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Phase relations and physical properties of $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$

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Abstract. $Li_2CuO_2\square$ and $MgCu_2O_3$, isomorphous to superconducting TiO, form solid solutions $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ with orthorhombic symmetry at $0 \leqslant r \leqslant 0.25$ and $0.90 \leqslant r \leqslant 1$ and three tetragonal phases α, β and γ at $r = 0.5$ with phase transitions at about 400 and about 800 °C. The O and the Li–Mg sublattices disorder at the α-to-β- and the β-to-γ-phase transitions, respectively, in tetragonal phases with lattice constants $a = 399.3$ pm, $c = 883.1$ pm (γ) and $a = 572.1$ pm, $c = 1239.5$ pm (α). The resistivity of samples is decreased at various r-values with semiconducting behaviour. The magnetic moment at Cu atoms is $1.3\mu_B$–$1.5\mu_B$ per Cu atom.

1. Introduction

The superconducting copper oxides $La_{2-r}Sr_rCuO_{4-x}$, $Ba_2YCu_3O_{6.5+x}$ and also the new $(Ca, Sr)_3Bi_2Cu_2O_{8+x}$ can be considered as interstitial alloys MZ_y of $Z \equiv O$ atoms at octahedral sites of a BCC derivative M lattice, where $M \equiv La_{2-r}Sr_rCu$, ($MoSi_2$ alloy structure), Ba_2YCu_3 or $(Ca, Sr)_3Bi_2Cu_2$ [1]. The O coordination of Cu atoms varies from octahedral to fivefold, fourfold or twofold. The present Cu oxides $Li_2CuO_2\square$ [2] and $MgCu_2O_3$ [3] can also be considered as MZ_y interstitial alloys, Z at octahedral sites but with a FCC $M \equiv Li_2Cu$ or $MgCu_2$ lattice with $MoPt_2$ alloy structure [1]. Both oxides are isomorphous to $TiO \equiv Ti_2\square O_2\square$ with vacancies $\square$ in the M and Z sublattices. The Cu atoms of $MgCu_2O_3$ and Li atoms of $Li_2CuO_2\square$ are on Ti positions of the $Ti_2\square O_2\square$ structure [1]. TiO is superconducting below $T_c = 2.3$ K [4], while brown–red Li_2CuO_2 and grey $MgCu_2O_3$ are non-metallic. The solid solution, $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ ($0 \leqslant r \leqslant 1$) of Li_2CuO_2 and $MgCu_2O_3$ is similar for example to the $La_{2-r}Sr_rCuO_{4-r/2+x}$ solid solution [5], where conductivity can be increased by substitution with low-valent M atoms, divalent Sr for trivalent La or monovalent Li for divalent Mg. The $x = 0$ reference O content $3 - r$ and $4 - r/2$ is defined for formally divalent Cu. The $Ba_2YCu_3O_{6.5+x}$ system had shown that x can be positive and negative for formally trivalent and monovalent Cu, respectively [6].

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2. Experimental details

Li_2O (obtained from LiOH at 700 °C and 10^{-3} bar), CuO and MgO were mixed in different ratios, sintered at 700–1100 °C in corundum or MgO crucibles. The oxygen partial pressure p_{O_2} could be varied from 0.01 to 1 bar by mixing O_2 and Ar with a gas-mixing pump at a constant flow rate.

The phases of Li_2CuO_2–$MgCu_2O_3$ solid solution were characterised by x-ray diffraction (the Bragg–Brentano or Guinier method), differential thermal analysis (DTA), thermogravimetric analysis (TGA), optical microscopy and scanning electron microscopy, resistivity (qualitatively with an ohmmeter and quantitatively with the four-point method at 10–300 K) and susceptibility measurements (with a Faraday balance at 4–300 K). The absolute O content was determined by the difference in weight after H_2 reduction for 10 h at 600 °C to a Li_2O–MgO–Cu mixture. Li_2CuO_2 impurities can be dissolved in aqueous ammonia to give a blue colour while the other phases, except Li_2O, dissolve only in acids.

3. Results

Li_2CuO_2–$MgCu_2O_3$ or Li_2O–MgO–CuO mixtures could be equilibrated to $MgCu_2O_3$–Li_2CuO_2 solid solutions after reaction for 10–20 h at about 1000 °C. The reaction of MgO and CuO is still very sluggish at these temperatures, although some of the Li_2O is volatile and samples with a high Li_2CuO_2 content are molten. The reaction of Li_2O–MgO–CuO mixtures at decreased temperatures or shorter annealing times yielded Li_2CuO_2–CuO–MgO reaction products because of favourable kinetics for Li_2CuO_2 formation. At 1000 °C, $MgCu_2O_3$–Li_2CuO_2 forms a solid solution $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ at $0 \leqslant r \leqslant 0.25$ (samples A), $0.90 \leqslant r \leqslant 1$ (samples B) and three modifications α, β and at $0.5 \leqslant r \leqslant 0.56$ (samples C).

The solid solution samples A at $0 \leqslant r \leqslant 0.25$ with a $MgCu_2O_3$ structure have a maximum extension at about 1000 °C. At this temperature the $r \simeq 0.25$ phase forms a eutectic melt with the $r = 0.5$ phase. The melting point increases to about 1120 °C for samples with low r. The a and b lattice constants of $MgCu_2O_3$ [3]—a = 400 pm, b = 319 pm and c = 935 pm—decrease by about 2% at increased $r = 0.25$ (b and c are chosen to be as in the Li_2CuO_2 structure [2]).

Samples with $r > 0.56$ are molten at 1000 °C. Black samples (B) of Li_2CuO_2 solid solutions are obtained by cooling the melt after annealing for about 15 h at 1000 °C, whereas mixtures of Li_2CuO_2 with unreacted MgO–CuO are formed at short annealing times or decreased temperatures. The a and b lattice constants of Li_2CuO_2 [2]—a = 366.2 pm, b = 286.3 pm and c = 939.6 pm—increase by about 1% for the maximum solution of $MgCu_2O_3$.

Samples C are three tetragonal modifications α, β and γ obtained at $0.5 \leqslant r \leqslant 0.56$ with phase transformations at about 400 °C and about 800 °C, depending on the oxygen partial pressure (figure 1). The γ-modification melts congruently at 1064 °C. It can be investigated at room temperature after quenching in liquid nitrogen. The phase transition to β-phase with an enthalpy $\Delta H_{\beta\gamma}$ of transformation of 253 ± 10 J g^{-1} on heating is reversible, e.g. at a decrease of 50–100 °C in the transition temperatures for a 5 °C min^{-1} cooling process. This phase transition is associated with the ordering of Li and Mg atoms as will be shown from an analysis of different x-ray patterns.

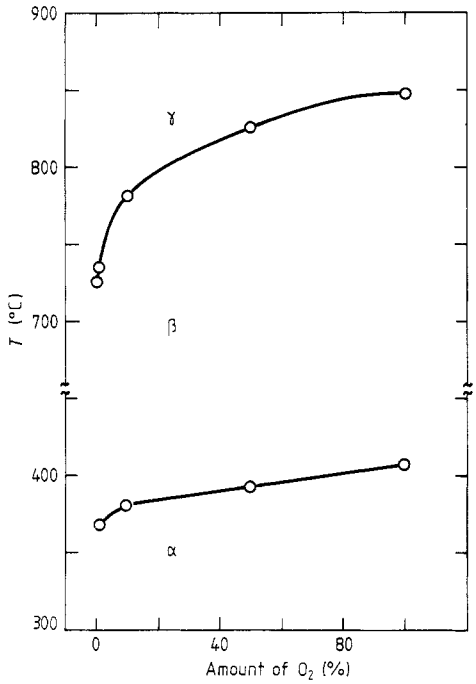

Figure 1. α-to-β-to-γ-phase transitions of $Li_8Mg_4Cu_{12}O_{20+x}$ for different percentages of O_2 in O_2–Ar gas mixtures at 1 bar.

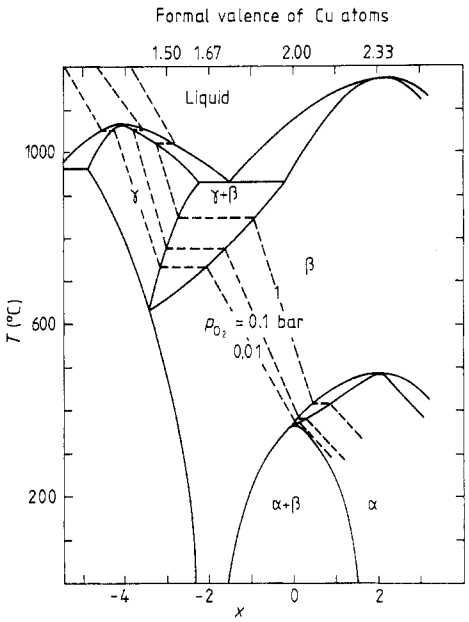

Figure 2. Schematic phase diagram of temperature against O content x of pseudo-binary oxide MO_x ($M \equiv Li_8Mg_4Cu_{12}O_{20}$) at different oxygen partial pressures (---).

The α-to-β-phase transition at about 400 °C seems to be related to the ordering of O atoms. The DTA experiments with varied oxygen partial pressure p_{O_2} on consecutive heating and cooling cycles show peaks only on heating with a change $\Delta H_{\alpha\beta}$ in enthalpy of 4–48 J g^{-1}, increasing at increased p_{O_2}. No peak was observed while heating in pure Ar. The peak, however, recovered at the appropriate temperature (figure 1) and increased to the usual magnitude after several cycles at increased p_{O_2}. This suggests the absence of the phase transition for low O content, as outlined in figure 2. The phase relations for low O contents are similar to those for tetragonal $Ba_2GdCu_3O_6$, which does not transform to the orthorhombic phase [6].

The phase transitions of the present system are first order and can be studied by DTA and TGA experiments. The free enthalpy of the ordering process for the α-to-β-phase transitions increases with increasing O content. The TGA shows a step-like decrease in O content in the two-phase regions, which can be explained by phase relations outlined in figure 2. The O content decreases at both phase transitions on heating. The β-to-γ-phase transition temperature increases even more markedly with increasing p_{O_2} (figure 1) and increasing O content (figure 2) than the α-to-β-phase transition temperature does. The ordering of the Li–Mg sublattice at the β-to-γ-phase transition seems to be important for occupation of O vacancies. The TGA experiments at $p_{O_2} = 1$ bar show a slightly increased O content in the melt, which can be explained by the phase relations in figure 2. The γ-phase of composition $Li_8Mg_4Cu_{12}O_{16}$ with $x = -4$ decomposes to $4Li_2CuO_2 + 4Cu_2O + 4MgO$ on inappropriate cooling, where kinetics are too slow to

increase the O content. Fast quenching in liquid nitrogen yields the γ-phase powder pattern, very slow cooling (3 °C min^{-1}) yields the α-phase, while cooling in air (after removing the quartz tube from the furnace) produces a mixture of α- and γ-phases and decomposition products. These experiments show that the lower limit of single-phase γ and β should be shifted to increased x at decreased temperatures (figure 2).

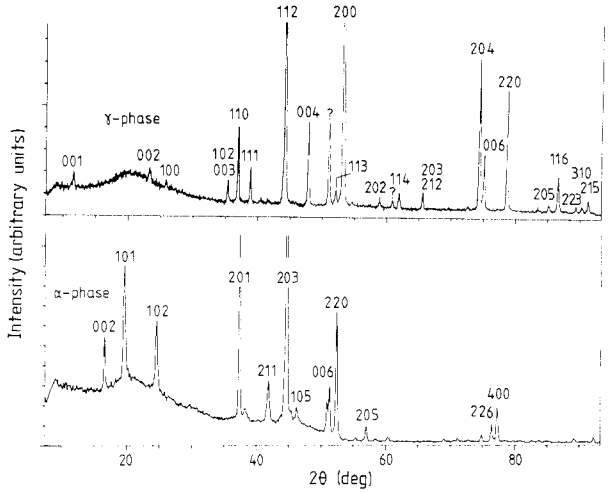

Figure 3. X-ray powder pattern (Co Kα_1 radiation) for new tetragonal α- and γ-phases of $Li_8Mg_4Cu_{12}O_{20-x}$.

The x-ray powder patterns of α- and β-phases are very similar because of the weak scattering of O atoms. The pattern of the γ-phase is different (figure 3). The strong 111, 200 and 220 'NaCl reflections' of pseudo-cubic MZ_y lattice are split differently for α–β- and γ-phase samples. Tetragonal unit cells were obtained for both patterns: $a = 399.3$ pm and $c = 883.1$ pm for the γ-phase; $a = 572.1$ pm and $c = 1239.5$ pm for the α-phase (after repeated annealing at $p_{O_2} = 1$ bar). The lattice parameters of the α-phase are slightly increased to $a = 572.8$ pm and $c = 1239.8$ pm on increased cooling rate and therefore decreased O content. The unit cell of the γ-phase is about twice the MZ_y NaCl unit cell with eight M- and eight Z-atom positions, while the unit cell of the α-phase with $a \simeq \sqrt{2}\,a$(NaCl) and $c \simeq 3a$(NaCl) contains 24 M- and 24 Z-atom positions. The composition of M and Z can be obtained from the r-values of single-phase $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$: $Li_{2.67}Mg_{1.33}Cu_4O_{6.67+x}$ at $r = 0.5$ and $Li_3Mg_{1.17}Cu_{3.83}O_{6.5+x}$ at $r = 0.56$ for the γ-phase; $Li_8Mg_4Cu_{12}O_{20+x}$ ($r = 0.5$) and $Li_9Mg_{3.5}Cu_{11.5}O_{19.5+x}$ ($r = 0.56$) for the α-phase. The $r = 0.5$ composition agrees with onefold, twofold, fourfold, eightfold and 16-fold positions at tetragonal symmetry. At $r = 0.56$ about 4% of the Cu atoms should be substituted by Mg atoms. However, the observation of identical phase transition temperatures (figure 1) for samples with nominally different r-values suggests negligible Mg substitution and therefore a constant $r = 0.5$ composition of the α-, β- and γ-phases. The increased Li content at $r = 0.5$–0.56 is probably volatile during the annealing process. The oxygen content $x = -3$ (γ-phase) and $x = 2$ (α-phase) correspond to two monovalent and two divalent Cu atoms in γ-$Li_{2.67}Mg_{1.33}Cu_2^+Cu_2^{2+}O_{5.7}$, and four trivalent and eight divalent Cu atoms in α-$Li_8Mg_4Cu_8^{2+}Cu_4^{3+}O_{22}$. All Cu atoms are divalent at $x = 0$ (figure 2).

Figure 4 shows the ordering of Li, Mg, Cu and O atoms in agreement with the observed tetragonal symmetry. Other configurations are possible—in particular for Li and O atoms in the α- and β-phase, which is difficult to determine by x-ray diffraction. The suggested ordering of Li atoms and O vacancies □ is similar to that in Li_2CuO_2□ [2]. The O vacancies □ in Li_2CuO_2□ are in the sequence □–Cu–□–Cu in the a axis direction (figure 4), so that all Cu atoms have planar fourfold O coordination. In α-$Li_8Mg_4Cu_{12}O_{22}$□$_2$ with a sequence O–Cu–O–Cu in the c axis direction, eight Cu^{2+} atoms have octahedral and four Cu^{3+} atoms have fourfold planar O coordination. The Cu^+ atoms in the γ-phase and β-phase at low x have twofold coordinations in the suggested structure (figure 4). The relative distance between Cu atoms decreases from $c/2a = 1.11$ in the γ-phase to $c\sqrt{2}/3a = 1.02$ in the α-phase—about 0.90 in $MgCu_2O_3$ and about 0.87 in Li_2CuO_2. In α-, β- and γ-phases and Li_2CuO_2 the Li atoms, which are close to the O vacancy positions, have smaller coordination numbers. The fourfold coordination in Li_2CuO_2 is tetrahedral [2]. The unit-cell content of the γ-phase ($Li_{2.67}Mg_{1.33}Cu_4O_{6.67+x/3}$ with $x \simeq -3$) suggests a disorder of Li–Mg and part of the O sublattice. 71% of the total O positions are occupied in the γ-phase, 83% in the α- and β-phases at $x = 0$, and 92% in the α-phase at $x = 2$. The $x = 0$ composition is similar to that for 83% occupation of the Z ≡ C positions in ordered or disordered V_6C_5□ or Nb_6C_5□ [1]. The C atoms of the disordered phase have short-range order, whereas the ordered phases have some disorder. This might be similar in the present system.

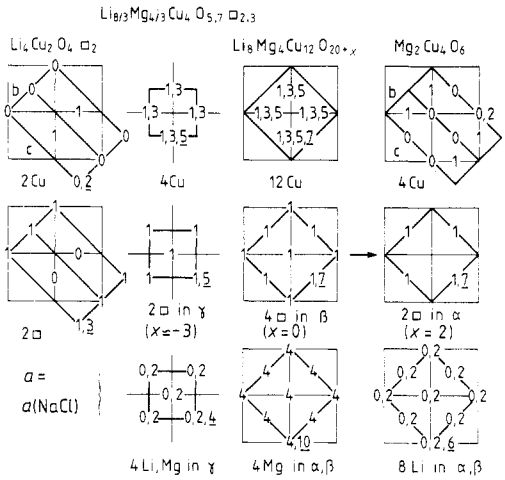

Figure 4. Projection of Cu, Mg, Li atoms and O vacancy □ positions in $Li_4Cu_2O_4$□$_2$–$Mg_2Cu_4O_6$ neglecting distortions [2, 3] and α-, β- and γ-$Li_8Mg_4Cu_{12}O_{20+x}$ unit cells on an NaCl lattice grid with a(NaCl) = 2. The underlined numbers show the periodicity in height.

Grey $MgCu_2O_3$ and reddish brown Li_2CuO_2 are insulating. The electrical resistivity decreases in the black samples of solid solutions A, B and C. All samples investigated so far show increased conductivity but are still semiconducting (figure 5). Magnetic measurements of the susceptibility were performed at 4–300 K for the α-phase. The data can be fitted to Curie–Weiss laws with $\mu_{eff} = 1.3\mu_B$–$1.5\mu_B$ per Cu atom and θ in the range from −31 to −40 K. A very small contribution from Pauli paramagnetism and the observed magnetic moment indicate localisation of the electrons in the d^9 configuration

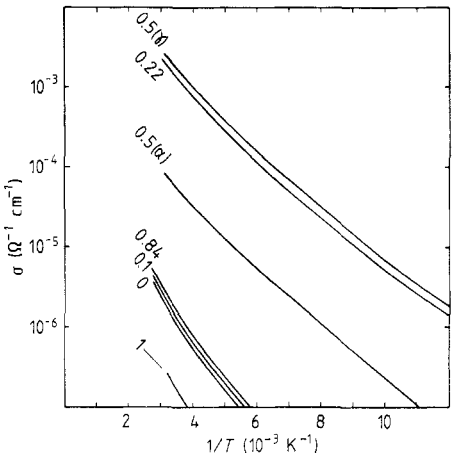

Figure 5. Conductivity of $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ samples with different r-values (shown as curve labels).

of divalent Cu. The magnetic moments do not order above 4 K. Li_2CuO_2 and $MgCu_2O_3$ have $\mu_{eff} = 1.9$ and >0.8 μ_B per Cu atom and order at the Néel temperatures 10 and 70 ± 0.5 K, respectively.

4. Conclusion

$Li_2CuO_2\square$ and $MgCu_2O_3$ form solid solutions with the formula $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ at $0 \leqslant r \leqslant 0.25$ (samples A), $0.90 \leqslant r \leqslant 1$ (samples B) and three modifications α, β and γ at $r = 0.5$ (samples C). There are miscibility gaps at $0.25 \leqslant r \leqslant 0.50$ and $0.50 \leqslant r \leqslant 0.90$. The metal sublattice can be considered to be FCC derivative structures: M ≡ $MgCu_2$ for $MgCu_2O_3$ solid solution (samples A) and M ≡ Li_2Cu for Li_2CuO_2 solid solution (samples B) have an orthorhombic $MoPt_2$ alloy structure, and M ≡ $(Li_2Mg)Cu_3$ for α-, β- and γ-phases (samples C) have a CuAu alloy structure (figure 4). The Li_2Mg sublattice is disordered in the γ-phase with tetragonal unit-cell lattice constants $a = 399.3$ pm and $c = 883.1$ pm and ordered in the tetragonal β-phase with $a = 572.1$ pm ($\approx\sqrt{2}a$(NaCl)) and $c = 1239.5$ pm. The O sublattice orders below about 400 °C in the α-phase.

$Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ samples A and B can be compared with the solid solution $La_{2-r}Sr_rCuO_{4-r/2+x}$, where the symmetry of the phases is maintained in certain ranges, e.g. the orthorhombic phase for $0 \leqslant r \leqslant 0.16$ and the tetragonal phase for $0.16 \leqslant r \leqslant 0.5$ [5]. Samples A and B in the present system have different O contents. $MgCu_2O_3$ solid solution samples consist of CuO_6 octahedra, which are linked by apices and edges, whereas Cu atoms of $Li_2CuO_2\square$ have a planar coordination of four O neighbours forming CuO_2 chains in the b axis direction (figure 4). The chains are linked by edges, whereas CuO_4 groups of Cu(1) atoms in $Ba_2YCu_3O_7$ are linked at apices.

The α-, β- and γ-phases with $r = 0.5$ (samples C) can be compared with the $Ba_2YCu_3O_{6.5+x}$ system. The ratio of Li : Mg : Cu = 2 : 1 : 3 is constant, while the O content x in $Li_8Mg_4Cu_{12}O_{20+x}$ can vary between −4 and 2 as outlined in figure 2. The α-to-β-phase transition at about 400 °C is probably absent at low O contents, as in tetragonal $Ba_2GdCu_3O_6$ which does not transform to the orthorhombic phase [6]. The Li–Mg sublattice becomes disordered at the β-to-γ-phase transition at about 800 °C; this might

be due to the small size and high mobility of Li atoms. The lattice constants $c = 2a$(NaCl) (γ-phase) and $c = 3a$(NaCl) (α-phase) are related to alternating Cu^{+}–Cu^{2+} layers (γ-phase with $x = -3$) and Cu^{3+}–Cu^{2+}–Cu^{2+} layers (α-phase with $x = 2$).

Despite the large variety of phases in the $Li_{2r}Mg_{1-r}Cu_{2-r}O_{3-r+x}$ system and some analogies to superconducting $Ba_2YCu_3O_{6.5+x}$ or $La_{2-r}Sr_rCuO_{4-r/2+x}$, the physics of the present system seem to be quite simple. All samples investigated so far are semiconducting. Measurements of magnetic properties show that the d electrons of divalent Cu atoms are localised in d^9 configuration without magnetic ordering above 4 K.

A physical property concerning the mechanical strength, namely the deterioration of bulk material after repeated loading and unloading with O seems to be new in oxide systems but is well known for interstitial alloys, e.g. $FeTiH_x$ [7]. The variation in volume of about 3.7% at the β-to-γ-phase transition (figures 1 and 2) causes internal strain. Large grains of the starting material for DTA and TGA runs at different p_{O_2}-values (figures 1 and 2) deteriorated to a fine powder after several cycles of O loading and unloading.

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