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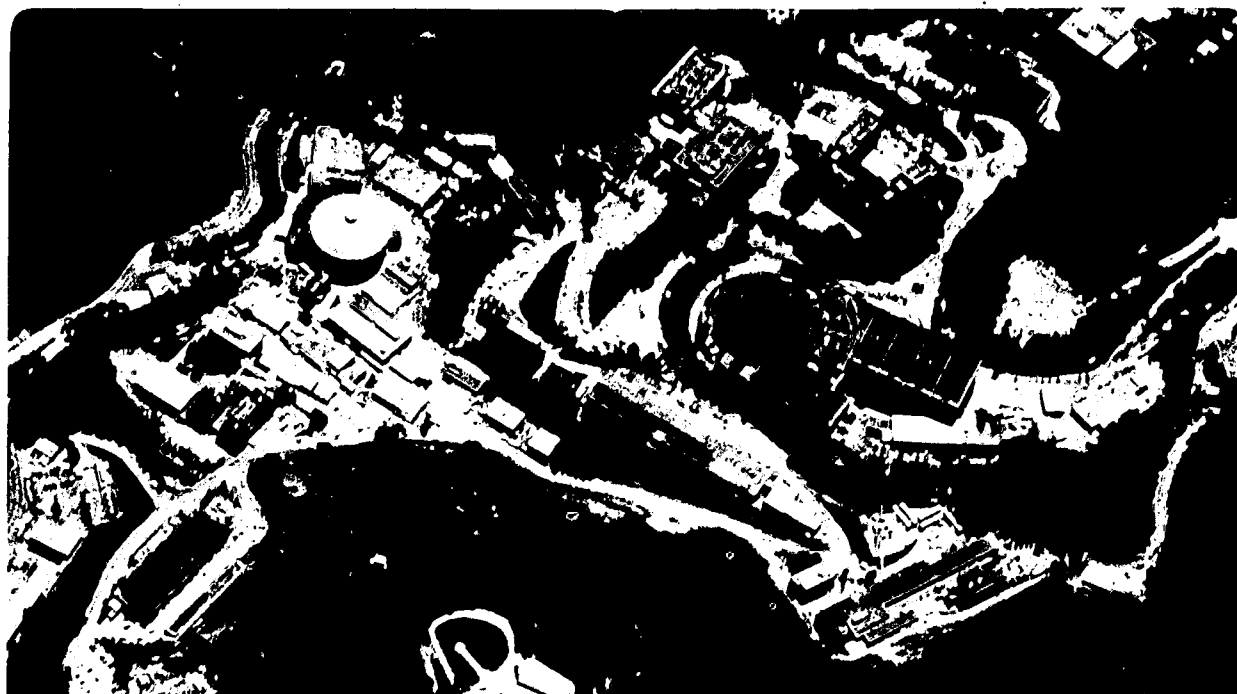
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D.E. Morris, N.G. Asmar, J.Y.T. Wei, and J.E. Post

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Stability of 124 and 247 superconductors

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Abstract

The 124 phase $\text{YBa}_2\text{Cu}_4\text{O}_8$ is synthesized by solid state reaction at $930\text{--}980^\circ\text{C}$ in $P(\text{O}_2) \geq 35$ atm. while the 123 phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is formed at $P(\text{O}_2) \leq 5$ atm. At intermediate $P(\text{O}_2)$ the 247 phase $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ is favored. In high $P(\text{O}_2)$, 124 is the only phase formed for a wide range of starting stoichiometries. When Dy or Ho (ionic radii close to Y) or Er (smaller) are substituted, the pressure ranges are similar. For the larger (lighter) rare earths Eu and Gd, higher pressures are required. Oxygen is more tightly bound in 124 than in 123, and slow cooling is not needed to optimize T_c . Oxygen is reversibly lost when 247 is heated, but much less than in 123. The T_c of 247 is 40-50 K, half that of 123 or 124. Synthesis of the 124 and 247 phases is relatively easy since very high oxygen pressures are not required; this may have considerable practical importance.

The 123, 124, and 247 phases of Y-Ba-Cu-O along with their rare earth analogues offer three isostructural families with incremental variations in lattice parameters and superconducting properties. For this reason, the rare earth 124 and 247 compounds may be helpful in testing theories of high temperature superconductivity. In earlier work⁶, we prepared the rare earth analogues $RBa_2Cu_4O_8$ ($R = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm$) with the 124 structure using high pressure oxygen $P(O_2) \approx 100$ atm. These compounds exhibit varying T_C 's correlated with the R ion radius and lattice parameters. We have now prepared the 247 rare earth analogues $R_2Ba_4Cu_7O_{15-x}$ ($R = Eu, Gd, Dy, Ho, Er$), using appropriate oxygen pressures.

The '124' superconductor $YBa_2Cu_4O_8$ has a more stable oxygen content than '123' ($YBa_2Cu_3O_{7-\delta}$), and its superconducting $T_C \approx 81$ K, is high enough to be useful. Its structure is similar to that of 123 but with a double Cu-O 'ribbon' in place of the single Cu-O chain^{1,2}. Unfortunately, 124 was difficult to synthesize, so it has not been studied extensively. It was first identified as an intergrowth³ in 123, and subsequently prepared as a distinct phase⁴ and as majority phase⁵ in epitaxial thin films. Recently, $YBa_2Cu_4O_8$ has been synthesized in bulk in pressurized oxygen^{6,7}, but very high oxygen pressure was thought to be necessary⁷. We have discovered that single phase 124 can be prepared at 930-980°C by the simple

solid state reaction method at moderate oxygen pressure, ~35 atm. There is no need for slow cooling or oxygen annealing of 124 to optimize its superconducting properties; this may have considerable practical importance.

124 is the only phase formed over a wide range of starting stoichiometries, when the oxygen pressure is sufficient. The 123 phase is stable only up to a few atm., and the '247' phase $Y_2Ba_4Cu_7O_{15-x}$ is favored at intermediate pressures. 247, which consists of 123 and 124 blocks alternating along the *c* axis, was also considered difficult to synthesize in bulk^{6,8,9}. This phase is also a superconductor, but surprisingly, $T_C \approx 40-50$ K, much lower than for 123 ($T_C \approx 93$ K) or 124 ($T_C \approx 81$ K). When rare earths are substituted for yttrium, the pressure ranges for the different phases shift somewhat. We have investigated synthesis conditions of all three phases in the *R*-Ba-Cu-O (*R* = Y, Eu, Gd, Dy, Ho, Er) systems, by varying $P(O_2)$ and starting stoichiometry. It has been reported⁷ that the 123 phase $YBa_2Cu_3O_{7-\delta}$ is stable up to ~200 atm., with the 124 and 247 phases co-existing at higher pressures. Our results show that this is not the case.

Samples were prepared by solid state reaction of Y_2O_3 or a rare earth oxide R_2O_3 (*R* = Nd, Sm, Eu, Gd, Er, Dy, Ho, Er, or Tm) (all 99.9%), with BaO(99.99%) and CuO(99.99%). In the first series of experiments, starting stoichiometry (cation ratio) was 1:2:4. All ingredients were fine powders (-325 mesh), which were ground

together in a mortar and pestle and pressed into 6 mm tablets at 3500 kg/cm². The samples were wrapped individually in Au foil and calcined for 8 hr in O₂ at pressures between 4 and 100 bar (1 bar ... 0.1 Mpa = 0.987 atm) in a commercially available externally heated high pressure oxygen furnace¹⁰. The calcining temperature was 930°C or 980°C, followed by slow cooling¹¹ to room temperature. Each sample was then re-ground, pressed and fired under the same conditions to maximize homogeneity.

The samples were examined by X-ray powder diffraction (XRD). The patterns (Fig. 1) indicated that in addition to one or more of the superconducting phases, most samples contained some CuO and BaO, as well as small quantities of the 'green phase' R₂BaCuO₅. The three superconducting phases were distinguished by their characteristic low angle powder diffraction peaks. The [0 0 2] peak of the 124 phase is found at d spacing ≈ 13.6 Å, clearly distinct from the position of the [0 0 1] peak of 123 at 11.7 Å and the [0 0 4] peak of 247 at 12.55 Å (Fig 2 and Ref 6). This method is quite sensitive, because the low angle reflections from the rare earth compounds are quite strong.

The preliminary phase diagram determined from the XRD studies is given in Figure 3. We find that the 123 phase in the Y-Ba-Cu-O system is stable only up to a few atm. At high pressure (> 30 bar) the stable phase is 124, while 247 is formed at intermediate

pressure. A similar pattern is found in the rare earth substituted systems, but the ranges of pressure over which the 123, 247, or 124 phase are formed depend on the radius of the R ion. In the Dy and Ho systems the pressure ranges correspond closely to those of the Y system. These three ions have nearly the same radii and their 124 and 247 compounds have nearly the same lattice parameters⁶. The T_C 's of their 124 phases are also similar⁶. The lighter rare earth ions (with larger radii) require somewhat higher pressures for synthesis of 247 and of 124. This accounts for our inability to synthesize single phase $\text{EuBa}_2\text{Cu}_4\text{O}_8$ and $\text{GdBa}_2\text{Cu}_4\text{O}_8$ at 100 bar (Fig 3 and Ref 6). When the $P(\text{O}_2)$ is not optimal for 247, ordering of the alternating 123 and 124 blocks is imperfect. The disorder is indicated by broadening of the low angle XRD peak (Fig 2b). Samples which contained two phases according to XRD (Fig 2d) showed two transitions, giving 'stepped' susceptibility curves (Fig 4e).

The orthorhombic distortion in 124 is smaller⁶ than in 123, and we find that it is still smaller in the 247 compounds. The distortion varies inversely with rare earth ion radius in 247 compounds in the same manner as in 124 and 123. The T_C of the 247 compounds also varies inversely with rare earth radius, as found earlier for the 124 series⁶. Details will be published elsewhere¹².

Superconducting diamagnetic transitions were measured on a SQUID magnetometer in fields of 3-8 oe. Y-Ba-Cu-O samples containing 123

exhibited Meissner flux expulsion at 93K, as opposed to 81 K for those containing 124. Our value of $T_c \approx 40-50$ K for the slow cooled¹⁰ 247 compound agrees with Ref 7, but not with the value ~ 86 K given in Ref 9 for the resistive transition of an oxidized ribbon of metallic precursors. Some 123 or 124 in their samples may have been responsible.

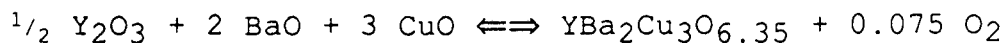
The oxygen in 124 is more tightly bound than in 123 (Refs 6 and 7). No reversible weight loss was observed upon heating $YBa_2Cu_4O_8$ at $50^\circ\text{C}/\text{min}$ in a Perkin-Elmer TG-7 thermogravimetric analyzer to $\sim 800^\circ\text{C}$ in 1 atm O_2 (Fig 5), demonstrating that the 'ribbon' oxygen in 124 is more tightly bound than is the 'chain' oxygen in 123. However, heating to higher temperatures caused irreversible loss. A sample of 124 which was quenched from $\sim 950^\circ\text{C}$ to 100°C within 5 minutes showed T_c and transition width substantially the same as for slow cooled samples (Fig 4), confirming that cooling rate is not critical for the 124 phase, in contrast to 123.

A second series of experiments, in which the starting cation ratio was varied over a wide range, showed that only the 124 phase is formed at $P(O_2) = 100$ atm. The synthesis temperature was 930°C . With Y:Ba:Cu ratios of 1:2:3, 1:2:3.5, 1:2:4, and 1:2:5, the 124 phase alone, without 123 or 247, was detected by low angle XRD. At still greater CuO content (1:2:6), and in samples richer in Ba (Y:Ba:Cu ratios 1:3:4, 1:3:5, 1:3:6), no low angle peaks appeared.

These experiments indicate that 124 is the stable phase in high $P(O_2)$ over a considerable range of starting compositions.

It is worth noting that all these cation ratios (except 1:2:3) lie within the "region of partial melting" shown in Ref 13 for the Y_2O_3 -Ba-CuO phase diagram at 950-1000°C and one atm. An attempt was made to grow single crystals of 1-2-4 by a melt-reaction of a Cu-O rich mixture. The Y:Ba:Cu starting stoichiometry was 2:6:15. After reacting at 980°C and 70 bar for 24 h and slow cooling at 3°C/h to 900°C, no melting or crystal growth was observed. To explore this further, Y-Ba-Cu-O with 1:2:4 cation ratio was reacted in $P(O_2) = 100$ bar at 1000°C. Again, no melting was seen.

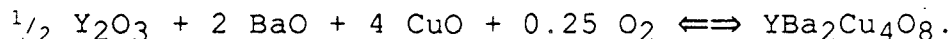
With the above information it is easy to understand why the 124 phase is more stable than 123 in high pressure oxygen at elevated temperatures ($T \approx 900$ -1000°C), and the reverse is true at lower oxygen pressures. As is well known, 123 loses oxygen rapidly and reversibly upon heating above ~400°C (Ref 14 and Fig 5). At synthesis temperature $T \approx 950$ °C in 1 atm oxygen, the stoichiometry is about $YBa_2Cu_3O_{6.35}$ (Ref 15). Therefore, the synthesis reaction is:



and oxygen is evolved during the synthesis. When the compound is slowly cooled after synthesis, it absorbs ~0.3 O_2 from its

surroundings to form $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$, the well known 123 superconductor. If the compound is quenched from synthesis temperature, the oxygen content will remain low, yielding the non-superconducting semiconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.35}$. In retrospect, the momentous discovery¹⁶ of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ was made because of the extraordinarily high oxygen diffusivity¹⁴, which enabled the semiconducting compound to oxidize during cooling.

In contrast, when synthesis is carried out under $P(\text{O}_2) > 30$ bar, the reaction proceeds as:



We see that oxygen is taken up during the synthesis, and the 124 compound is fully oxidized during formation. The thermodynamic stability of 124 under these conditions is indicated by the fact that it forms in preference to 123 even when the starting cation ratio is 1:2:3.

At lower temperatures, the difference in oxygen content of 123 and 124 (compared to their constituent oxides) is smaller and the oxygen pressure required to stabilize the 1-2-4 phase should be lower. Furthermore, diffusion of the cations is much slower than the oxygen. This may explain the formation of 1-2-4 in thin films prepared with the appropriate stoichiometry and processed at lower

temperatures^{4,5}. At still lower temperature (<400°C) the excess oxygen content of both 123 and 124 is the same (relative to their constituent oxides), and it is not clear at present which compound is thermodynamically more stable at ambient temperature and pressure.

The stability of 247 at intermediate oxygen pressures can also be understood. Only the oxygen in the single chains in the 123 blocks is expected to be weakly bound, while the oxygen in the 1-2-4 blocks will be more tightly bound. Consequently, the oxygen loss on heating 247 should be only about half that of the 123 compound at the same temperature and oxygen partial pressure. Therefore, the oxygen content of 247 at high temperatures should be intermediate between that of 123 and 124. This was confirmed by TGA measurements (Figure 5) which showed a reversible oxygen loss from $Y_2Ba_4Cu_7O_{15-x}$ which is much smaller than for $YBa_2Cu_3O_{7-\delta}$, which is shown for comparison.

The 124 superconductor may be technologically useful because of its greater thermal stability. Since no oxygen is lost or gained during heating or cooling, the thermal expansion parameters should be better behaved than 123, and no tetragonal-orthorhombic phase transition is expected during cooling from synthesis temperature. The orthorhombic distortion of 124 is only half that of 123 (Ref 6), which may also be helpful in minimizing thermal stresses.

It is well known that when 123 is processed above ~940°C in one

atm O_2 , non-superconducting phases form at the grain boundaries¹⁷. This is a handicap in producing high density ceramic 123, since the sintering temperature cannot be increased. Note that the 123 compound at $T \geq 950^\circ C$ and $P(O_2) = 1$ atm contains less oxygen than do the green phase Y_2BaCuO_5 and other decomposition products of 123 (e.g. $BaCuO_2$). One might attempt to stabilize the 123 phase up to higher temperatures by heating in high $P(O_2)$ to increase the oxygen content to above 6.5, which is higher than that of the decomposition products. Unfortunately, our results show that the 123 phase is not stable under those conditions and will gradually convert into 124. The inhibition of melting in elevated $P(O_2)$ (see above) will prevent densification by liquid phase sintering. However, it may be possible to prepare dense 124 material with enhanced J_c by sintering in high $P(O_2)$ at significantly higher temperatures.

Another technique for making high density ceramic material is hot isostatic pressing (HIP). If 123 is synthesized, sealed in an Ag, Au or Pt container and HIPed, a large internal oxygen pressure will develop as the compound loses oxygen, and the 123 will convert slowly to 124 plus excess Yttrium and Barium oxides. Then the oxygen pressure inside the sample container will fall to a value (~ 5-30 bar) just sufficient to sustain the stability of the 124 phase, which has absorbed the rest of the oxygen released from the 123 compound. A more practical procedure would be to prepare 124, and then HIP it. The conversion of 124 into 123 will be stopped by the

rising internal O_2 pressure.

The most important use for the 124 compound may be as a precursor for preparation of 123. After synthesis of single phase 124, and high temperature processing for densification, subsequent thermal treatment in air or vacuum would remove enough oxygen to cause the 124 to convert into 123 plus excess CuO , which may migrate to the grain boundaries. However, the diffusion of the cations is much slower than of the oxygen, so if the low $P(O_2)$ treatment is done at low temperature, or for a short time, the Cu will not reach the grain boundaries, but will be left within the 123 grains as CuO 'islands'. These intragranular non-superconducting islands may be effective as flux pinning centers to increase J_c .

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Figure captions

Fig. 1. X-ray powder diffraction patterns for the 124 and 247 phases in the Dy-Ba-Cu-O system. Each pattern shows a single phase, except for additional peaks identified as CuO.

Fig 2. Low angle X-ray powder diffraction curves taken with Cu $k\alpha$ radiation: (a) Dy-Ba-Cu-O synthesized in 34 bar O_2 ; the peak at d spacing = 13.6 Å indicates the 124 phase. (b) Dy-Ba-Cu-O synthesized in 17 bar O_2 ; the peak at 12.55 Å indicates the 247 phase. (c) Dy-Ba-Cu-O synthesized in 5 bar O_2 ; the peak at 11.7 Å indicates the 123 phase. (d) Eu-Ba-Cu-O processed in 100 bar O_2 . The two peaks at 13.6 Å and 12.55 Å indicate that the sample contains both 124 and 247 phases. Note the broadening of the 12.55 Å peak, indicating imperfect order in the sequence of alternating 123 and 124 layers or presence of extra 123 or 124 layers.

Fig. 3. Pressure ranges for thermodynamic stability of the 123, 247, and 124 phases: $RBa_2Cu_3O_{7-\delta}$, $R_2Ba_4Cu_7O_{15-x}$, and $RBa_2Cu_4O_8$ ($R = Y, Eu, Gd, Dy, Ho, Er$) at 930-980°C, as determined from the position of the low angle X-ray peak. For each rare earth system, the phases present are indicated as a function of oxygen pressure during synthesis. The fraction of each phase between 0 and 1.0 is plotted on the vertical axis. In all cases, the 123 phase is stable up to 5-15 bar, the 124 phase is stable above 35-200 bar

depending on the R ion radius, and the 247 phase is stable at intermediate oxygen pressures.

Fig. 4. Meissner flux expulsion curves for (a) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, (b) $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$, and (c) $\text{YBa}_2\text{Cu}_4\text{O}_8$, all slow cooled. Curve (d) is for $\text{YBa}_2\text{Cu}_4\text{O}_8$ synthesized under the same conditions as (c) ($T = 980^\circ\text{C}$, $P[\text{O}_2] = 70 \text{ atm}$), but rapidly cooled in $\sim 5 \text{ min}$ to 100°C ; the T_c was unaffected. Curve (e) is for a Eu-Ba-Cu-O sample processed at 34 bar. Note the two 'steps' at $\sim 37 \text{ K}$ and $\sim 60 \text{ K}$. Meissner curves for $\text{RBa}_2\text{Cu}_4\text{O}_8$ ($R = \text{Nd, Sm, Eu, Gd, Dy, Ho, Er}$) were published in Ref 6, and curves for $\text{R}_2\text{Ba}_4\text{Cu}_8\text{O}_{15-x}$ ($R = \text{Y, Eu, Gd, Dy, Ho, Er}$) are given in Ref 12.

Fig 5. Thermogravimetric (oxygen loss) curves for 124, 123, and 247 phases of Y-Ba-Cu-O up to 800°C . Heating and cooling rates were 30 deg/min . (a) $\text{YBa}_2\text{Cu}_4\text{O}_8$ - oxygen content remains nearly constant, with a small irreversible weight loss at high temp. (b) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ - oxygen loss is large and nearly reversible. (c) $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-x}$ - oxygen loss at 800°C is much smaller than for 123, and is partially reversible. The oxygen loss appears to begin at a higher temperature ($\sim 500^\circ\text{C}$) than in 123 ($\sim 400^\circ\text{C}$).

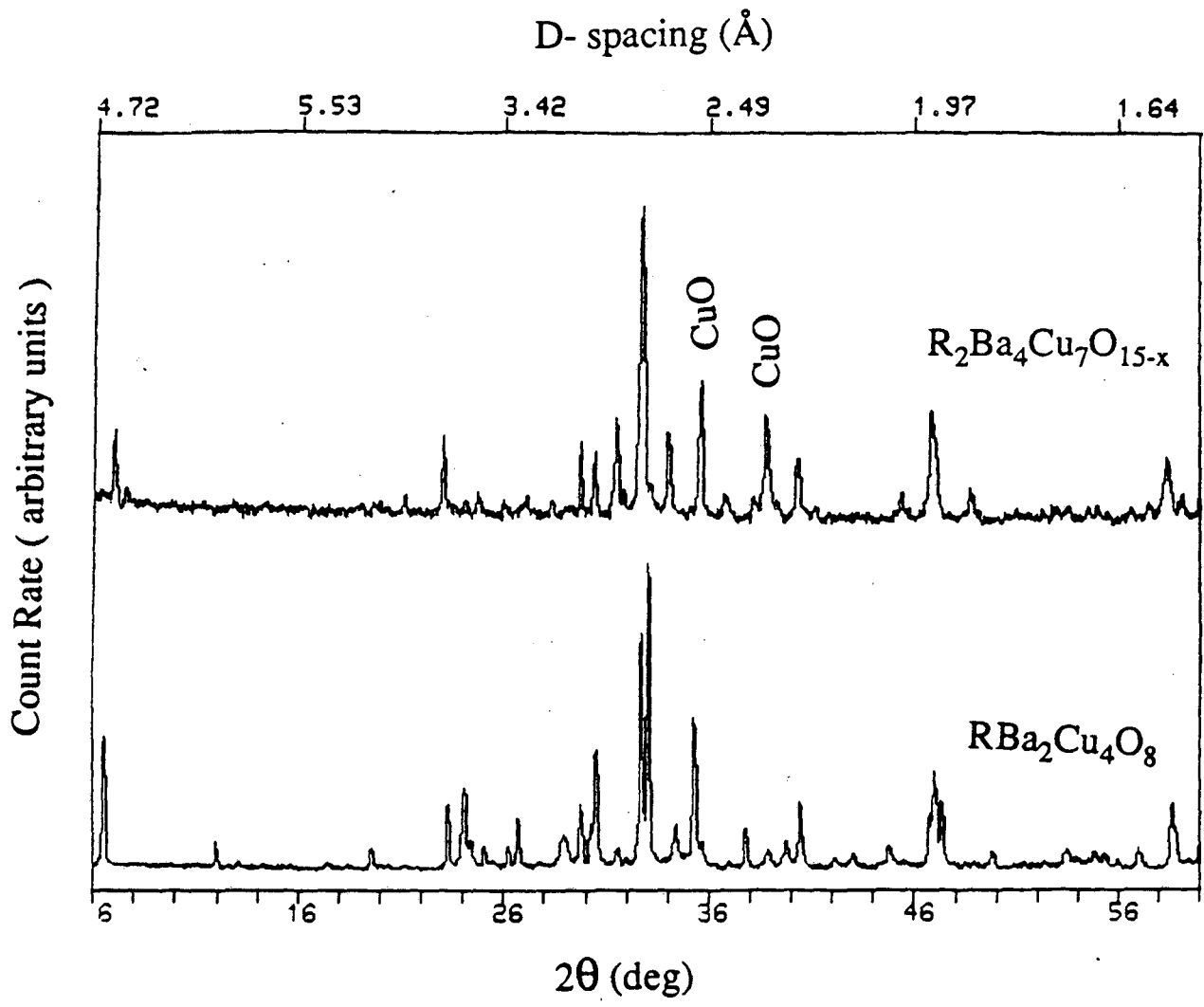


Fig. 1

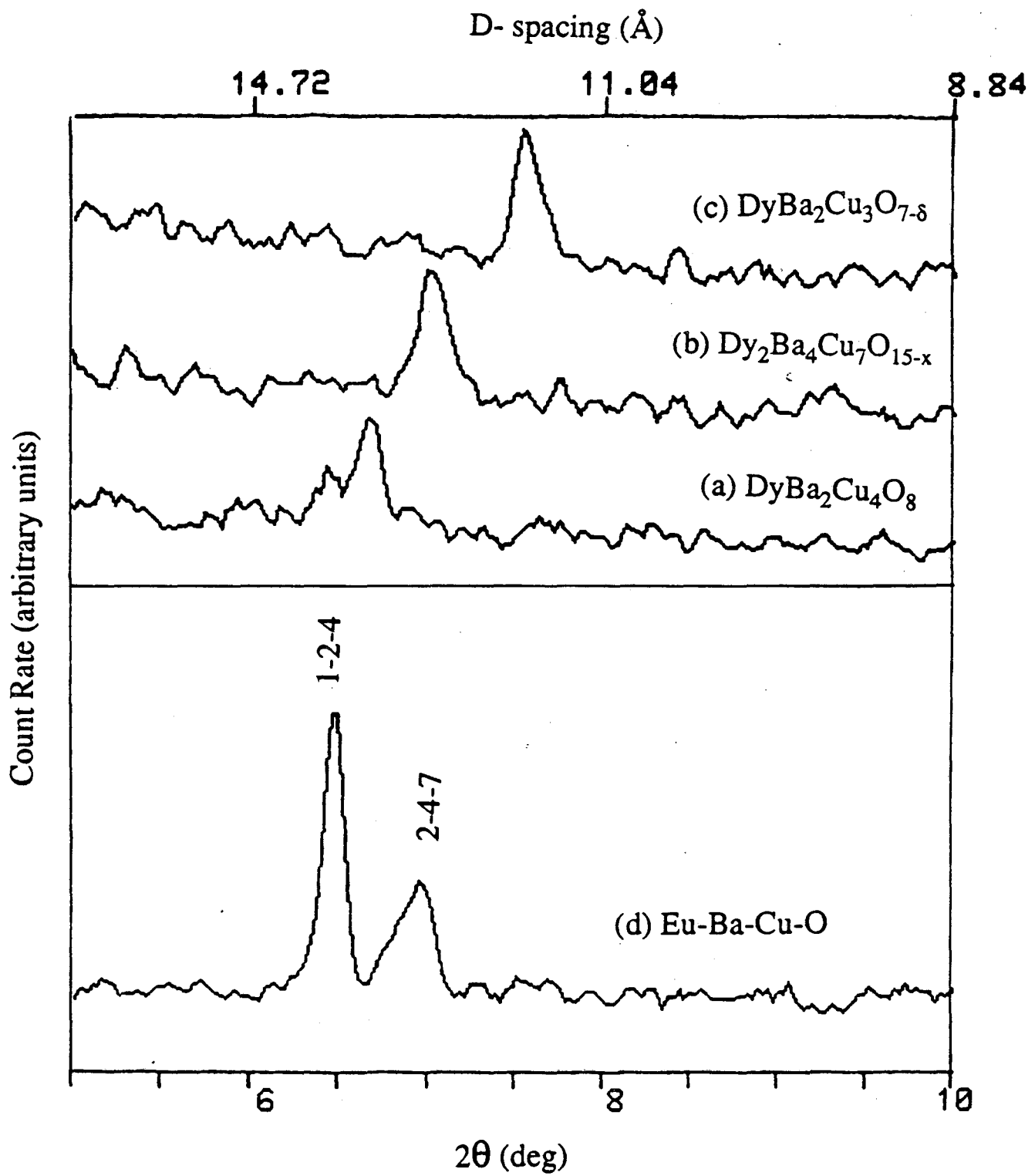


Figure 2

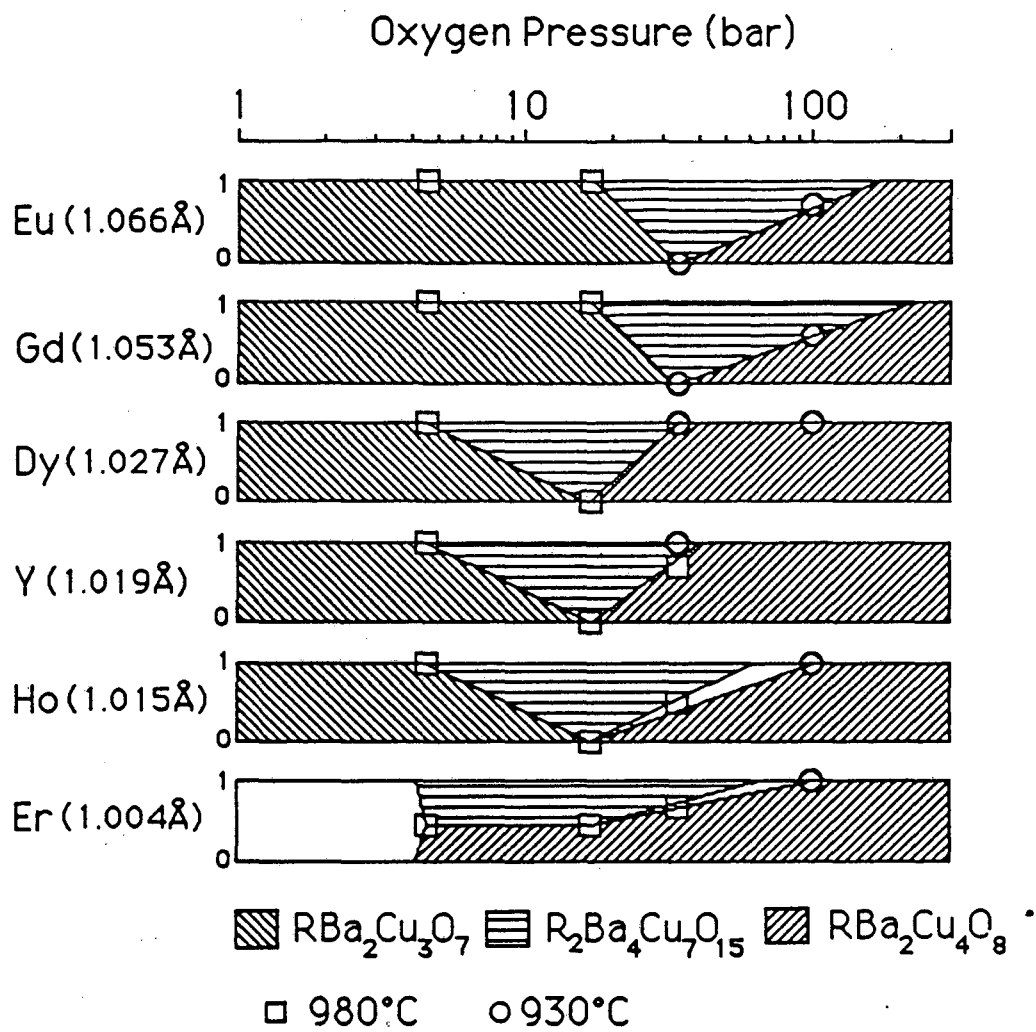


Fig. 3

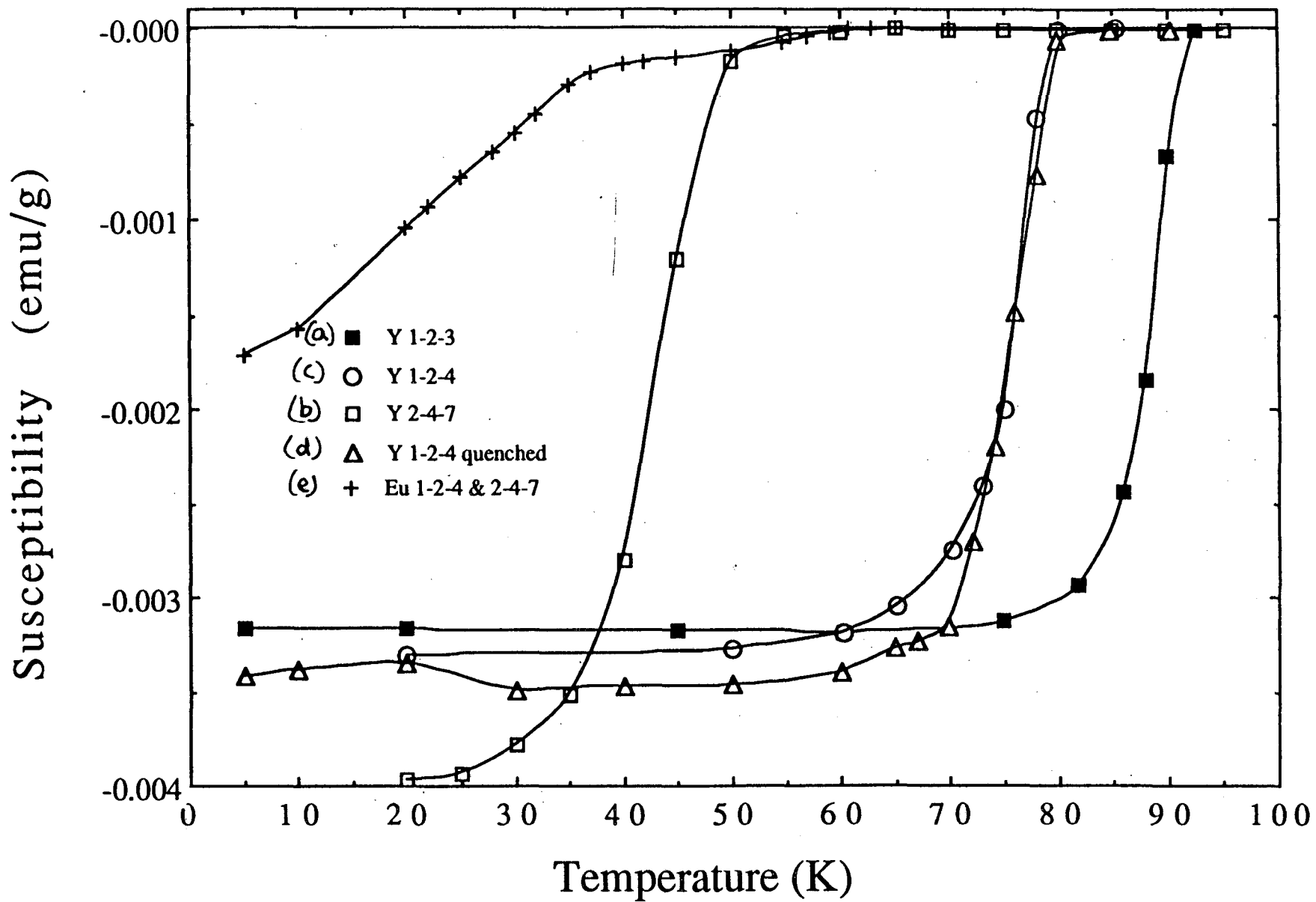


Figure 4

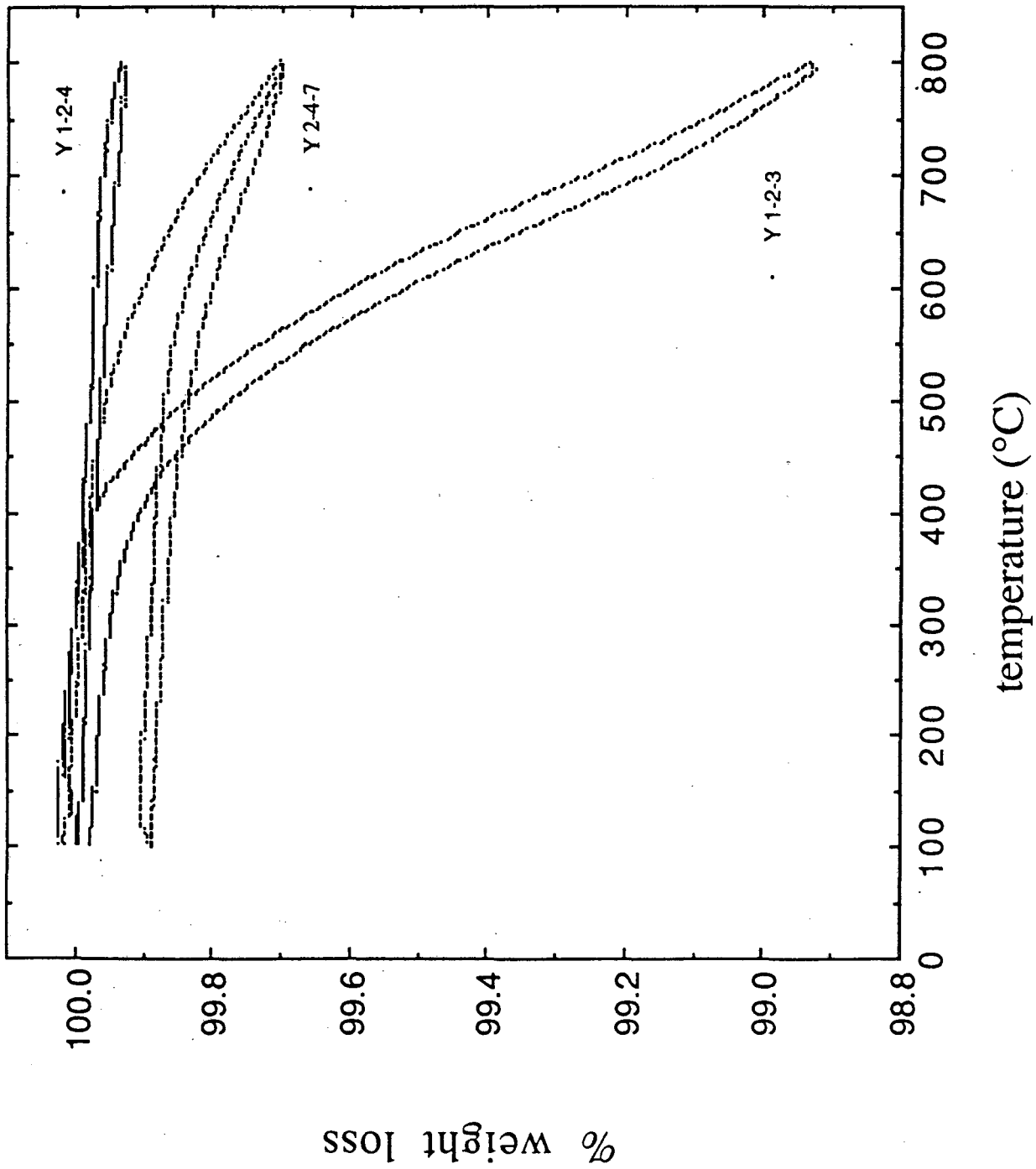


Figure 5

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