1.54056\text{\AA}$ ). Lattice parameters are reported in Table 1. Thin films prepared by PLD averaged about 300 nm thick. The observed reflections from films obtained by  $\theta$ -2 $\theta$  scans are reported in Table 1. Deposition parameters are as follows: KrF excimer laser ( $\lambda=248\text{ nm}$ ) was used at a pulse repetition rate of 10 Hz and a laser fluence of 1-2  $\text{J}/\text{cm}^2$  at the target. The chamber was maintained at an oxygen pressure of 13.6 Pa and the heater block holding the substrates was held at 850 °C. Deposition times were about 10 minutes. Samples were cooled rapidly to 650 °C and then to 400 °C in 5.17 kPa of oxygen in 1/2 hr. The substrates employed in this investigation were single

crystal (211) GGG, (100) LaAlO<sub>3</sub>, and (100) LSAT (a solid solution of 30 mole % LaAlO<sub>3</sub>-70 mole % Sr<sub>2</sub>AlTaO<sub>6</sub>) [8,9]. The superconducting transition temperature and transition width were measured using an ac Eddy current apparatus. Bulk or thin film samples were mounted on a sapphire block in which a detecting pick up coil has been imbedded. The sample is mounted on the sapphire block above the detecting coil. An exciting coil driven at 100 MHz is placed above the sample. The sapphire block is in contact with the thermal sink of a closed cycle helium cryostat.

TABLE 1. Properties of La<sub>3-2</sub>Me<sub>2</sub>Ba<sub>3</sub>Ca<sub>1-v</sub>Cu<sub>7</sub>O<sub>16+x</sub> Compounds.

Compound	Lattice Parameter (Å)		Onset T <sub>c</sub> (K)	ΔT <sub>c</sub> (K)	Observed Reflections
	c	a			
La <sub>3</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub>	11.650 11.680*	3.865	72 80*	4	
La <sub>3</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LSAT	11.665				003,005,006,007,0012
La <sub>3</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /GGG	11.540				003,005,006,007,009
La <sub>3</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LaAlO <sub>3</sub>	11.660		35	15	003,004,005,006,007, 009,0011,0012
La <sub>2</sub> YBa <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub>	11.580	3.850	72	3	
LaY <sub>2</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub>	11.630	3.868	74	6	
LaY <sub>2</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LSAT	11.703				002,005,006,007
Nd <sub>3</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub>	11.614	3.874	42		
Nd <sub>3</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LSAT			40	20	
La <sub>2</sub> YbBa <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub>	11.530	3.843	74	5	
La <sub>2</sub> YbBa <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LSAT	11.628		45	>20	003,005,006,007, 009,0010,0011
La <sub>2</sub> YbBa <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LaAlO <sub>3</sub>	11.630				003,005,006,007,008, 009,0010,0011
La <sub>2</sub> YbBa <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /GGG	11.683				003,005,006,007
La <sub>2.5</sub> Na <sub>0.5</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub>	11.630	3.870	68	18	[multiphase]
La <sub>2.5</sub> Na <sub>0.5</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /LaAlO <sub>3</sub>	11.662		65	>40	003,005,006,007
La <sub>2.5</sub> Na <sub>0.5</sub> Ba <sub>3</sub> CaCu <sub>7</sub> O <sub>16+x</sub> /GGG	11.664				006,009
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Cd <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub>	11.661	3.881	55		
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Cd <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub> /LSAT	11.720				003,006
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Cd <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub> /LaAlO <sub>3</sub>	11.265		70	>45	003,006
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Cd <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub> /GGG	11.730				003,006,007
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Mg <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub>	11.661	3.890	35	15	
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Mg <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub> /LaAlO <sub>3</sub>	11.650				003,005,006,007, 009,0010,0011
La <sub>3</sub> Ba <sub>3</sub> Ca <sub>0.5</sub> Mg <sub>0.5</sub> Cu <sub>7</sub> O <sub>16+x</sub> /GGG	11.692				003,005,006,007,0011

\*Reference [3].

Desorption of oxygen from several films was investigated as a function of temperature using thermal desorption mass spectrometry. This involves detecting desorbing  $O_2$  using a double focusing mass spectrometer. The spectrometer has high mass resolution which allows the oxygen signal to be separated from other interfering species such as hydrocarbons of the same nominal mass (i.e., 32 AMU). For analysis, a piece of a thin film coated substrate was introduced into a tantalum foil cell. Spotwelded to the cell was a 0.005 in. 5%Re-W/26%Re-W thermocouple. The cell was attached to a vacuum feedthrough that allowed samples to be moved into a roughing chamber and then into an analysis chamber containing the mass spectrometer. The base pressure of the analysis chamber at the onset of the desorption was in the mid  $10^{-9}$  Torr range. This provided a low oxygen background and an increased sensitivity for detecting oxygen originating from the contents of the cell. The cell temperature could be ramped to 1500 °C, but typically a maximum of 800 °C was used. A linear temperature ramp of 1.4 K/sec was maintained using a feedback temperature controller and a 100 amp power supply. The area of the film was determined by computer processing a scanned image of the sample. The sample thickness was determined by fracturing a coated substrate and measuring the film cross section using scanning electron microscopy. The oxygen desorption spectra were then normalized to the calculated volume of the film for each sample respectively.

## RESULTS

All substitutions for either La or Ca resulted in the preservation of the tetragonal structure. In bulk samples, changes in intensity of x-ray diffraction lines are consistent with the increase or decrease in the scattering power of the substituent. Very small changes in the  $c$  lattice parameter are also noted, consistent with the changes in ionic radii of substituent ions, while the  $a$  parameter exhibited a slight expansion. For thin films, contractions in the  $c$  parameter were observed when the substrate was  $LaAlO_3$ ; slight expansion was found when LSAT or GGG substrates were used. The results of lattice expansion or contraction of the film are consistent with known lattice parameters for the substrates. All films showed the same epitaxial relationship regardless of substrate:  $La_{3-z}Me_zBa_3Ca_{1-v}Nc_vCu_7O_{16+x}$  (00 $l$ ) on (100) $LaAlO_3$ , on (100)LSAT or on (211)GGG, Table 1. The strongest reflection from each of these films was always (006). The best quality films obtained, as judged by the presence of higher order reflections, were those deposited on  $LaAlO_3$ . This may be due to the fact that of all the substrates employed, only  $LaAlO_3$  placed the films in compression, or film deposition conditions were not optimized.

## CONCLUSIONS

All substituent compounds exhibited high  $T_c$  superconductivity, although the transition temperatures were lower than in the unsubstituted compounds. The highest transition temperatures were obtained when rare earth ions replaced La. Engelsberg found that the substitution of Mg for Ca resulted in a reduced  $T_c$  [3]. We observed a  $T_c=35$  K upon the replacement of half of the Ca by Mg; this was close to what Engelsberg observed. On the other hand, the substitution of half the Ca by Cd in this investigation resulted in a much higher transition temperature, 55 K. The fact that divalent Cd is much larger than Mg and has an ionic radius close to Ca suggests that ionic size might be a major factor influencing superconductivity. However, the nature of the bonding is probably a major factor as well.

All the thin film compounds prepared in this investigation desorb very little oxygen when heated compared with YBCO, Fig. 1(A). When some La is replaced by Na the largest desorption for any substituted compound was observed, Fig. 1(C). The substitution of Cd for Ca has a smaller effect, Fig. 1(E). It appears that occupancy by light rare earths (large ionic radii), in the rare earth site for this triple perovskite structure, strongly influences the retention of oxygen with heating.

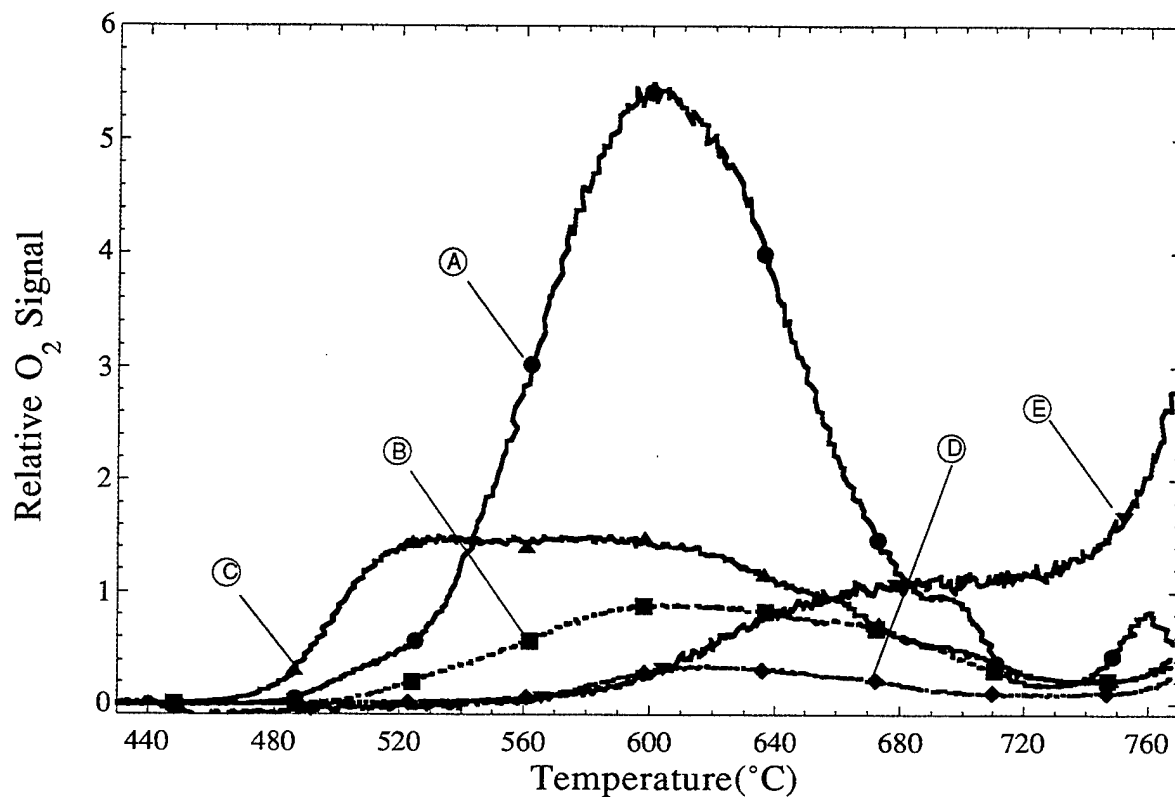


Figure 1. Desorption of oxygen from thin films: (A)  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , (B)  $\text{Nd}_3\text{Ba}_3\text{CaCu}_7\text{O}_{16+x}$ , (C)  $\text{La}_{2.5}\text{Na}_{.5}\text{Ba}_3\text{CaCu}_7\text{O}_{16+x}$ , (D)  $\text{La}_3\text{Ba}_3\text{CaCu}_7\text{O}_{16+x}$  and (E)  $\text{La}_3\text{Ba}_3\text{Ca}_{.5}\text{Cd}_{.5}\text{O}_{16+x}$ .



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