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Thermochemistry of $YBa_2Cu_{3-x}M_xO_y$ (M = Ni, Zn)

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Abstract

The partial molar enthalpy of incorporation of oxygen (ΔH_{ox}) and enthalpy of formation from the oxides (ΔH_f) have been measured via high-temperature reaction calorimetry for $YBa_2Cu_{3-x}M_xO_y$ (where M = Ni, Zn) in the composition range $0.0 < x < 0.18$. ΔH_{ox} and ΔH_f values were nearly independent of dopant for both Ni and Zn, with enthalpies of oxidation in the range of -86 to -110 kJ/mol $\frac{1}{2}O_2$ and enthalpies of formation in the range of -110 to -118 kJ/mol. The independence of thermodynamic behavior from superconducting properties is consistent with an electronic mechanism for T_c suppression in Zn doped YBCO superconductors. Oxygen contents, lattice parameters, and T_c measurements are also reported.

Introduction

Many studies have investigated the behavior of transition metal dopants in the $YBa_2Cu_3O_{7-\delta}$ "123" superconductors [1-8]. Much of this research has focused on the effects of metal ions such as Co, Fe, Zn, Ni when they are substituted for the copper ions at Cu(1) and Cu(2) sites, commonly referred to as the chain and plane sites, respectively. Trivalent ions such as Co^{+3} and Fe^{+3} have been shown to behave similarly in their substitution effects, displaying site preference on the Cu(1) site [3-8]. This site preference has been established with the use of techniques such as neutron diffraction and Mossbauer spectroscopy [4,5]. Thermogravimetry, electron diffraction, and analysis of lattice parameters as a function of dopant also yield results consistent with those of the structural studies with respect to the chain site preference of both Co and Fe [3,4,6-8]. The very fast convergence of **a** and **b** lattice parameters to that of the tetragonal structure, occurring at x = 0.3 Co dopant (i.e. $YBa_2Cu_{2.7}Co_{0.3}O_{7-\delta}$) for high-oxygen-content samples, coupled with information derived from diffuse scattering and oxidation behavior of these samples, has been described in detail by several authors in terms of the Co and Fe ions creating "microchains" at Cu(1) sites within the 123 compound [4,7-8]. The Cu(1) site dopants decrease T_c at a rate of 2 to 5 K/at. %, varying to some extent with site preference [4,9].

Both Ni and Zn appear to substitute in the 123 structure, but in marked contrast to Co and Fe. When Ni and Zn cations are substituted for Cu, they apparently have a site preference for the plane site and maintain an orthorhombic structure even at the highest solubility levels (i.e. x= 0.2) in high oxygen content samples [1-3,9]. This is an apparent site preference since there is general consensus in the literature that Zn and Ni prefer the Cu(2) plane site, but directly measuring the dopant site location is exceedingly challenging [10-18]. The considerable difficulty in studying the site locations of the dopants is due to their low concentration and the similarity in scattering factors for Cu, Ni and Zn. It is notable that the solubility of Ni and Zn within the 123 phase is substantially lower than that of Co and Fe. This implies a different behavior for Zn and Ni dopants (compared to Co and Fe) and lends support to the likelihood of different site preference for the (2+) vs (3+) cations.

Several authors [19-21] have published enthalpies of solution in molton oxide solvents for the undoped $YBa_2Cu_3O_y$ as a function of oxygen content. These studies indicated that the enthalpy was not affected (by more than 2-4 kJ/mol) by the tetragonal/orthorhombic phase transition and that enthalpies of oxidation changed linearly with oxygen content, implying a constant partial molar enthalpy of oxygen incorporation. With this observation in mind, study of doped 123 samples is a logical extension of the previous work. In this way, it would be possible to test whether or not the energetics of oxygen in the 123 superconductor structure was significantly affected by the presence of the Zn and Ni dopant.

The anomalously large decrease of T_c by Zn doping (normally greater than 10 K/at. % dopant) [9,22-25] led to an investigation of the interactions of Zn in the 123 compound as a function of oxygen content [23]. Previous research [23] has demonstrated that Zn-substituted samples with varying oxygen content (i.e. from $y = 6.9$ to 6.3), do not appear to modify the structural characteristics in terms of oxygen-ordering and lattice constants. In other words, a Zn doped structure (at a given oxygen content, y) looks basically the same as the 123 structure (of the same oxygen content, y) regardless of dopant level [23]. Ni behaves similarly in terms of its structural effects but it does not have as dramatic an effect on T_c as Zn [16.24].

The purpose of this investigation is to compare the energetic effects of the Zn and Ni dopants, as well as the corresponding behavior of oxygen within these structures, to contribute to better understanding of the nature of superconductivity for these compounds. The determination of enthalpies of oxidation, enthalpies of formation, lattice parameters, and T_c values, for these compounds as a function of dopant level are reported.

Experimental Procedure

Sample Preparation:

Sample preparation technique have been detailed elsewhere [23]. Briefly, Zn and Ni doped compounds were prepared by solid-state reaction of oxides and $BaCO_3$. Stoichiometric amounts of reagents were homogenized and milled under ethanol, in an agate container. Repeated heating in air at 930 °C and mechanical grinding were performed, until homogeneous and x-ray impurity-free materials were obtained. X-ray diffraction patterns indicated phase pure compounds for samples of $x < 0.2$ dopant level. Samples above this dopant concentration contained secondary phases indicative of exceeding the solubility limit. Powders having phase pure diffraction patterns were then pressed and sintered in air at 930 °C. Annealing was carried out in flowing O_2 at 480 °C for 150 hours. Reduction was done in vacuum, by gettering oxygen with metallic zirconium. Two or three pellets of similar weight (about 0.7 grams each) and 2.5-cm-high zirconium strips of various lengths (from 1 to 15 cm) were sealed in evacuated Pyrex ampoules (35-40 cm^3 capacity) and treated at 448 °C for 120 hours. An inverse proportionality was reproducibly found between the zirconium surface area and the residual content of oxygen in the compounds, independent of dopant level. Within experimental error, the specimens from the same ampoule exhibited uniform stoichiometry and electronic and structural characteristics.

Characterization

The oxygen content of the samples was determined by iodometric titration[26]. Details of the procedure have been given elsewhere [19,23]. All oxygen contents were calculated based on a divalent oxidation state of Zn and Ni dopants. Oxygen contents for O_2 annealed samples were typically in the range of 6.92 – 6.98; gettered samples were normally in the range of 6.35 - 6.40.

Diffraction patterns were collected on prepared samples using a Scintag PAD V diffractometer equipped with Cu $K\alpha$ radiation and a solid-state Ge detector. The scan parameters were 10-70° 2θ at a 0.02° step-size and a 2-3 second count-time. Sample powders were mounted on zero-background sample holders. An external standard calibration was applied using silicon (NIST SRM#640b) to correct for instrumental errors. Least-square refinements were performed using 6-12 well-resolved reflections to determine the **a**, **b**, and **c** lattice parameters for each sample. All samples refined as orthorhombic (P*mmm*).

Calorimetry

Calorimetric measurements were made using a Tian-Calvet type calorimeter; further discussion of this instrument as well as a more detailed procedure of the drop-solution calorimetry technique can be found elsewhere [27]. Samples were prepared as 20-30 mg pellets pressed from Zn and Ni doped 123 powders. The samples were dropped from room temperature into the calorimeter where they were dissolved by lead borate (30g) solvent held at 701 °C. Flowing gas (dry air) at a rate of 0.06-0.12 l/min was used to maintain a dynamic gas environment above the solvent; the gas flow helped to reduce problems associated with baseline shifts, due to gas evolution, as the 123 samples dissolved. The partial enthalpies of oxidation, ΔH_{ox} were calculated according to the following thermodynamic cycle using two samples of differing oxygen content, y and z, which dissolve in lead borate to give dissolved oxides with all transition metals divalent ions in solution:

$YBa_2Cu_{3-x}R_xO_y$(s,298 K) ☞ 1/2 Y_2O_3 (diss, T) + 2BaO (diss., T)

+ (3-x)CuO (diss., T) + xRO (diss., T) + (y-6.3) 1/2 O_2 (g, T) $\Delta H1$ (1)

$YBa_2Cu_{3-x}R_xO_z$(s,298 K) ☞ 1/2 Y_2O_3 (diss, T) + 2BaO (diss., T)

+ (3-x)CuO (diss., T) + xRO (diss., T) + (z-6.3) 1/2 O_2 (g, T) $-\Delta H2$ (2)

(z-y) 1/2 O_2 (g, 298 K) ☞ (z-y) 1/2 O_2 (g, T) $\Delta H3$ (3)

$YBa_2Cu_{3-x}R_xO_y$ (s, 298 K) + (z-y) 1/2 O_2(g, 298 K) ☞

$YBa_2Cu_{3-x}R_xO_z$ (s, 298 K) $\Delta H4$ (4)

$$\Delta H(1/2\ O_2) = \Delta H4 / (z-y) \qquad (5)$$

In the above equations, the 6.3 oxygen content was an arbitrary reference state. A correction had to be made to drop solution values for samples containing less than a 6.5 oxygen content (i.e. gettered). A sample with a 6.5 oxygen content corresponds to all Cu having the formal oxidation state of (2+). Upon reduction of oxygen content below 6.5 the 123 material contains some fraction of Cu as (1+). Since the final state of all the Cu in the lead borate solution is (2+) when an atmosphere of flowing air is used [19,28], the fraction of Cu oxidizing from Cu^{+1} to Cu^{+2} must be accounted for. This was easily done by adding the factor (6.5-z)*2*(-75.1 ± 3.1 kJ/mol) to the observed drop-solution value as outlined by Zhou et. al.[19].

Enthalpies of solution (ΔH_{ds}) for ZnO and NiO were also measured. Pellets were prepared from high purity (99.99%) grade ZnO and NiO. These pellets were measured in an identical manner as the superconductor samples described above. The measured ΔH_{ds} values for ZnO and NiO were 50.8 ± 1.2 kJ/mol and 37.2 ± 2.5 kJ/mol, respectively.

Enthalpies of formation (ΔH_f) of Ni and Zn doped 123 materials from the oxides (BaO, CuO, Y_2O_3, CuO and ZnO or NiO) were calculated according to the following equation:

$$-\Delta H\ YBa_2Cu_{3-x}R_xO_y(\text{diss.}) + \Delta H\ \tfrac{1}{2}\ Y_2O_3\ (\text{diss.}) + 2\ \Delta H\ BaO\ (\text{diss.}) + (3-x)\ \Delta H\ CuO\ (\text{diss.})$$
$$+ (x)\ \Delta H\ RO\ (\text{diss.}) + \Delta H\ O_2\ (y-6.5)/2 = \Delta H_f\ YBa_2Cu_{3-x}R_xO_y\ (s, 298\ K) \qquad (6)$$

ΔH_{ds} for BaO, Y_2O_3, CuO, and O_2 were obtained from Zhou, et. al.[19]

T_c measurements

T_c measurements were performed on all samples according to standard methodology [23]. Resistivity as a function of temperature was measured between 300 and 12 K, in a closed-cycle helium cryostat, with a four-point probe technique.

Results and Discussion

Tables 1 and 2 present the enthalpy of drop solution (ΔH_{ds}), oxygen content, lattice parameters, and T_c obtained on Zn doped (Series 1) and Ni doped (Series 2) samples containing high (near 7) oxygen contents. Likewise, Table 2 contains the results for reduced (near 6.3) oxygen content samples. Both Series 1 and Series 2 had an undoped sample ($x = 0$). Since there is some variability of the oxygen content as a function of dopant (due to sample preparation), drop solution enthalpies have been adjusted to an oxygen content of $y = 7$ in Table 1 and $y = 6.3$ in Table 2 so that data could be directly compared. These values are denoted as ΔH_{ds}(cor) in Tables 1 and 2.

One can clearly see the stronger drop in T_c with Zn substitution as compared to Ni in figure 1 which plots the onset of T_c vs dopant level for Ni and Zn doped samples having oxygen contents near 7. The change in T_c with dopant level confirms the presence of the dopant within the structure of the host 123 phase. Similar results have been presented by Ting, et. al.[16]. In Table 2, there is an apparent inconsistency in the data for the undoped ($x = 0$) samples in Series 1 and 2. The T_c value for the (Series 1, $x = 0$) sample is 30 K, while the T_c value for the (Series 2, $x = 0$) sample is 50 K. This discrepancy can be accounted for when one recognizes that the oxygen contents for these two samples are substantially different, $y = 6.357$ in (Series 1, $x = 0$) while $y = 6.413$ in (Series 2, $x = 0$). There is not much other evidence that Ni and Zn are doped within the structure other than the T_c measurements and the lack of observed second phases in the diffraction patterns. Lattice parameter values in Tables 1 and 2 show very little variation with dopant, clearly illustrating the elusive way in which Zn or Ni substitutes for Cu. This small variation is also a reminder of the low concentration of dopant substituted in these materials.

Drop solution calorimetric data from Tables 1 and 2 were used to calculate the partial molar enthalpy of oxidation for Zn and Ni doped samples according to equations (1-5). Table 3 and figure 2 present the resulting partial molar enthalpies of oxidation as a function of Zn and Ni dopant. The addition of dopant does not alter the oxidation behavior of either the Zn or Ni doped samples; rather, the enthalpy of oxidation is constant within experimental errors and independent of dopant level. There is a slight deviation in ΔH_{ox} of the Zn doped samples at very low Zn concentrations that may be the result of a hidden ordering phenomenon often present in samples having very low dopant concentrations.

Drop solution calorimetric data from Table 1 were used to calculate the enthalpy of formation for Zn and Ni samples according to equation (6). Figure 3 plots the enthalpy of formation, ΔH_f vs. dopant level for both the Ni and Zn doped samples. The ΔH_f from the oxides is independent of Zn or Ni dopants within the error of measurement. The addition of either dopant has no effect on the thermodynamic stability of the structure as compared to the undoped $YBa_2Cu_3O_7$ structure.

It is clear from the results that structural parameters and thermochemical properties of 123 are not affected by Zn or Ni dopants. Apparently, the mechanism for influencing superconductivity in Zn doped 123 is not dependent on structural transitions, changes in average inter-atomic distances (as evidenced by lattice parameters), thermodynamic behavior of oxidation, or thermochemical stability. This suggests that the mechanism for T_c suppression in Zn and Ni doped samples is strictly electronic in nature. The superconductive transition temperature in cuprate superconductors has been shown to be highly dependent on the hole carrier density in the CuO_2 planes [29]. Hence, perturbation of the hole carriers will strongly influence the superconducting performance. Recently, Gupta et. al. [30] discussed the suppression of T_c by zinc in terms of the collapse of the antibonding Cu-O band. This collapse has the effect of causing perturbations that extend beyond the localized Zn site and induces non-homogeneity in the carrier density in the CuO_2 planes [30]. Our observation of the independence of structural and thermochemical properties from T_c behavior is consistent with this recently proposed mechanism. This change in electronic structure is apparently too small to measurably affect enthalpies of formation or oxidation. Ni is also likely to have a perturbing effect on the band structure as demonstrated by the decrease in T_c as a function of dopant. However, the degree of disruption appears to be substantially smaller than in the Zn doped samples. Therefore it is speculated that Ni does not have the same damaging effect on the Cu-O antibonding band and does not reduce the hole carriers as severely as Zn. This difference in behavior for Ni and Zn likely has its origin in the differing orbital configuration of Ni and Zn cations.

Conclusions

ΔH_{ox} values were found to be nearly independent of dopant for both Ni and Zn, having enthalpies of oxidation in the range -89.4 ± 10.9 to -109.1 ± 4.9 kJ/mol $\frac{1}{2}O_2$. The only exception to this was the slight increase in ΔH_{ox} for very low concentration Zn doped samples. This observation was attributed to an ordering phenomenon typical in small doped concentrations. ΔH_f values were found to be independent of dopant for both Ni and Zn as well; the values ranged from -110.3 ± 10.2 to -117.5 ± 7.8 kJ/mol. Additionally, lattice parameters showed no dependence on dopant concentration for either Ni or Zn; no variation of the orthorhombic structure was observed for samples at approximately the same oxygen content. The independence of thermodynamic and structural behavior from dopant concentration is consistent with an electronic mechanism for T_c suppression in these materials.

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Table 1. Observed Thermodynamic and Structural Data for $YBa_2Cu_{3-x}R_xO_y$ (R= Ni or Zn and y ~7)

Series	x	ΔH_{ds} (J/g)	Err* (J/g)	ΔH_{ds}(cor)# (kJ/mol)	Err* (kJ/mol)	y	**a** (angstroms)	**b** (angstroms)	**c** (angstroms)	T_c (K)
1	0	249.6	3.1	170.0	2.2	6.961(4)	3.820(2)	3.888(2)	11.674(3)	91.5
1	Zn 0.0075	251.1	2.8	170.3	1.9	6.971(4)	3.819(2)	3.888(2)	11.678(4)	89
1	Zn 0.015	251.2	5.4	167.4	3.3	6.982(4)	3.820(2)	3.888(3)	11.680(5)	85
1	Zn 0.0225	250.5	4.5	170.5	3.1	6.964(5)	3.821(1)	3.889(2)	11.678(3)	83
1	Zn 0.045	248.5	4.7	168.0	3.2	6.971(6)	3.820(2)	3.889(2)	11.681(5)	74
1	Zn 0.06	247.2	3.8	169.1	2.6	6.952(4)	3.820(1)	3.890(2)	11.677(3)	71
1	Zn 0.12	239.3	2.5	165.4	1.7	6.933(3)	3.821(2)	3.891(5)	11.681(4)	60.5
2	0	240.7	1.9	165.3	1.8	6.925(3)	3.821(2)	3.893(2)	11.673(6	92.8
2	Ni 0.03	238.5	6.3	163.8	4.3	6.933(3)	3.822(2)	3.890(2)	11.678(6)	88.5
2	Ni 0.06	241.4	2.0	165.4	1.5	6.934(4)	3.822(2)	3.889(2)	11.676(3)	84
2	Ni 0.12	239.8	3.6	162.0	2.5	6.942(3)	3.822(2)	3.888(2)	11.675(4)	80
2	Ni 0.18	239.9	2.8	165.6	2.0	6.922(3)	3.824(2)	3.887(2)	11.670(5)	74

#(Enthalpies of drop-solution corrected to oxygen content of 7 –for direct comparability)

*(Error calculated as 2σ of the mean)

Table 2. Observed Thermodynamic and Structural Data for $YBa_2Cu_{3-x}R_xO_y$ (R = Ni or Zn and y ~6.3)

Series	x	ΔH_{ds} (J/g)	Err* (J/g)	ΔH_{ds}(cor)# (kJ/mol)	Err* (kJ/mol)	y	**a** (angstroms)	**b** (angstroms)	**c** (angstroms)	T_c (K)
1	0	185.1	7.0	94.3	4.7	6.357(4)	3.844(2)	3.873(2)	11.774(5)	30
1	Zn 0.0075	174.8	3.4	87.3	2.4	6.364(5)	3.844(2)	3.874(2)	11.776(5)	26
1	Zn 0.015	170.7	5.7	85.0	3.9	6.369(4)	3.844(2)	3.875(2)	11.774(6)	24
1	Zn 0.0225	178.8	3.1	90.6	2.2	6.370(2)	3.846(2)	3.874(2)	11.769(4)	20
1	Zn 0.045	185.0	6.6	96.6	4.5	6.391(5)	3.841(2)	3.877(2)	11.768(6)	26
1	Zn 0.06	186.3	4.6	96.5	3.2	6.377(3)	3.846(2)	3.877(2)	11.772(4)	-
1	Zn 0.12	184.7	4.8	94.4	3.3	6.356(6)	3.849(2)	3.875(2)	11.775(4)	-
2	0	185.8	3.9	98.8	2.4	6.413(4)	3.842(3)	3.875(3)	11.771(9	50
2	Ni 0.03	180.0	5.1	96.7	3.5	6.439(4)	3.842(2)	3.878(2)	11.758(6)	30
2	Ni 0.06	186.1	4.3	100.5	3.2	6.430(4)	3.841(2)	3.877(2)	11.752(3)	28
2	Ni 0.12	174.1	5.2	92.6	3.4	6.447(3)	3.842(2)	3.879(1)	11.750(3)	22
2	Ni 0.18	179.5	2.2	92.7	1.6	6.398(5)	3.847(2)	3.876(2)	11.749(3)	15

#(Enthalpies of drop-solution corrected to oxygen content of 6.3 –for direct comparability)

*(Error calculated as 2σ of the mean)

Table 3. Calculated Thermodynamic Data for $YBa_2Cu_{3-x}R_xO_y$ (R=Ni or Zn)

dopant	x	ΔH_f (kJ/mol)	ΔH_f err* (kJ/mol)	ΔH_{ox} (kJ/mol ½ O_2)	ΔH_{ox} err* (kJ/mol ½ O_2)
None#	0	-113.7	7.3	-93.9	6.9
Zn	0.0075	-117.5	7.8	-109.1	4.9
Zn	0.015	-115.9	9.5	-108.2	8.2
Zn	0.0225	-117.5	9.2	-104.9	6.2
Zn	0.045	-116.4	9.4	-92.9	9.3
Zn	0.06	-116.0	8.6	-94.7	6.9
Zn	0.12	-111.9	7.7	-92.4	6.3
Ni	0.03	-110.3	10.2	-89.4	10.9
Ni	0.06	-113.1	6.1	-86.1	6.9
Ni	0.12	-113.8	7.3	-95.9	8.4
NI	0.18	-115.9	6.6	-98.3	4.6

average of data from undoped samples in series 1 and 2

*(Error calculated as 2σ of the mean)

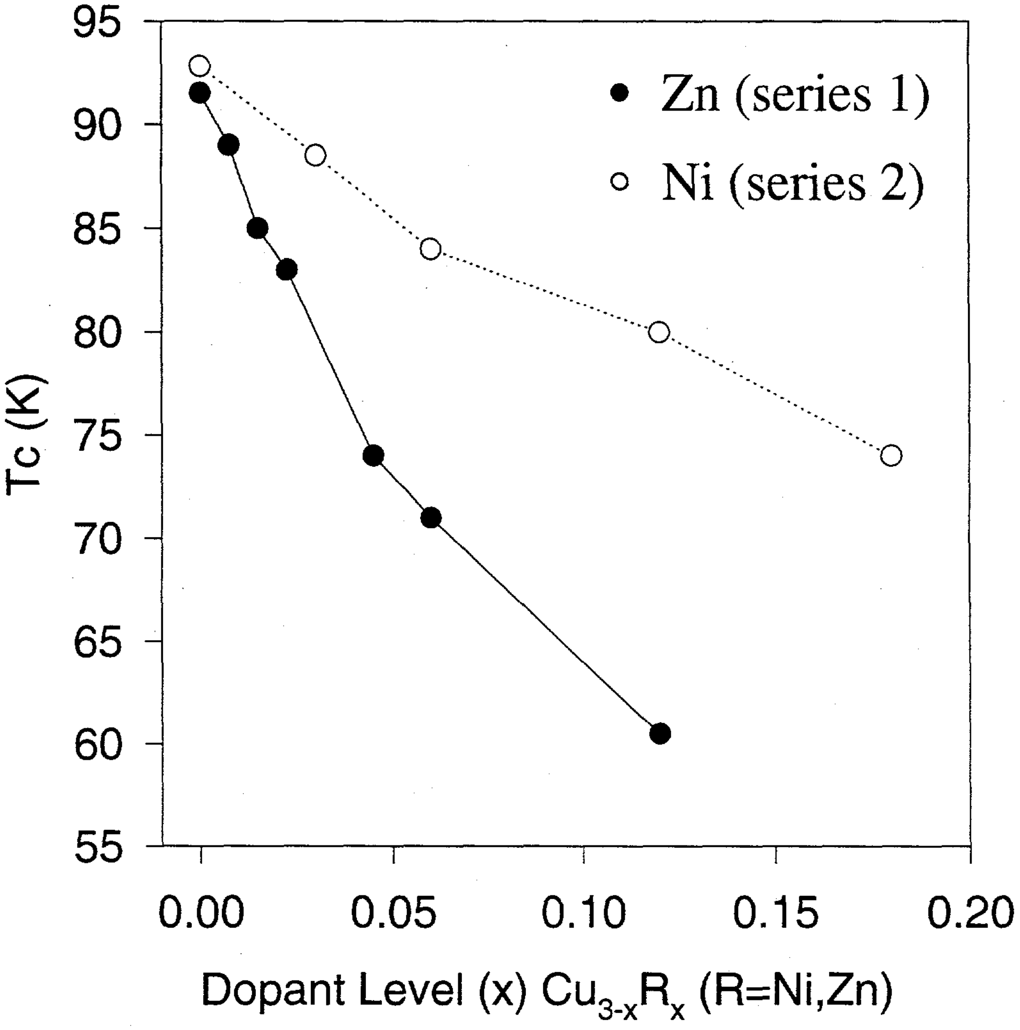

Figure 1. T_c onset vs. dopant level for Ni and Zn doped samples. T_c shows much stronger dependence on Zn substitution.

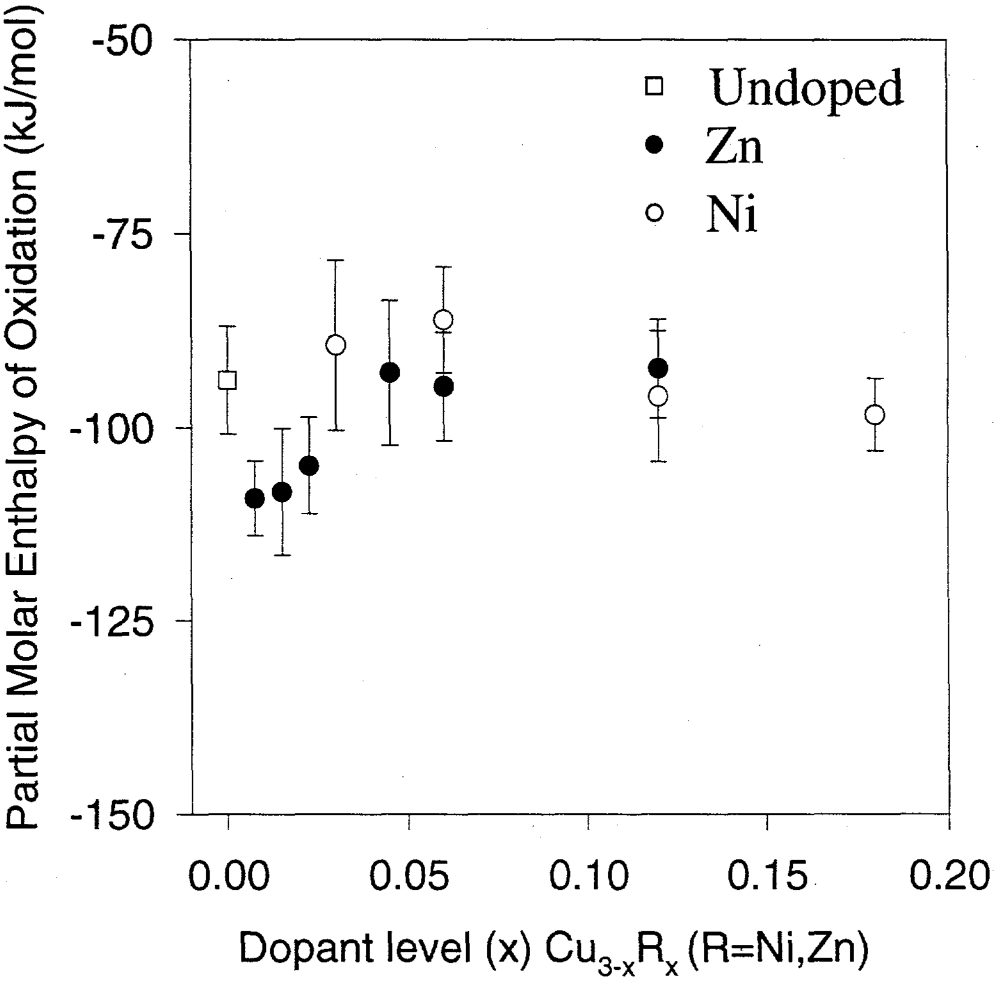

Figure 2. Partial molar enthalpy of oxidation vs. dopant level for Ni and Zn doped samples. Error bars are 2σ of the mean.

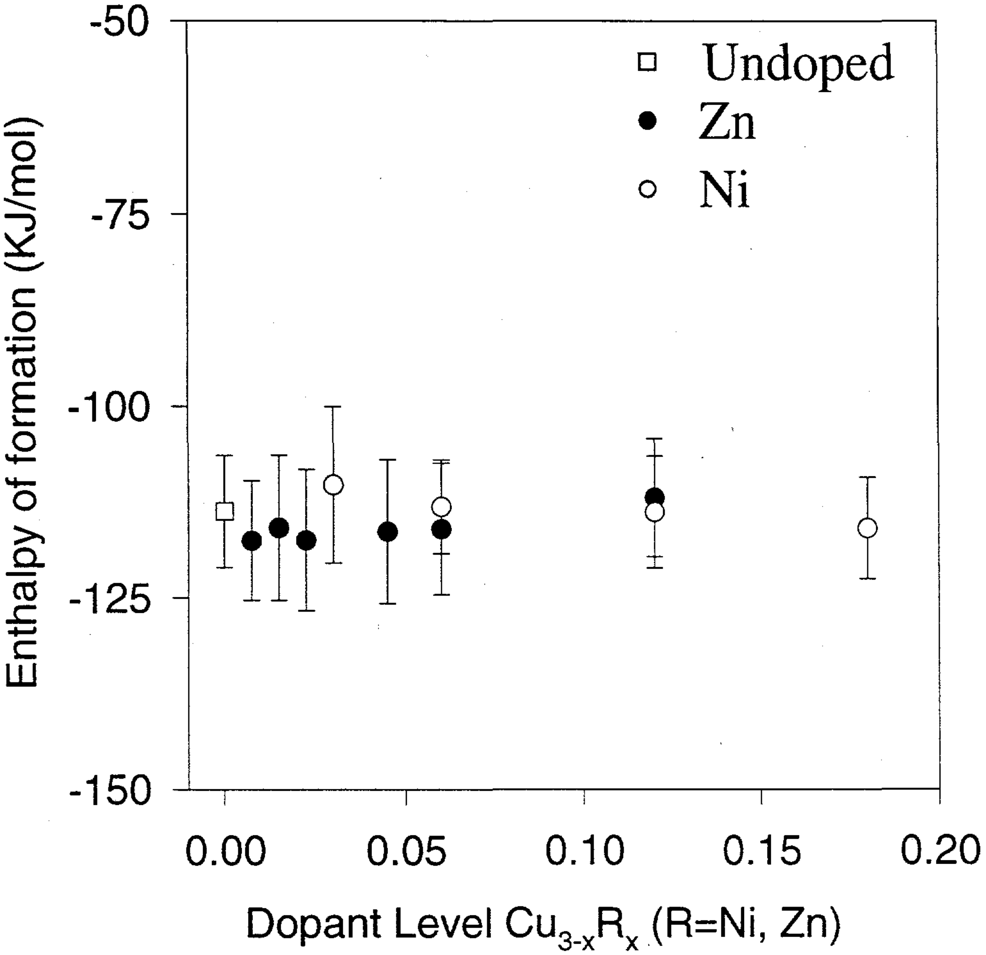

Figure 3. Enthalpy of formation vs. dopant level for Ni and Zn doped samples. Error bars are 2σ of the mean.