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Professor Sleight

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Department of Chemistry  
Oregon State University  
Corvallis, Oregon 97331-4003

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The objective of the project was the discovery of new materials which might be useful as superconductors, useful in superconducting devices, or useful in other electronic applications. Some insulating cuprates have been converted to superconductors by intercalation with oxygen, e.g., La<sub>2</sub>CuO<sub>4-x</sub> and YBa<sub>3</sub>Cu<sub>3O<sub>6-x</sub></sub>. In these cases an insulator is converted to a p-type conductor. We tried the opposite approach, i.e., cation intercalation to produce n-type conductors. Layered cuprates of the type A<sub>2</sub>Cu<sub>2O<sub>2-x</sub></sub> and A<sub>3</sub>Cu<sub>2O<sub>4X2</sub></sub> (A = Ca or Sr; X = Cl, Br) were the starting points. Lithium intercalation was attempted by reaction of these materials with n-butyl lithium. Although some intercalation appeared to occur, no superconductivity was observed in the products.

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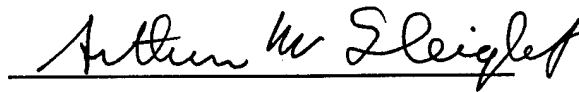
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**New Materials for Electronic Applications**



Arthur W. Sleight, P.I.  
Department of Chemistry  
Oregon State University  
Corvallis, Oregon 97331-4003

The objective of the project was the discovery of new materials which might be useful as superconductors, useful in superconducting devices, or useful in other electronic applications.

Some insulating cuprates have been converted to superconductors by intercalation with oxygen, e.g.,  $\text{La}_2\text{CuO}_{4+x}$  and  $\text{YBa}_3\text{Cu}_3\text{O}_{6+x}$ . In these cases an insulator is converted to a p-type conductor. We tried the opposite approach, i.e., cation intercalation to produce n-type conductors. Layered cuprates of the type  $\text{A}_2\text{Cu}_2\text{O}_{2+x}$  and  $\text{A}_3\text{Cu}_2\text{O}_4\text{X}_2$  (A = Ca or Sr; X = Cl, Br) were the starting points. Lithium intercalation was attempted by reaction of these materials with n-butyl lithium. Although some intercalation appeared to occur, no superconductivity was observed in the products.

Phases of the type  $\text{Li}_x\text{NbO}_2$  and  $\text{Na}_x\text{NbO}_2$  are known to be superconducting for certain values of x. We conducted proton exchange reactions with  $\text{Li}_x\text{NbO}_2$  to produce a series of  $(\text{Li,H})_x\text{NbO}_2$  materials. None of these materials was superconducting above 4.2 K.

Compounds of the type  $\text{A}_x\text{WO}_3$  and  $\text{A}_x\text{MoO}_3$  (A = Li, Na, K, Rb, Cs, Ca, Sr, and Ba) can be metallic and superconducting. Compounds of the type  $\text{Ba}_x\text{NbO}_3$  and  $\text{Sr}_x\text{NbO}_3$  are also known, but they are not superconducting. We found that phases of the type  $\text{Ca}_x\text{NbO}_3$  had not been reported. We have prepared such compounds with x ranging from 0.6 to 0.95. Although these materials are reasonably good electrical conductors, the temperature dependence of conductivity is never metal like. Also, we did not observe superconductivity for any value of x. Superficially,  $\text{Ca}_x\text{NbO}_3$  phases have a very simple cubic structure. However, close examination of our X-ray diffraction data reveals a large superstructure which changes as x changes. This suggests a mechanism for electron localization in this system where delocalized electron behavior might be expected. The  $\text{Ca}^{2+}$

cations are in fact ordered leading in effect to a charge density wave in a lattice which otherwise would be simple cubic. This charge density wave likely creates a periodic potential which traps the 4d electrons of Nb.

We thoroughly investigated a report of superconductivity at 20 K in the Ba/Nb/O system. We concluded that the superconducting phase reported was actually essentially NbN. Details of this work are given in our last report.

Superconductivity at temperatures as high as 34 K have been observed in (K,Ba)BiO<sub>3</sub> phases with the perovskite structure. We have produced new mixed valent compounds of bismuth by ion exchanging NaBiO<sub>3</sub>·nH<sub>2</sub>O with Sr and Ba. This has led to perovskite phases such as (Ba<sub>0.44</sub>Bi<sub>0.56</sub><sup>3+</sup>)(Na<sub>0.34</sub>Bi<sub>0.66</sub><sup>5+</sup>)O<sub>2.77</sub>. However, none of these new perovskite phases showed superconductivity above 4.2 K.

Much of our work during the last year of this project has been on materials with low dielectric constant that might be used as substrates or interlayers in superconducting devices. Some of this work was on thin films prepared by sputtering. Films of Sr<sub>2</sub>MgWO<sub>6</sub>, Ca<sub>2</sub>MgWO<sub>6</sub>, Sr<sub>2</sub>AlNbO<sub>6</sub>, Sr<sub>2</sub>AlTaO<sub>6</sub>, and Sr<sub>2</sub>GaNbO<sub>6</sub> were prepared because all of these have a good lattice match to the cuprate superconductors. The substrate was either MgO or LaAlO<sub>3</sub>. Both on- and off-axis conditions were studied. Texture was evaluated by X-ray diffraction, and the morphology of the films was characterized by SEM and AFM. The most promising films were of Sr<sub>2</sub>GaTaO<sub>6</sub> and Sr<sub>2</sub>AlTaO<sub>6</sub>. Thus, films of YBCO were grown on top of these films; T<sub>c</sub>'s as high as 87 K were obtained in such films.

LaAlO<sub>3</sub> has good properties as a substrate for cuprate superconductors. However, it has problems due to a phase transition and related twinning. Above about 500°C, LaAlO<sub>3</sub> is cubic. Below this temperature, it is rhombohedral. If films are grown on LaAlO<sub>3</sub> above 500°C, this phase transition in LaAlO<sub>3</sub> can seriously damage the films. Even if films are grown below 500°C on LaAlO<sub>3</sub>, there

is a problem due to the twinning which is directly caused by the phase transition. We have found that the phase transition in  $\text{LaAlO}_3$  can be completely suppressed by substitution of Sr for La. Materials of the type  $\text{La}_{1-2x}\text{Sr}_{2x}\text{O}_{3-x}$  were prepared for a wide range of x values. It was found that x must be about 0.36 to suppress the phase transition. The dielectric properties of these substituted  $\text{LaAlO}_3$  phases have been measured and found to be essentially unchanged from those of  $\text{LaAlO}_3$ . Thus,  $\text{La}_{0.64}\text{Sr}_{0.36}\text{O}_{2.82}$  is a promising new substrate material.

Attempts were also made to prepare phases of the type  $\text{A}_2\text{MgMO}_5\text{F}$  (A = Ca, Sr, or Ba; M = Nb or Ta). In the case of A = Ba, good results were obtained. These may be useful dielectric materials because the polarizability of  $\text{F}^-$  and less than that of  $\text{O}^{2-}$ .