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THE THERMAL STABILITY OF $RBa_{2-x}K_xCu_3O_z$ (R = Y and Eu)

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ABSTRACT

The thermal stability of ceramic compounds $RBa_2Cu_3O_z$ R=Y and Eu where Ba^{++} is replaced by K^+ is investigated here by TG analysis. The release of oxygen in $RBaKCu_3O_z$ compounds starts at about 700°C, which is much higher than for undoped samples. Two major steps in the TG curves are observed for $RBa_{1.5}K_{0.5}Cu_3O_z$ samples, corresponding to the oxygen-release temperatures of undoped and doped samples, respectively.

INTRODUCTION

Many experimental studies of superconductivity in $YBa_2Cu_3O_z$ have investigated the effects of substituting different ions at various sites in the lattice. In recent studies [1-2] we substituted monovalent K^+ for divalent Ba^{2+}; they have similar ionic radii, 1.33Å and 1.35Å, respectively. In most cases the introduction of impurity atoms other than rare earths into the $YBa_2Cu_3O_z$ lattice drastically reduces T_c and shifts the crystal symmetry from orthorhombic to tetragonal[3]. In the case of $YBa_2Cu_3O_z$, up to 50% of the Ba has been replaced by K without noticeably affecting T_c, crystal symmetry, or lattice parameters. On the other hand, the $EuBa_{2-x}K_xCu_3O_z$ system behaves quite differently. A progressive decrease in T_c is observed with increasing K^+ concentration (Table 1), leading ultimately to a non-superconducting compound, $EuBaKCu_3O_z$. X-ray powder diffraction showed[2] all these samples to be single-phase with an orthorhombic unit cell for pure $EuBa_2Cu_3O_z$, whereas a tetragonal structure is induced in the K^+ doped samples.

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In the present paper it is shown that, although the superconducting behavior of $RBa_{2-x}K_xCu_3O_z$ systems differs for R=Y and R=Eu, the thermal stability patterns for both systems are quite similar. It is evident that both $RBaKCu_3O_z$ compounds are much more stable than the corresponding $RBa_2Cu_3O_z$ compounds. In the undoped systems oxygen loss starts at 450-500°C, while in the K-doped systems oxygen is not released below about 700°C. At intermediate concentrations two major steps are observed in the TG curves.

EXPERIMENTAL DETAILS

Experimental details concerning sample preparation and susceptibility measurements to determine T_c are given in ref. 2. Thermogravimetry in a reducing atmosphere was carried out with a Mettler Thermal Analyzer at a constant temperature increment rate of 10°C/min.

RESULTS AND DISCUSSION

The oxygen weight losses of some samples investigated are shown in Figs. 1 and 2. The TG curves obtained for undoped $YBa_2Cu_3O_z$ and $EuBa_2Cu_3O_z$ (not shown) are similar to curves reported by others[4-6]. On exposure to the laboratory environment some water is absorbed, causing the slight decrease in weight observed at low temperatures. Oxygen begins to be liberated in significant quantities at about 450°C, indicated by a weight loss of 1.6% at the first step of the $YBa_2Cu_3O_z$ curve (Fig. 1), corresponding to a loss of 0.66 oxygen atoms per formula unit (Table 1). Progressive weight loss continued up to 800°C, resulting in a nonsuperconducting phase.

For the $RBaKCu_3O_z$ compounds, the thermal stability behavior is quite different. Beside the slight decrease in weight observed at low temperatures, no weight loss is observed for either sample up to 600°C (Fig. 1-2). A minor step in the curves is observed at 700° and 760° for R=Y and Eu, respectively. Most of the oxygen is released at 810° and 860°C, respectively (Table 1). It is worth noting that no weight loss is observed in any of the $RBaKCu_3O_z$ samples at 450-500°C, independent of whether the sample is superconducting - ($YBaKCu_3O_z$) or not ($EuBaKCu_3O_z$). In the intermediate composition

TABLE 1

Lattice parameters, T_c and thermal stability data for $RBa_{2-x}K_xCu_3O_z$ compounds.

	a(Å)	b(Å)	c(Å)	T_c(K)	oxygen weight loss T°(C)	% atom	T°(C)	% atom
$YBa_2Cu_3O_z$	3.822	3.891	11.67	90	450	0.66		
$YBa_{1.5}K_{0.5}Cu_3O_z$	3.826	3.893	11.67	90	450	0.25	800	0.25
$YBaKCu_3O_z$	3.835	3.889	11.64	88	600	0.11	810	0.78
$EuBa_{1.5}K_{0.5}Cu_3O_z$	3.863		11.59	64	520	0.33	820	0.58
$EuBaKCu_3O_z$	3.859		11.67	-	760	0.12	860	0.95

$RBa_{1.5}K_{0.5}Cu_3O_z$ two major steps in the TG diagrams are observed: the first at about 450-520 °C, corresponding to about 0.3 oxygen atoms per unit cell; and the second, at about 800°C, at which an additional oxygen is released. The total weight loss represents less than one oxygen atom per unit cell. Note

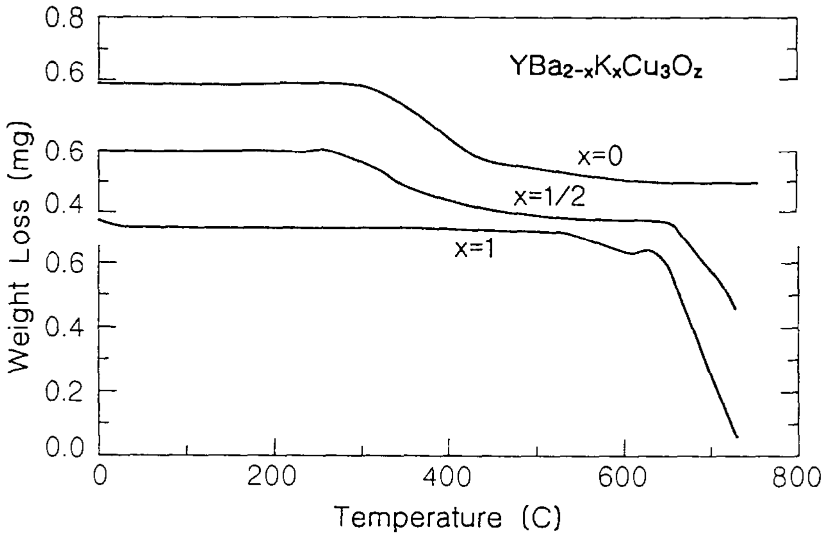

Fig. 1 Thermogravimetric curves or $YBa_{2-x}K_xCu_3O_z$ compounds.

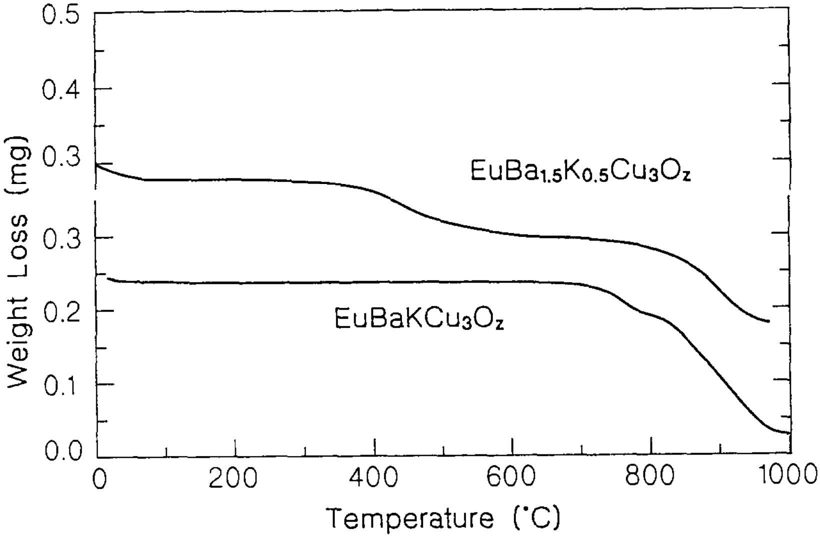

Fig. 2 Thermogravimetric curves of $EuBa_{2-x}K_xCu_3O_z$ compounds.

that both steps occur in the same temperature ranges as those of the $RBa_2Cu_3O_z$ and $RBaKCu_3O_z$ systems mentioned above.

In a previous paper[2] it was shown that in the $RBa_{2-x}K_xCu_3O_z$ system a single-phase structure persists up to x=1. Above this concentration a multi-phase system is observed. Our conclusion is that in the orthorhombic $RBa_2Cu_3O_z$ unit cell, which contains two equivalent Ba sites, it is possible to replace only one Ba ion with K. It thus appears that the thermal stability of the oxygen depends on whether the unit cell contains K or not. In the pure system oxygen from the Cu-O chains along the b-axis begins to be liberated when heated to above 450°C. This oxygen atom is surrounded only by Cu and Ba atoms. On the other hand, in $RBaKCu_3O_z$ each unit cell contains one K^+ ion, so that oxygen in the chains is surrounded by K ions as well. Apparently the $RBa_{1.5}K_{0.5}Cu_3O_z$ system has two distinct kinds of unit cell, one containing K ions, the other without them: in unit cells which do not contain K^+, oxygen is released at 450-500°C, as in the pure $RBa_2Cu_3O_z$ system; the second major weight loss, at about 800°, is related to those unit cells in which Ba^{++} is replaced by K^+ ions. Note that the amount of oxygen released at each step is the same in the case of R=Y. As Ba^{++} is substituted for K^+ in $RBa_2Cu_3O_z$, charge compensation may be achieved either by reducing the formal oxygen valence to O^-, or by decreasing the oxygen content, or by a combination of both. The greater thermal stability of the samples containing K does not in itself resolve this dilemma, and more research is needed.

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