

Thermodynamics of high-T_c superconductors

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Abstract - Phase relationships in the Y-Ba-Cu-O system and thermodynamic properties of the comprising substances, including high-T_c superconductors, are discussed. Phase equilibrium calculations for the same system are presented.

INTRODUCTION

Despite the flood of publications on high-T_c superconductors, thermodynamic investigations still play a modest role. Nevertheless, since thermodynamics is the physico-chemical basis of inorganic syntheses, we would like to draw attention to the results already published in this field and the ensuing possibilities, and also, to stress that much still remains to be done. This report discusses heat capacity, enthalpy and phase equilibrium in high-T_c oxide systems.

HEAT CAPACITY

Most measurements of the low temperature heat capacity of oxide superconductors have been made in connection with other investigations (electric, magnetic, etc.). The main aims of C_p(T) studies have been:

- to determine the thermodynamic properties;
- to make sure that the electric conductivity and heat capacity jumps are concurrent;
- to measure the absolute value of the C_p jump and calculate the superconductor parameters on this basis;
- to look for other C_p anomalies;
- to establish the nature of the temperature dependence of the electronic heat capacity in the range of superconductivity from the shape of C_p(T) curves at low temperatures;
- to measure the jump parameters (T_c, ΔC_p) as a function of the ceramic composition.

C_p(T) measurements have rarely been used to calculate the thermodynamic properties, probably because preparation of these compounds is a multistage process and the resulting and initial compositions are not the same. In addition, the superconducting ceramics is usually a mixture of several phases in an unknown ratio with different (even if close) compositions, while the thermodynamic properties are attributable to a single compound. Hence the problem is to obtain a single-phase sample and identify it as completely as possible.

The existing high- T_c oxide superconductors can be divided into three types:

- 1) $\text{La}_{2-x}\text{M}_x\text{CuO}_4$, where M is an alkaline earth metal;
- 2) $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$, where Ln is Y or a rare-earth element;
- 3) multinary oxides of bismuth (or thallium), alkaline earth metals and copper in different ratios (2:1:2:2, 2:2:2:3, 1:1:2:2).

The characteristic feature of these compounds is that they show metallic conductivity at ambient temperatures (ref. 1)

$\text{La}_{2-x}\text{M}_x\text{CuO}_4$ compounds. According to the pioneer publication (ref. 2) these are based on the La_2CuO_4 parent and become superconductors at temperatures below 30 K. Their heat capacity measurements show a C_p jump in a diffused and not very large T_c range (about $1 \text{ J mol}^{-1} \cdot \text{K}^{-1}$). The mean temperature of this jump has been variously reported as 34-37 K. This was somewhat different from the T_c obtained from electric conductivity data. Thermodynamic properties have been determined for La_2CuO_4 and $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$. As can be seen from Table 1, addition of an alkaline earth metal does not have any noticeable effect. Comparison of the corresponding $C_p(T)$ curves (Fig. 1) shows that at $T < 50 \text{ K}$ the values for La_2CuO_4 exceed those for $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ while at $T > 50 \text{ K}$ the C_p sequence is the opposite. From Fig. 1 the absolute jump value is $C_p/T = 30 \text{ mJ mol}^{-1} \text{ K}^{-2}$.

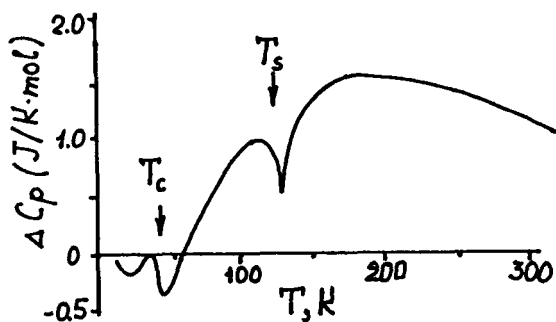


Fig. 1. The difference in C_p between $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ and La_2CuO_4 .

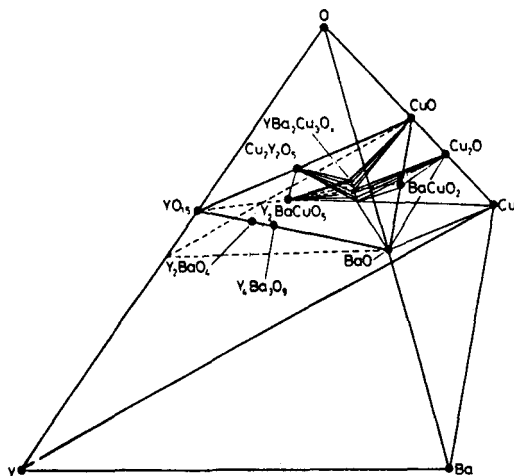


Fig. 2. Y-Ba-Cu-O system (ref. 20)

$\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ compounds. These are known as 1:2:3 compounds. Their preparation is much more complicated and involves several heating-grinding cycles to increase the oxygen concentration since it has been well established that samples with $x < 0.5$ are not complete superconductors. Accordingly, appropriate identification of the samples becomes even more pressing if thermodynamic characteristics are to be measured. The thermodynamic properties in Table 1 are taken from several publications and are in reasonable agreement. The C_p jump was reported at the superconducting transition point from the measurements at 50-150 K. Its absolute value differs from 2.3 to $5.5 \text{ J mol}^{-1} \text{ K}^{-1}$, as well as its temperature interval (0.5 to 7 K) and the T_c value (79 to 94 K). The essential differences in these values can be attributed to the quality of the measured samples. For example, Gavrichev et al. (ref. 5-7) reported changes after several heating-cooling cycles and ascribed them to the non-equilibrium state of the samples immediately after preparation. In particular, the oxygen distribution might have been non-uniform, leading to diffusion during the temperature recycling. It has also been shown that in the temperature range 45-83 K the $C_p(T)$ curve may exhibit multiple maxima, probably due to superconducting phase transitions for the phases with different oxygen non-stoichiometry. The C_p anomalies in these samples were in agreement with those of electric conductivity.

TABLE 1. Heat capacity, entropy and enthalpy of high-T_c superconductors at T = 298.15 K

Compound	C _p ^o (T)	S ^o (T)	H ^o (T)-H ^o (0)	Reference
	J mol ⁻¹ K ⁻¹	J mol ⁻¹ K ⁻¹	J mol ⁻¹	
La ₂ CuO ₄	151.3	178.1	27750	3
La _{1.8} Sr _{0.2} CuO ₄	152.4	179.7	27990	4
YBa ₂ Cu ₃ O _{7-x}	285.8	323.5	51230	5
	282.1	321.7	50790	6
HoBa ₂ Cu ₃ O _{7-x}	290.6	344.3	52620	7
	292.4	342.5	54850	6
YbBa ₂ Cu ₃ O _{7-x}	291.0	338.7	52270	6
GdBa ₂ Cu ₃ O _{7-x}	316.1	345.4	56040	8
Bi ₂ Sr ₂ Ca _{1.2} Cu _{1.8} O _{8+δ}	346.7	406.7	62640	9
Tl _{0.7} Ba _{2.1} Ca ₂ Cu _{3.3} O _{8+δ}	372.2	424.5	66320	10

Heat capacity measurements for this type of superconductors at very low temperatures showed that:

- 1) C_p(T) curves may have maxima at temperatures below 10 K;
- 2) the electronic term can be described by a linear function.

The first finding could have been expected from the properties of the rare earth. The second, however, has no definite explanation (as well as in the case of La_{2-x}M_xCuO₄ compounds). The low temperature C_p maxima observed by Junod (ref. 11) were ascribed to magnetic ordering. The maximum C_p values for different rare earths were observed in the temperature range 0.5-10 K. Two points must thus be stressed:

- 1) for single-phase samples with a high oxygen index, only one C_p anomaly is observed in the temperature range 10-300 K;
- 2) there is no evidence that the linear heat capacity dependence at very low temperatures is connected with impurities rather than with the substance itself.

Bismuth and thallium ceramics. Very few publications have examined the C_p of these materials (ref. 9, 10 & 12-14). All the measurements have been made on multiphase samples, probably on account of the complicated preparation process, and the reported data must obviously be regarded as rough estimates. The heat capacity curves involve several C_p maxima in the range 85-150 K. The properties of the samples are strongly dependent on the thermal processing (ref. 14). The data for bismuth ceramics are widely discordant. For example, the linear term in the C_p temperature dependence reported in refs. 9 & 13 was not observed in ref. 12.

ENTHALPY OF FORMATION AND ENTROPY

Investigation of these thermodynamic properties of high-T_c superconductors has barely begun. The standard enthalpy of formation of Cu-(Ba,Y,La) oxides, as well as the ternary oxides, has been measured by calorimetric investigation of solutions in HClO₄ (ref. 15) or HCl (ref. 16). Depending upon oxygen non-stoichiometry, the value of Δ_fH^o(YBa₂Cu₃O_y, s, 298.15 K) obtained by Morss *et al.* (ref. 15) ranged from (-2671±17) kJ mol⁻¹ for y=6.25 to (-2713±17) kJ mol⁻¹ for y=6.93. The interpolation to y=6.5 gave the value (-2675±20) kJ mol⁻¹ for standard enthalpy of formation from the elements, or (-143) kJ mol⁻¹ from binary oxides (Table 2).

TABLE 2. Enthalpy and entropy changes for formation of compounds from simple oxides.

Compound	T	$\Delta H(T)$	$\Delta S(T)$	Method	Reference
	K	kJ mol ⁻¹	J mol ⁻¹ K ⁻¹		
La ₂ CuO ₄	298.15	-28	-	calorimetry	15
BaCuO ₂	298.15	-98.08	-	calorimetry	16
	1000-1100	-53.8±12.1	-17.9±3.0	emf	17
Y ₂ Cu ₂ O ₅	298.15	-55.97	-	calorimetry	16
	1100-1300	12.8±1.7	18.4±1.4	emf	17
	1173-1340	20.7±2.5	22.8±2.7	emf	18
	1097-1292	10.91	13.41	emf	19
YBa ₂ Cu ₃ O _{6.5}	298.15	-143	-	calorimetry	15
YBa ₂ Cu ₃ O _{7-x}	298.15	from -154.6 to -231.9	-	calorimetry	16
	1073-1173	-66.6±20.2	-9.4±7.6	emf	17
	298.15	-78.3	-	calorimetry	16
Y ₂ BaCuO ₅	298.15	-78.3	-	calorimetry	16
	1073-1173	-48.4±11.9	-6.6±2.1	emf	17

Pivovarov *et al.* (ref. 16) reported values (Table 2) strongly dependent on the method of preparation of YBa₂Cu₃O_{7- δ} samples. These results are strongly discordant with those of Morss (ref. 15). Enthalpies of formation for BaCuO₂, Y₂Cu₂O₅ and Y₂BaCuO₅ from binary oxides are also shown in Table 2. The emf method (ref. 17-19) gave ΔH and ΔS for reactions of formation of substances from simple oxides at elevated temperatures. As can be seen in Table 2, these results are not in accord with the calorimetric data.

PHASE EQUILIBRIA

In all the Ln-Ba-Cu-O systems, only the LnBa₂Cu₃O_{7-x} compounds were observed. The system Y-Ba-Cu-O has been studied in greater detail (Fig. 2), (ref. 20), though attention has been almost entirely directed to the CuO-Y₂O₃-BaO section. The main experimental methods were X-ray, DTA and TG. This section can be considered a quasi-ternary system with a compositional deviation from the plane of triangle due to the oxygen non-stoichiometry.

Oxides with 1:1 stoichiometry were found in all the binary systems: Y₂Cu₂O₅, Y₂BaO₄ and BaCuO₂, along with other binary oxides namely Y₄Ba₃O₉, Y₂Ba₄O₇, Y₂Ba₂O₅, BaCuO₃, Ba₃CuO₄. The difference in ternary oxide stoichiometry is still more pronounced. In addition to YBa₂Cu₃O_{7-x} and Y₂BaCuO₅, some new substances have been synthesised: YBa₃Cu₂O_x, Y₃Ba₈Cu₅O_{17.5+x}, YBa₄Cu₃O_{8.5+x}, Y₂Ba₃Cu₅O_{11+x}, Y₂BaCu₃O_{7-x}. The oxygen non-stoichiometry in oxides was studied by TG, mainly for YBa₂Cu₃O_{7-x}. The range of x in the formula was found to be 0 < x < 1. Due to serious complications in the experimental study of four-component systems, special attention must be given to thermodynamic simulation of phase equilibria. The first attempt to use this method for YBa₂Cu₃O_y was made by Moiseev *et al.* (ref. 21). Because of the absence of suitable thermodynamic data for this system, YBa₂Cu₃O_y was considered to be an ideal associated solid solution of simple oxides and BaCuO₂. It was shown that depending on the model and compounds in the mixture, the y value may be limited by 6.5 at ca. 1300 K, while at 1100-2000 K it increased up to 7. We used the thermodynamic simulation method and all published data to reconstruct the phase equilibria in the Y-Ba-Cu-O system by solving a direct thermodynamic problem at P = 1 atm, T = 473-1773 K.

The individual condensed phases (properties in Tables 1 & 2) were taken into account, together with the ideal condensed solutions between simple oxides. Individual condensed and vapour phase compounds with known standard thermodynamic functions were also considered. A total of 13 condensed and 15 vapour phase compounds were involved. The calculations were made at 22 points of the concentration triangle CuO-Y₂O₃-BaO along the sections: Y₂Cu₂O₅-BaCuO₂, Y₂Cu₂O₅-Y₂BaCuO₅, Y₂O₃-BaCuO₂, CuO-Y₂BaCuO₅, CuO-YBa₂Cu₃O_y (y = 6.5 and 7) as well as for CuO-BaO and CuO-Y₂O₃ systems.

TABLE 3. Equilibrium condensed phases (in mol kg⁻¹) for the overall composition YBa₂Cu₃O_{6.5}

T/K	Individual phases				Solution	
	Cu ₂ O	BaCuO ₂	YBa ₂ Cu ₃ O _{6.5}	BaO	Y ₂ O ₃	CuO
473	1.473·10 ⁻⁶	1.8231	-	2.04·10 ⁻⁵	0.45580	0.91156
573	1.473·10 ⁻⁶	1.8229	-	2.162·10 ⁻⁴	0.45583	0.91176
673	1.473·10 ⁻⁶	1.8220	-	1.144·10 ⁻³	0.45579	0.91269
773	1.475·10 ⁻⁶	1.8191	-	3.9725·10 ⁻³	0.45572	0.91551
873	1.815·10 ⁻⁶	1.8126	-	1.0508·10 ⁻²	0.45574	0.93466
973	2.1083·10 ⁻⁵	1.7999	-	2.316·10 ⁻²	0.45577	0.92204
1073	-	6.058·10 ⁻⁷	0.91152	3.244·10 ⁻⁸	3.5766·10 ⁻⁷	3.5146·10 ⁻⁷
1173	-	-	0.91152	2.315·10 ⁻⁸	1.4632·10 ⁻⁷	6.676·10 ⁻⁸
1273	-	-	0.91152	1.3645·10 ⁻⁷	2.3262·10 ⁻⁷	5.6675·10 ⁻⁸
1373	-	-	0.91152	2.0623·10 ⁻⁶	7.2706·10 ⁻⁷	2.8093·10 ⁻⁷
1473	-	-	0.91128	5.208·10 ⁻⁴	1.3056·10 ⁻⁴	5.9772·10 ⁻⁵
1573	-	-	0.91060	1.8403·10 ⁻³	4.6152·10 ⁻⁴	1.9508·10 ⁻⁴
1673	1.1485·10 ⁻²	-	0.90296	1.7123·10 ⁻²	4.2886·10 ⁻³	1.6371·10 ⁻³
1773	4.2417·10 ⁻²	-	0.87988	6.314·10 ⁻²	1.5823·10 ⁻²	6.3218·10 ⁻³

TABLE 4. Equilibrium condensed phases (in mol kg⁻¹) for the overall composition (0.5CuO + 0.5YBa₂Cu₃O_{6.5})

T/K	Individual phases				Solution	
	Cu ₂ O	BaCuO ₂	YBa ₂ Cu ₃ O _{6.5}	BaO	Y ₂ O ₃	CuO
473	1.538·10 ⁻⁶	1.6265	-	2.5286·10 ⁻⁵	0.40664	1.6265
573	1.538·10 ⁻⁶	1.6263	-	2.6792·10 ⁻⁴	0.40661	1.6268
673	1.538·10 ⁻⁶	1.6251	-	1.4174·10 ⁻³	0.40668	1.6279
773	1.542·10 ⁻⁶	1.6216	-	4.9195·10 ⁻³	0.40659	1.6314
873	2.2429·10 ⁻⁶	1.6135	-	1.3·10 ⁻²	0.40660	1.6395
973	4.1834·10 ⁻⁵	1.5979	-	2.8598·10 ⁻²	0.40663	1.6550
1073	1.279·10 ⁻³	0.89490	0.34636	3.893·10 ⁻²	0.23346	1.3165
1173	3.218·10 ⁻²	3.7648·10 ⁻²	0.77876	3.136·10 ⁻²	1.7252·10 ⁻²	0.81476
1273	0.31619	-	0.80882	8.893·10 ⁻³	2.223·10 ⁻³	0.19422
1373	0.40663	-	0.81326	7.393·10 ⁻¹¹	7.078·10 ⁻¹⁰	1.363·10 ⁻⁹
1473	0.40663	-	0.81326	1.165·10 ⁻⁹	1.161·10 ⁻⁸	9.257·10 ⁻⁹
1573	0.40659	-	0.81326	2.14·10 ⁻⁸	1.55·10 ⁻⁷	6.42·10 ⁻⁸
1673	0.40639	-	0.81326	3.76·10 ⁻⁷	1.662·10 ⁻⁶	4.11·10 ⁻⁷
1773	0.40554	-	0.81324	5.512·10 ⁻⁶	1.385·10 ⁻⁵	2.842·10 ⁻⁶

It was shown that the enthalpies of formation from simple oxides reported by Pivovarov (ref. 16) for $Y_2BaCu_3O_{7-x}$ ($-116.8 \text{ kJ mol}^{-1}$) and $Y_2Ba_3Cu_5O_{11+x}$ (-284.2 to $-343.04 \text{ kJ mol}^{-1}$ for different preparation conditions) disagreed with all the published data on phase equilibrium in Y-Ba-Cu-O: no existence field for $YBa_2Cu_3O_y$ was found within the CuO - Y_2O_3 - BaO triangle at 473-1573 K and $Y_2BaCu_3O_{7-x}$ was also absent. Probably these measurements were made on multiphase or non-equilibrium samples and hence were excluded from subsequent calculations.

The high- T_c superconductors are frequently regarded as thermodynamically metastable substances, whereas prolonged sintering at 1073 K in oxygen or air is known to stabilize $YBa_2Cu_3O_y$. Since the ΔH and ΔS values for $BaCuO_2$ and $Y_2Cu_2O_5$ agree (ref.17-19) and the absolute standard entropy of $YBa_2Cu_3O_{7-x}$ is also known (Tables 1 & 2), it was interesting to estimate the minimum $\Delta_f H^\circ$ ensuring its thermodynamic stability at $T \geq 1073 \text{ K}$. It was found that the low temperature limit of stability for this compound is 1073 K if $\Delta_f H^\circ(YBa_2Cu_3O_{7-x}, s, 298.15 \text{ K}) = -2596 \text{ kJ mol}^{-1}$ which corresponds to -62 kJ mol^{-1} for the enthalpy of formation from simple oxides. Tables 3 & 4 show the equilibrium compositions calculated at two points of the compositional triangle: $YBa_2Cu_3O_{6.5}$ and $(0.5CuO + 0.5YBa_2Cu_3O_{6.5})$. Comparison of Tables 1, 2 & 3 shows that the accepted value for $\Delta_f H^\circ(YBa_2Cu_3O_{6.5})$ leads to thermodynamic metastability below 1073 K, while at $T > 1073 \text{ K}$ its stability is due to the entropy term.

In conclusion, the extensive literature phase equilibria in oxide systems with high- T_c superconductors has by no means clarified the position. The final solution of this problem demands complete thermodynamic characterization of all the substances involved.

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