with the nitridation time, showing that the N atoms enter the Si substrate even at the initial stage of nitridation. This difference in the initial $\Delta\phi$ might arise from the different geometrical structures of the surfaces. Namely, the (111) surface has the most closely packed structure while the (100) surface has an open structure, and therefore N atoms diffuse into the Si (100) substrate more easily than into the (111) substrate. Similar work function changes were observed in the oxidation of the Si (111) and (100) surfaces.[39]

For forming relatively thick nitride films, reorganization of the surface Si atoms must occur, and thus the structures of the nitride surfaces as well as the bulks formed on the Si (100) and (111) substrates are thought to be the same. On the other hand, the nitride/Si interfacial regions are likely to have different structures due to the difference in diffusion coefficient of N atoms in the (100) and (111) substrates, causing different $\Delta\phi$ after the formation of the relatively thick nitride layers. The Si 2p peak at 100.1 eV may be caused by the N atoms which diffuse into Si.

E_{FB} for the 2-nm-thick nitride-covered Si electrodes is shifted in the anodic direction after sweeping the electrode potential in the 1 M acetonitrile solution of $LiClO_4$ as shown in Figure 5. This indicates that the barrier height in Si can be controlled by this simple electrochemical method. A similar shift is observed for the Si electrodes covered with the thin Si oxide layers,[25] but the amount of the shift is about one-third of that for Si nitride.

After the potential sweep, the nitride-induced Si 2p peak shifts from 101.9 to 103.0 eV (Figure 6b), indicating that the Si atoms in the layer are more positively charged. Simultaneously, the intensity of the O 1s peak is increased. These results indicate that Si oxynitride is formed from Si nitride, probably by the reaction of the nitride film with a small amount of residual water in the acetonitrile solution.

After the potential sweep, a Li 1s main peak and a shoulder are observed at 55.8 and 57.8 eV, respectively. The 55.8-eV peak is assigned most probably to Li bound to other atoms, and the 57.8-eV peak to free Li^+ ions.[25] The shift in E_{FB} caused by the former species is thought to be very small since the dipole moments of the bonds are randomly oriented. On the other hand, free Li^+ ions in the layer will shift E_{FB} because they generate a potential drop in this layer. As the Si band edges are fixed with respect to the band edges of Si oxynitride, the Si band edges are shifted by the same amount as that of the potential drop in the oxynitride layer. If one assumes that Li^+ ions are present uniformly in the layer of the 2-nm thickness and the dielectric constant of the layer is 4, the density of Li^+ ions to cause a 1.5-V shift in E_{FB} is estimated to be 1.7×10^{20} cm^{-3}. The Li^+ ions are thought to be included in the film during the transformation from nitride to oxynitride. This is supported by the fact that the shift becomes smaller when the as-produced Si nitride layer contains a large amount of oxygen.

Our recent work[25] shows that Li^+ ions can be included in the Si oxide layer only during the formation of the layer in the solution, but cannot after the formation. Contrary to this case, inclusion of Li^+ ions in the nitride layer is possible after the film formation.

Conclusion

The rate of the Si nitride formation by the reaction of Si with nitrogen plasma at 700 °C is at least 2 orders of magnitude higher than that by the reaction with ammonia at 900 °C, and consequently contamination during the film formation can be minimized. This procedure may be applicable to the mass product of Si nitride (or Si oxynitride) films in MIS solar cells as well as in LSI. The work function of the Si (111) surface increases slightly in the very initial nitridation stage and decreases by further nitridation. The work function of the (100) surface decreases monotonically. The amount of the work function lowering of the (100) surface is more than twice of that of the (111) surface, due to the open surface structure. E_{FB} for the nitride-covered Si electrode is shifted toward the anodic (maximum 1.5 V) after the electrode potential sweep in the acetonitrile solution of $LiClO_4$. This shift is caused by the inclusion of the Li^+ ions in the Si oxynitride layer which is formed from Si nitride during the potential sweep. This electrochemical procedure can be applied to the MIS and PEC solar cells to enhance the energy barrier and the photovoltage.

Registry No. Si, 7440-21-3; N, 7727-37-9; Li, 7439-93-2; silicon nitride, 12033-89-5; silicon oxynitride, 12033-76-0.

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Oxygen Stoichiometry and Expansion of $YBa_2Cu_4O_8$

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The effects of temperature and oxygen partial pressure on the oxygen stoichiometry, expansion, and electrical resistivity of $YBa_2Cu_4O_8$ have been determined. Samples prepared by two low-pressure synthesis methods—prolonged reaction between $YBa_2Cu_3O_7$ and $Cu(NO_3)_2$ and reaction between $BaCO_3$, Y_2O_3, and CuO at 4 Torr of oxygen—behave similarly. Heating to 800 °C in oxygen produces a loss of 0.08 atom of oxygen, which is completely recovered during cooling. At 500 °C a change of the ambient gas from pure oxygen to 0.25% oxygen causes a release of 0.055 atom of oxygen and an expansion of ~200 ppm. Two diamagnetic transitions, a weak one at 81 K and a strong one at 70 K, are observed. The average thermal expansion between 25 and 800 °C is 13.2 ppm/°C in oxygen.

Introduction

Early reports on the $YBa_2Cu_4O_8$ high-temperature superconductor (124) suggested that it possesses a relatively high T_c (~81 K) and an oxygen stoichiometry nearly independent of temperature. This latter behavior was expected to present a major advantage over $YBa_2Cu_3O_7$ (123) since oxygen replacement would not be required after high-temperature processing. In the course of preparing samples of 124, we have found that the samples exhibit two diamagnetic transitions, a weak one at 81 K and a strong one near 70 K.[1] There is also a small but measurable oxygen stoichiometry variation with temperature. This report will characterize the oxygen stoichiometry of 124 material prepared by two different methods.

The structure of 124 is similar to 123 with a double CuO chain along the *b* axis instead of a single CuO chain. At atmospheric pressure, preparation of homogeneous 124 material is more difficult than that of 123 because the reaction to form 124 must be conducted at lower temperatures. The use of higher oxygen pressures permits higher synthesis temperatures and presumably should enhance homogeneity. Methods for preparing 124 can be categorized as high pressure[2-4] and atmospheric or low pressure.[5-7] Ceramic or powder samples, parepared at high pressure, show a strong diamagnetic transition at 80 K, but a single crystal, also prepared at high pressure, exhibited a sharp[8] transition at 71 K. Karpinski et al.[2] obtained powder samples whose neutron diffraction pattern showed a few weak impurity lines and whose TGA showed an irreversible weight loss of ~0.23% when heated to 770 °C for 50 h in oxygen. The samples of Morris et al.[3] showed small amounts of CuO, BaO, and 211 second phases, and smaller (0.08%) reversible weight loss was observed during heating to 800 °C in oxygen. A superconducting phase $Y_2Ba_4Cu_7O_{15-x}$ (247), which is formed at a higher temperature, was identified by X-ray diffraction (XRD); it showed a reversible oxygen loss of 0.3% when heated and had $T_c \simeq 50$ K. Miyatake et al.[4] prepared samples that were single phase by XRD and showed negligible weight loss during heating at 800 °C.

Syntheses at atmospheric or low pressure have yielded powder samples that have a strong diamagnetic transition at either ~70 or ~80 K. Cava et al. used alkali-metal carbonate mineralizers to prepare Y-,[5] Er-,[9] and Ho-124.[9] The Y material contained some second phases and had a T_c of 77 K, whereas the Er and Ho samples were single phase with the major transition near 70 K and a weak transition near 80 K. Balachandran et al.[6] used a partial vacuum at 750–800 °C to promote decomposition of $BaCO_3$ followed by heating at 800 °C in oxygen to effect synthesis of 124 powder. These samples show a diamagnetic $T_c \sim 80$ K and a weight loss (presumably reversible) of ~0.16 wt % during heating to 800 °C in oxygen. Pooke et al.[7] utilized a prereaction at 900 °C to form 123 followed by prolonged heating at 790–830 °C to yield 124. A second preparation scheme utilized alkali-metal nitrate as a fugitive mineralizer to enhance the rate of formation. Both methods yielded samples that were predominately single-phase 124 and had a $T_c \sim 80$ K. No data on oxygen stoichiometry were reported for the 124 compound, but it was observed that a 247 compound that formed at slightly higher temperature shows a large variation in oxygen content that affects its T_c. In summary, there is considerable disagreement on the T_c of the major diamagnetic transition in 124 and the extent of any oxygen loss during heating.

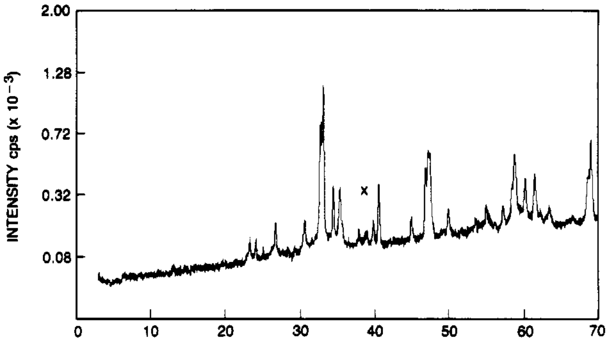

Figure 1. XRD pattern for $YBa_2Cu_4O_8$ prepared at 4 Torr of oxygen 800 °C and annealed in oxygen 800 °C. × indicates the CuO line.

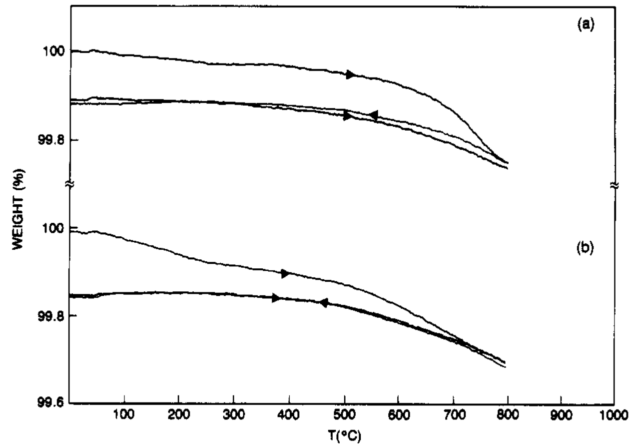

Figure 2. TGA for $YBa_2Cu_4O_8$ in oxygen, heating rate 5 °C/min: (a) type I; (b) type II.

Experimental Section

Two types of 124 powder were investigated. Both were synthesized at atmospheric or low pressure. Type I used 123 as a precursor to which a $CuNO_3$ solution was added.[10] Several heatings at 800 °C after regrinding and pressing for a 17-day total reaction period yielded 124. Type II samples were prepared from $BaCO_3$, Y_2O_3, and CuO by using the Balachandran method.[6] Prior to the initial heating, the raw materials were vibratory milled with ZrO_2 media under propanol for 16 h. [The authors are indebted to T. B. Lindemer, who directed them to the need for reducing the particle size of the CuO prior to the 124 reaction.] The milled powder had the following particle size distribution: 10 wt %, <0.8 μm; 50 wt %, <1.55 μm; <90 wt %, <2.8 μm. Spectrochemical analysis indicated that there was no measurable ZrO_2 pickup during milling (total ZrO_2 <0.003 wt %) and no impurities except Sr (~0.3%) above 0.1%. After heating at 800 °C for 1 h in 4 Torr of flowing oxygen and at 750 °C for 16 h in 1 atm of oxygen, the powders were reground and reacted at 800 °C in atmospheric oxygen for 20 h. XRD showed that after the partial vacuum treatment and 750 °C anneal, the powder was largely 124 with some CuO, $BaCuO_2$, and 123 phases. After the anneal at 800 °C in oxygen, XRD showed only 124 and slight CuO. Sintered bars were obtained by firing pressed powder at 825 or 850 °C in oxygen for 12 h. The XRD patterns for both types of material were identical, and Figure 1 shows one pattern.

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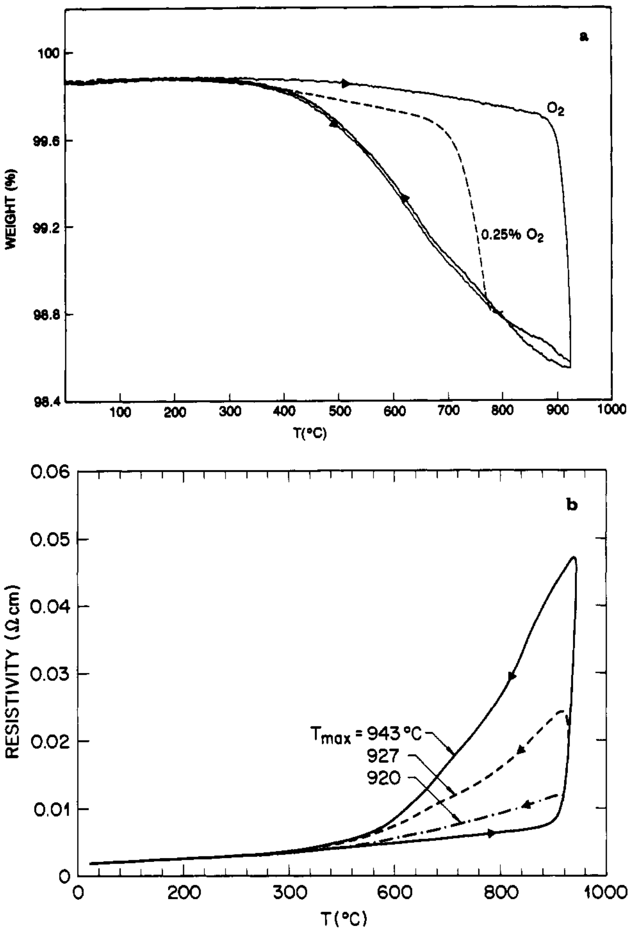

Figure 3. (a) TGA for $YBa_2Cu_4O_8$ starting material in oxygen (—) and 0.25% oxygen in nitrogen (---); the heating rate is 5 °C/min. (b) Electrical resistivity of 124 material on heating in oxygen to T_{max} = 920, 927, and 943 °C, and subsequent cooling to room temperature. Heating and cooling rates are 5 °C/min.

Thermogravimetric analyses (TGA) using an atmopshere of either pure oxygen or 0.25% oxygen in nitrogen were performed with a Perkin-Elmer TGA7 system. The samples were ~100-mg sintered bars, and heating and cooling rates were 5 °C/min. Isothermal gravimetry measurements were made at 500 °C on the same TGA system while the atmosphere was changed from pure oxygen to nitrogen with 0.25% oxygen. Since the large volume of the balance system required long purge times to change the atmosphere in the vicinity of the sample, the partial pressure in the exit gas was monitored with an oxygen monitor to verify that the purge was effective. Isothermal dilatometry using a Theta Research dilatometer was performed at 500 °C on sintered samples as the same atmospheres were switched. Electrical resistance measurements were performed on type I samples using as contacts 0.0025-cm-diameter Au wire embedded in the powder during compaction.

Results

TGA data in oxygen (flow rate 25 cm^3/min) are shown in Figure 2 for types I and II sintered samples. The samples were held 1 h at 800 °C before cooling. Both materials exhibit a small irreversible weight loss during the initial heating as well as a reversible weight change. For type I, the irreversible weight loss amounts to 0.09%, and the reversible portion is ~0.15%. When corrected for buoyancy, the reversible change amounts to ~0.075 oxygen atom per 124 molecule. The type II sample shows a larger irreversible weight loss (0.17%) but an equivalent reversible change (0.16% or 0.08 oxygen atom). Neither sample showed any weight change during the 800 °C hold. A faster heating rate (20 °C/min) produced an identical TGA for the reversible weight change. Isothermal gravimetric analysis showed that at 500 °C a 124 sample that had been equilibrated in flowing 0.25% oxygen in nitrogen gained 0.11 wt % when the atmopshere is changed to 100% oxygen. This weight gain was equivalent to 0.055 oxygen atom, and the weight change is reversible as long as the temperature does not exceed the temperature at which 124 decomposes into 123. Figure 3a shows that a large loss of oxygen (i.e., decomposition to 123 + CuO) begins near 875 °C in oxygen and 650 °C in 0.25% oxygen. The samples in oxygen were held at 925 °C for 45 min before cooling and reheating. It is seen that during cooling, the entire weight loss was recovered so that the sample weight returned to its original value. The electrical resistivity, Figure 3b, is observed to begin a steep rise at ~880 °C on heating, which becomes even more steep in the temperature range 920–950 °C. On subsequent cooling, the resistivity returns to lower values near ~500 °C.

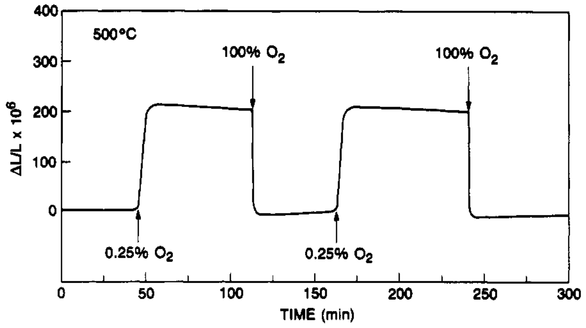

Figure 4. Isothermal expansion of $Ba_2YCu_4O_8$ at 500 °C as the atmosphere is switched between 100% oxygen and 0.25% oxygen at 500 °C.

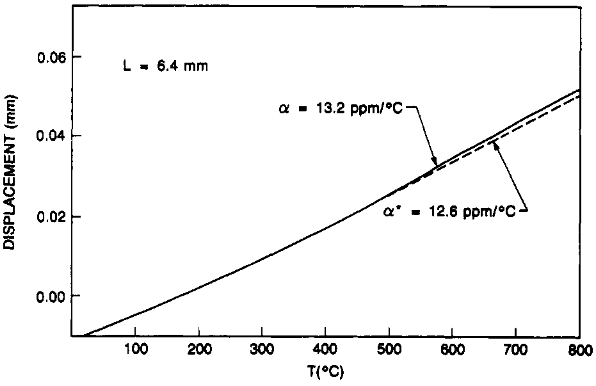

Figure 5. Thermal expansion of $YBa_2Cu_4O_8$ in oxygen, heating rate 5 °C/min. Expansion coefficients have been corrected for the contribution of the silica holder. α^* is calculated for constant oxygen content.

Small changes in oxygen content have been found to produce large dimensional changes in 123, $Pb_2Sr_2(Y,Ca)Cu_2O_8$, and Bi-2212 type ceramics.[11] The results of isothermal dilatometry while the sample atmosphere was switched between oxygen and 0.25% oxygen in nitrogen are shown in Figure 4 for 124. There is an expansion in low P_{O_2} and contraction in 100% oxygen with the amount of change being ~220 ppm for both samples. High-temperature XRD data taken to identify the lattice parameter change that causes this compositional expansion indicated only that the removal of oxygen increased the *c* axis. Data were not accurate enough to permit a quantitative measure. Figure 5 shows the thermal expansion in oxygen between 25 and 800 °C for 124. The data have been

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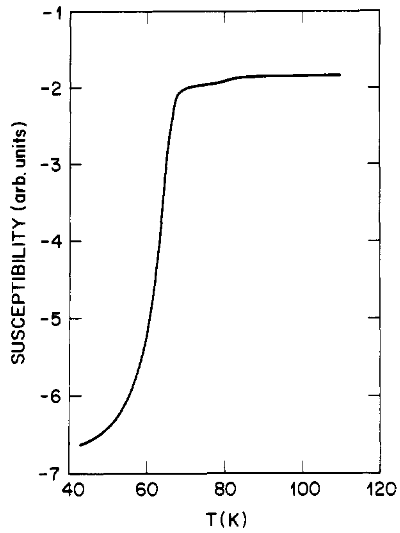

Figure 6. Susceptibility of type II sintered 124 as a function of temperature.

corrected for the contribution from the silica holder.

Discussion

In all respects, i.e., XRD, T_c, TGA, and dilatometry, the 124 specimens prepared by the two techniques are similar. No evidence of any 123 or 247 has been found, while the ac susceptibility measurements always showed a weak 81 K transition and a strong 70 K transition for slowly cooled samples (Figure 6). The irreversible weight losses observed during the initial heating are likely caused by adsorbed water and/or CO_2. The type II material not heated above 850 °C has a smaller grain size (~1 μm) than type I (~2 μm), and therefore its larger irreversible losses can be understood in terms of its greater surface area. Once either sample has been heated to 800 °C, no further irreversible weight change occurs as long as there is no contact with air. Cooling and reheating data (Figure 2) for both materials show the reproducibility and reversibility of the subsequent (0.16%) weight changes. At 500 °C, the expansion with atmospheric change is ~4000 ppm/oxygen atom for both materials. Therefore, for these two preparation methods there is no difference in T_c, phase formation, oxygen stoichiometry, or compositional/thermal expansion.

The reversible oxygen loss on heating to 800 °C in oxygen represents a variable oxygen stoichiometry. Although its magnitude (0.16 wt % or 0.08 atom of oxygen) is ~0.1% larger than observed by most other investigations, this probably represents the higher precision in our data of the TGA measurement rather than a sample difference. Balachandran[6] also obtained 0.16% weight change by heating to 800 °C.

The TGA and resistivity data in Figure 3 represent the effect of decomposition and oxygen unloading in accordance with the reactions

$$YBa_2Cu_4O_8 \rightarrow YBa_2Cu_3O_7 + CuO \quad (1)$$

$$YBa_2Cu_3O_7 \rightarrow YBa_2Cu_3O_{7-x} + (x/2)O_2 \quad (2)$$

As the temperature is raised above 875 °C, 123 forms. Since its equilibrium oxygen content ranges from $x = 0.61$ at 896 °C to $x \simeq 0.67$ at 925 °C,[12] a large weight loss is observed as this oxygen is unloaded. The rate of reaction 1 is slow compared to that of reaction 2, and oxygen unloading continues during the hold at 925 °C, but the cooling and reheating curves for 100% oxygen are identical.

An increase in resistivity accompanies the unloading of oxygen by the 123 phase. As the amount of 124 decreases (with successively higher T_{max}), the high-resistivity, oxygen-deficient 123 phase dominates the resistivity. On cooling, the 123 regains oxygen and the resistivity decrease is similar to the TGA curve. Measurement of the electrical resistivity as a function of temperature is therefore a useful monitor of the conversion from 124 to 123.

The cooling curve for the 100% oxygen TGA (Figure 3a) shows that all the oxygen unloaded during heating to and holding at 925 °C can be recovered. This is in agreement with the reverse of reaction 2 and means that the sample can recover its oxygen quickly. Earlier work[8] that showed a net 0.23% weight loss after heating to 770 °C and cooling is not understood.

The thermal expansion data in Figure 5 show an increase in the coefficient of expansion with temperature. Although this expansion appears to be caused only by temperature, there is actually a significant contribution from the compositional expansion that results from oxygen unloading. With the value of expansion/oxygen atom removed (~220/0.055 ppm) and the oxygen loss as a function of temperature from Figure 2, the expansion at constant oxygen content can be calculated, assuming that the expansion/oxygen atom removed is temperature independent. This expansion appears as the dotted line on Figure 6 and yields an average coefficient of 12.6 ppm/°C for 25–800 °C.

The reversible weight loss that occurs for 124 during heating to 800 °C in oxygen begins above 400 °C and is much smaller than for 123 (0.07–0.08 oxygen atom vs 0.505[12]). Although the accompanying compositional expansion for 124 is much smaller, it has the same sense as 123 (i.e., contraction in the more oxidizing atomosphere) and is about the same magnitude when normalized for the oxygen stoichiometry change (~4000/atom of O for 124 and for 123).[11] Thus, one might suspect that the 124 sample contains a significant amount of 123. A comparison of the relative effects of the weight and length changes would place the amount of 123 at 10–15%. Such an amount should have been observable by XRD and should have given a susceptibility response at 91 K. The absence of both effects indicates that if present, the 123 has a special form, perhaps an intergrowth. TEM has not been able to observe such intergrowths in the 124.[1] Therefore, it is unlikely that the oxygen stoichiometry variations are caused by 123.

Our earlier work,[1] which showed a strong dependence of T_c on quenching temperature, can be understood in terms of the variation of oxygen stoichiometry with temperature (Figure 2). This oxygen variation and the lower T_c as compared to 123 mitigate the potential processing advantage of 124. For the maximum T_c of 70 K samples must be fully oxygenated, i.e., the 0.08 oxygen atom evolved by heating to 800 °C must be returned to the structure.

Registry No. $YBa_2Cu_4O_8$, 114104-80-2.

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