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LETTERS TO THE EDITOR

Semiconducting $Li_2MgCu_3O_{5+x}$ and $Li_2CaCu_3O_{5+x}$ with Face Centered Cubic Metal Lattice

J. HAUCK, K. BICKMANN, B. BISCHOF, AND S. IPTA

Inst. f. Festkörperforschung, KFA Jülich, D-5170 Jülich, Federal Republic of Germany

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Semiconducting $Li_2MgCu_3O_{5+x}$ and $Li_2CaCu_3O_{5+x}$ were obtained in three modifications from Li_2CuO_2/$MgCu_2O_3$ or $CaCu_2O_3$ mixtures. The Li/Mg or Li/Ca sublattices of γ-phases are disordered in tetragonal distorted NaCl lattices (a = 399–401 pm, $c/2$ or $c/4$, resp. 442–443 pm). The phase transitions to α and β phases depend on oxygen partial pressure indicating O atoms ordering.

The crystal structures of superconducting La_2CuO_4 (*1, 2*), $Ba_2YCu_3O_{6.5+x}$ (*3*), and $Ca_2Sr_4Bi_4Cu_4O_{16+x}$ (*4*) consist of M = La_2Cu, Ba_2YCu_3, or $Ca_2Sr_4Bi_4Cu_4$ metal lattices with structures of ordered body centered cubic (bcc) alloys, e.g., with $MoSi_2$ alloy structure of La_2Cu (*5*). The oxygen atoms are on interstitial octahedral sites similar, e.g., to H in VH_x or $FeTiH_x$ interstitial alloys (*5*). We have prepared new quaternary oxides $Li_2MgCu_3O_{5+x}$ and $Li_2CaCu_3O_{5+x}$ with small metal atoms Li, Mg, and Ca on Au positions of CuAu alloy structure, which is an ordered face centered cubic (fcc) alloy. The oxygen atoms are on interstitial octahedral sites similar to H atoms on PdH_x interstitial alloys. The structures consist of tetragonal layers as in La_2CuO_4, $Ba_2YCu_3O_6$, or $Ca_2Sr_4Bi_4Cu_4O_{16}$ (Fig. 1). Each fcc layer contains two M atoms, each bcc layer one M atom. Therefore the lattice constants (and Cu–O bond distances) are increased in ordered fcc M structures, though Li, Mg, and Ca atoms are smaller than Ba, Y, Bi, and La atoms. All compounds investigated so far display semiconducting behavior, probably because of the increased Cu–O bond distances.

The $Li_2MgCu_3O_{5+x}$ and $Li_2CaCu_3O_{5+x}$ phases with $-0.7 \lesssim x \lesssim 0.4$ were obtained from mixtures of Li_2CuO_2 (*6*) and $MgCu_2O_3$ (*7*) or $CaCu_2O_3$ (*8*) by 10 hr annealing at 960–1000°C. Both compounds occur in three modifications with two phase transitions depending on oxygen partial pressure as was determined by X-ray diffraction at room temperature after quenching in liquid nitrogen, by thermogravimetric analysis and differential thermal analysis (Fig. 2). The phase transition temperatures of $Li_2MgCu_3O_{5+x}$ (*9*) are about 100°C ($\beta \rightarrow \gamma$) or 400°C ($\alpha \rightarrow \beta$) lower than in $Li_2CaCu_3O_{5+x}$. The oxygen sublattice of $Li_2MgCu_3O_{5+x}$ is disordered in β phase, the Li_2Mg sublattice disordered in γ phase. The

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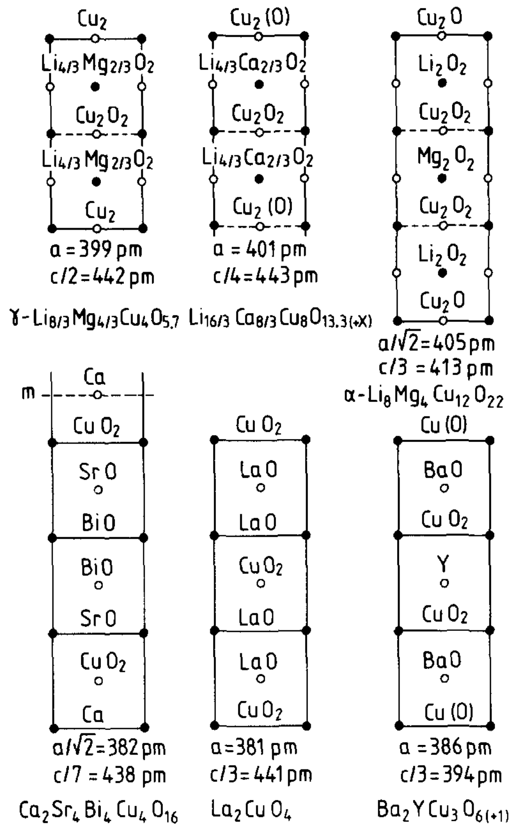

FIG. 1. Schematic drawing of $Li_2MgCu_3O_{5+x}$ and $Li_2CaCu_3O_{5+x}$ structures with fcc metal lattice compared to $Ca_2Sr_4Bi_4Cu_4O_{16}$, La_2CuO_4, and $Ba_2YCu_3O_{6(+1)}$ structures with bcc metal lattice. (● and ○, Metal atoms at projection height 0 and 0.5, respectively.) Only one-half of $Li_2CaCu_3O_{5+x}$ and $Ca_2Sr_4Bi_4Cu_4O_{16}$ structures is shown; m = mirror plane.

samples must be annealed for ~1 hr below the $\beta \rightarrow \gamma$ phase transition so that the Li_2Mg sublattice is ordered and the oxygen content can increase at 400–700°C. Otherwise the sample with low oxygen content decomposes at decreased temperatures to Li_2CuO_2, MgO, and Cu_2O. It is suggested that the oxygen content of one Cu plane increases in a manner similar to that in $Ba_2YCu_3O_{6(+1)}$ structures, so that the coordination number of these Cu atoms changes from twofold at low oxygen content ($x \sim -0.75$) to fourfold at high oxygen content ($x \sim 0.5$).

Buerger precession photographs on γ-$Li_2CaCu_3O_{5+x}$ platelets (Fig. 3) show superstructure reflections corresponding to $c \approx 4a$ (NaCl). The strong reflections of X-ray powder pattern are as in tetragonal distorted NaCl lattice with lattice constants similar to γ-$Li_2MgCu_3O_{5+x}$ (Fig. 1). The determination of superstructure reflections from powder patterns of α and β phases is somewhat difficult because of the three modifications and of impurities with crystal structures related to NaCl lattice (CaO, $CaCu_2O_3$, Li_2CuO_2).

The Cu–O–Cu bond distances a or $a' = a/\sqrt{2}$ (Fig. 1) in tetragonal planes of $Li_2MgCu_3O_{5+x}$ (399–405 pm) and $Li_2CaCu_3O_{5+x}$ (401 pm) are larger than in La_2CuO_4 (381 pm), $Ba_2YCu_3O_{6(+1)}$ (~386 pm), or $Ca_2Sr_4Bi_4Cu_4O_{16+x}$ (382 pm). The c' values perpendicular to tetragonal planes are increased by ~10% in γ-$Li_2MgCu_3O_{5+x}$ and γ-$Li_2CaCu_3O_{5+x}$, similar to $Ca_2Sr_4Bi_4Cu_4O_{16+x}$ and La_2CuO_4, but are only 2%

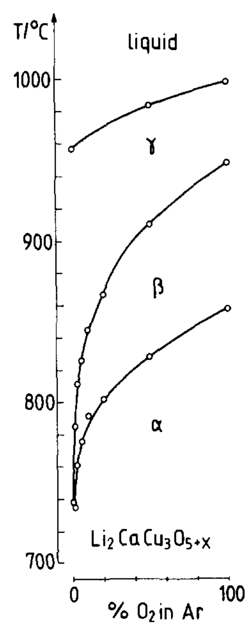

FIG. 2. Phase transitions of α, β, γ-$Li_2CaCu_3O_{5+x}$ at different oxygen partial pressures of O_2/Ar mixtures at 1 bar total pressure.

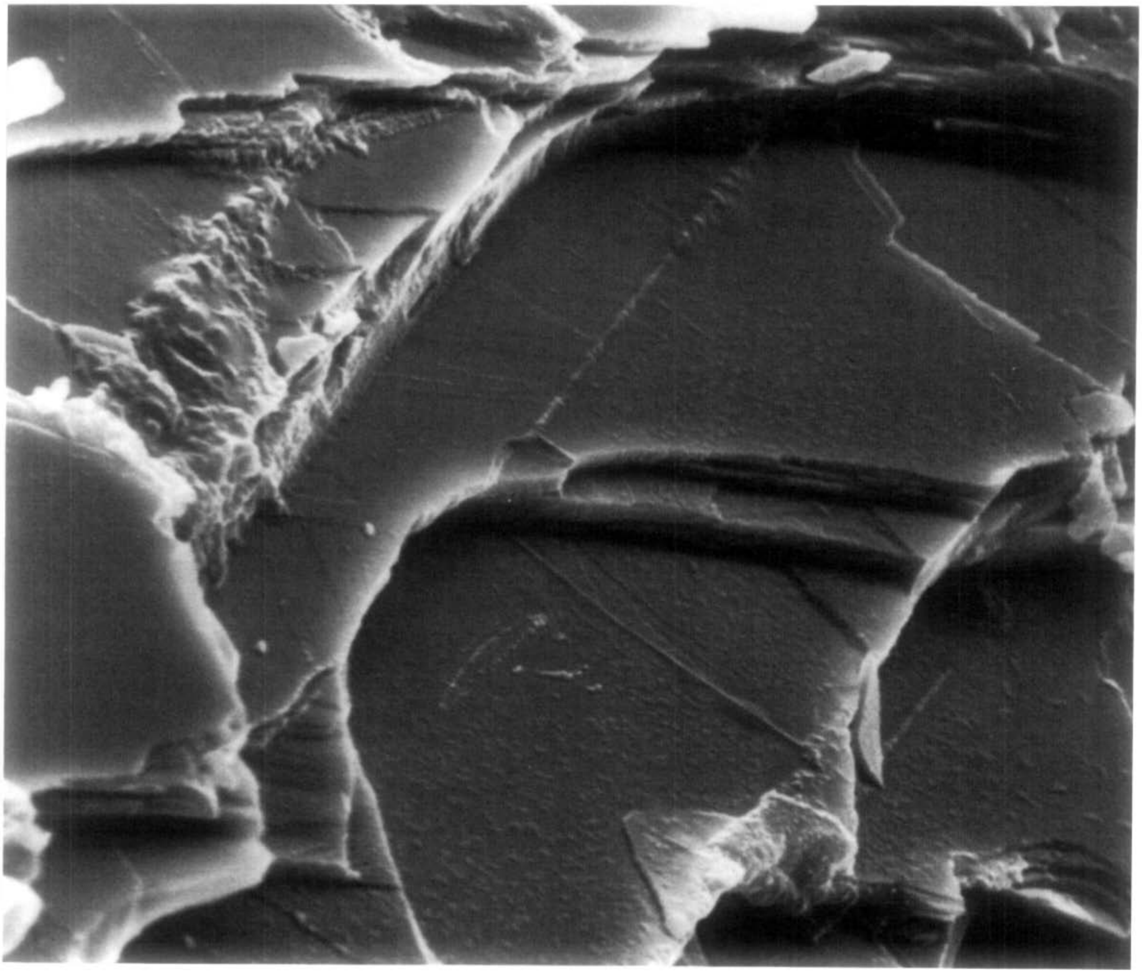

FIG. 3. Scanning electron micrograph of γ-$Li_2CaCu_3O_{5+x}$.

larger than a' values in α-$Li_8Mg_4Cu_{12}O_{22}$ and $Ba_2YCu_3O_6$ (Fig. 1).

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