

## Relative thermodynamic stabilities of constituent oxides of high $T_c$ superconductors

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**Abstract.** A thermodynamic scale of the relative stabilities of constituent oxides can help the choice of stoichiometric multi-component compositions and can provide guidance for judicious selection of heat-treatment conditions for high- $T_c$  superconductors. A thermodynamic analysis was undertaken to study  $Y_2O_3$ -BaO-CuO, BaO-K<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>-SrO-NiO systems. The relative stability of the oxides was expressed in terms of two ratios,  $S_v$  and  $S_p$ , computed using free-energy of formation and vapour pressure data. CuO, Bi<sub>2</sub>O<sub>3</sub> and NiO were taken as reference oxides for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> , Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub> and La<sub>1.9</sub>Sr<sub>0.1</sub>NiO<sub>4</sub> respectively. Thermodynamically, the reference oxide was found to be the least stable amongst the constituent oxides in each of these systems.

**Keywords.** Gibb's free-energy of formation; vapour pressure; equilibrium oxygen pressure; thermodynamic stability.

### 1. Introduction

The discovery of possible high  $T_c$  superconductivity followed by worldwide research has resulted in three potential groups of materials, viz. Cuprates (Wu *et al* 1987), Bismuthates (Cava *et al* 1988; Mattheiss *et al* 1988) and the controversial Nickelates (Rao *et al* 1989). The thermodynamic stability of high  $T_c$  superconductors is the most debated topic of the hour. Experimental observations of different research groups on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> , the most studied superconductor at present, do not agree well.

Lindemer *et al* (1989) experimentally determined the non-stoichiometry of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (1-2-3 compound) over the range  $573 < T < 1173$  K and  $10^{-5} < P_{O_2}^* < 1.0$  ( $P_{O_2}^*$  = oxygen pressure in MPa divided by standard-state pressure 0.101 MPa). The authors presented an excellent review of data on this aspect and elaborated thermodynamic representations to relate the interdependence of  $T$ ,  $x$  and the chemical potential of oxygen using the Ellingham diagram. Limited availability of thermodynamic information is the major problem. Williams and Chaudhury (1988) established procedures and guidelines that would enable research workers to choose materials which would not react chemically with the oxide superconductors using thermochemical predictions. These authors determined the most stable elemental metals in contact with the copper-oxide superconductors and examined the possible integration of these superconductors with Si-devices. It was shown that most elements would reduce CuO to elemental Cu and would react chemically with any of the copper-oxide superconductors as well. The authors analysed the stability of 1-2-3 compound with respect to the solid elements and several oxides and pointed out the importance of thermochemical properties in the processing of copper-oxide superconductors. Tretyakov (1990) emphasized the great differences in melting points, volatility,  $G$  and  $H$  of formation of Cu, RE, Bi, Pb and other binary oxides to understand the behaviour of superconductive materials upon preparation and exploitation. The present paper

is an attempt to form a thermodynamic scale of the relative stability of constituent oxides which can help judicious choice of composition and heat-treatment conditions.

## 2. Thermodynamic analysis

A thermodynamic analysis was undertaken to study the relative stability of the constituent oxide. Three systems, viz.  $Y_2O_3$ -BaO-CuO, BaO-K<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>-SrO-NiO were considered to represent YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> , Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub> and La<sub>1.9</sub>Sr<sub>0.1</sub>NiO<sub>4</sub> respectively. The vapour pressure indicates the volatilization while equilibrium partial pressure indicates the reducibility of the oxides. These two factors should be considered in the analysis. It is worthwhile to point out here that the atmosphere often contains CO<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub> during processing of high  $T_c$  superconductors. Temperature dependence of standard Gibb's free energy of formation ( $\Delta G_f^0$ ) of the oxides was determined. The rate of volatilization ( $V = P/K$ ) was calculated using vapour pressure and  $\Delta G_f^0$  data (Kubaschewski and Alcock 1979). The equilibrium oxygen pressure of constituent oxides at 700°C, 800°C and 900°C was also determined. The relative stability was expressed in the form of two ratios,  $S_v$  and  $S_p$ . CuO, Bi<sub>2</sub>O<sub>3</sub> and NiO were taken as reference oxides for Y<sub>2</sub>O<sub>3</sub>-BaO-CuO, BaO-K<sub>2</sub>O-Bi<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>-SrO-NiO systems respectively. The ratio of rate of volatilization of reference oxide to that of other oxides in the respective systems ( $S_v = \log V_x / \log V_y$ ,  $x = \text{CuO}$ , Bi<sub>2</sub>O<sub>3</sub> or NiO) at various temperatures was computed. Similarly, the ratio of equilibrium oxygen pressure of reference oxide to that of other oxides in the respective systems ( $S_p = \log P_x / \log P_y$ ,  $x = \text{CuO}$ , Bi<sub>2</sub>O<sub>3</sub> or NiO) at 700°C, 800°C and 900°C was also computed. Table 1 shows the calculated  $S_p$  values for 800°C.

**Table 1.** Equilibrium oxygen pressure and relative stability ( $S_p$ ) of constituent oxides (temperature = 800°C)

Constituent oxide	Equilibrium oxygen pressure $P$ (atm.)	$\log P_x$ or $\log P_y$	Relative stability $S_p = \log P_x / P_y$
<b>I. YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-<math>\delta</math></sub></b>			
* CuO	$1.1081 \times 10^{-3}$	-2.9554	1.0000
Cu <sub>2</sub> O	$1.5868 \times 10^{-9}$	-8.7995	0.3359
BaO	$1.6626 \times 10^{-44}$	-43.7898	0.0675
Y <sub>2</sub> O <sub>3</sub>	$4.1172 \times 10^{-47}$	-46.3854	0.0637
<b>II. Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub></b>			
* Bi <sub>2</sub> O <sub>3</sub>	$3.2756 \times 10^{-10}$	-9.4847	1.0000
BiO	$6.8836 \times 10^{-11}$	-10.1622	0.9333
K <sub>2</sub> O	$5.4830 \times 10^{-20}$	-19.2610	0.4924
BaO	$1.6226 \times 10^{-44}$	-43.7898	0.2166
<b>III. La<sub>1.9</sub>Sr<sub>0.1</sub>NiO<sub>4</sub></b>			
* NiO	$2.2618 \times 10^{-14}$	-13.6455	1.0000
SrO	$3.5083 \times 10^{-48}$	-47.4549	0.2875
La <sub>2</sub> O <sub>3</sub>	$1.2032 \times 10^{-48}$	-47.9197	0.2848

\* Reference oxides ( $x = \text{CuO}$ , Bi<sub>2</sub>O<sub>3</sub> or NiO)

3. Results and discussion

Figure 1 shows the temperature dependence of  $\Delta G_T^0$ . There are two distinct groups of oxides. CuO, Cu<sub>2</sub>O, Bi<sub>2</sub>O<sub>3</sub>, BiO and NiO form one group having  $\Delta G_T^0$  more than -100 kcal, while BaO, Y<sub>2</sub>O<sub>3</sub>, SrO and La<sub>2</sub>O<sub>3</sub> form the other group having  $\Delta G_T^0$  less than -200 kcal. The oxides of the former group are relatively low in stability and those of the latter group, high in stability. At 1200°C, Cu<sub>2</sub>O, Bi<sub>2</sub>O<sub>3</sub> and BiO have overlapping  $\Delta G_T^0$  values, i.e. about -50 kcal.  $\Delta G_T^0$  of K<sub>2</sub>O, which is about -150 to -100 kcal up to 700°C, increases steeply above 800°C. Above 1255°C, K<sub>2</sub>O becomes less stable than all other oxides except CuO. CuO is the least stable oxide throughout up to 1100°C. It would be appropriate to point out here that the presence of CO<sub>2</sub> or H<sub>2</sub>O can seriously affect these equilibrium states.

Figure 2 shows the temperature dependence of rate of volatilization of constituent oxide systems. Cu-CuO and Bi-Bi<sub>2</sub>O<sub>3</sub> systems are more or less equally volatile over a temperature range of 300-1000°C closely followed by Bi-BiO and subsequently by Cu-Cu<sub>2</sub>O, K-K<sub>2</sub>O and Ni-NiO. Ba-BaO and Sr-SrO are orders of magnitude less volatile. The volatilizability of Cu-CuO and/or Bi-Bi<sub>2</sub>O<sub>3</sub> systems must be kept in mind while processing of high *T<sub>c</sub>* superconductor compositions containing CuO and/or Bi<sub>2</sub>O<sub>3</sub>. Thermodynamically, these species are the first ones to come out of the system thus making the atmosphere rich in Cu-CuO and Bi-Bi<sub>2</sub>O<sub>3</sub>, in turn

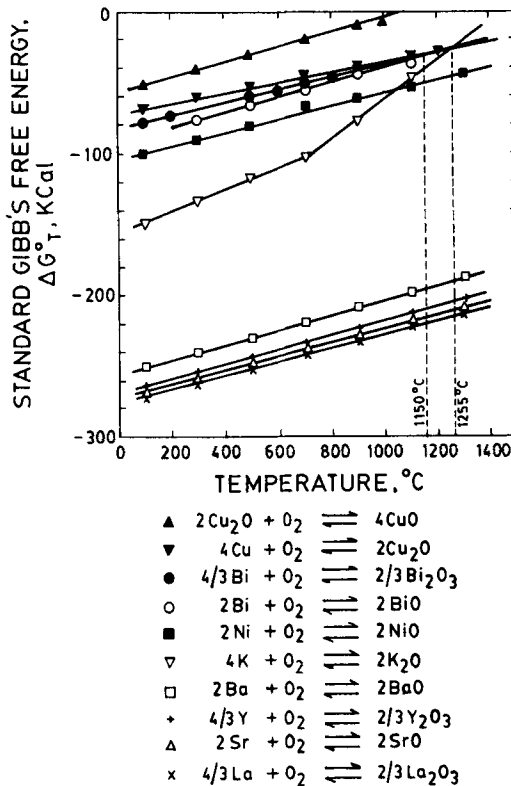


Figure 1. Standard Gibb's free energy vs temperature diagram for constituent oxides.

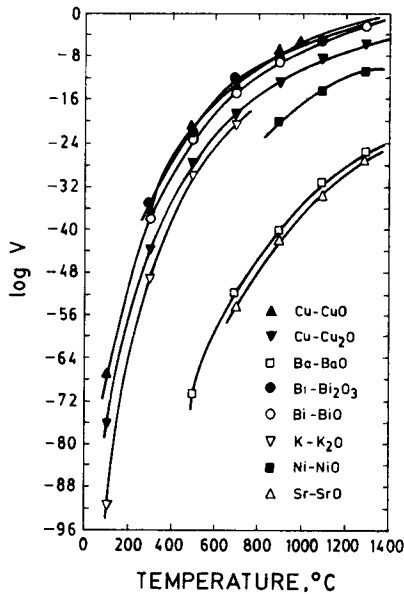


Figure 2. Temperature dependence of rate of volatilization of constituent oxides.

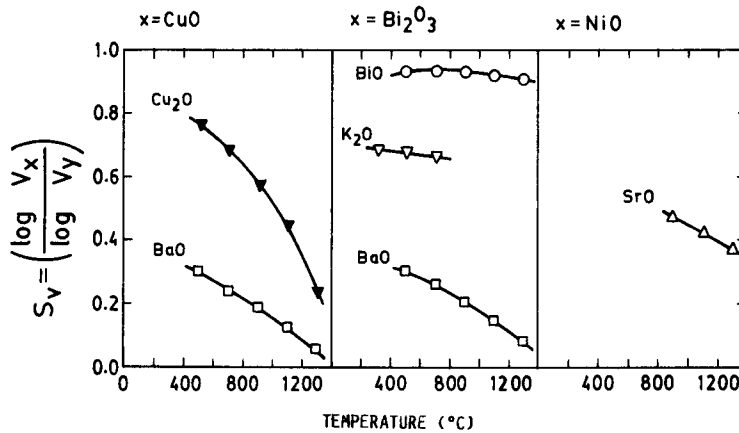


Figure 3. Relative stability ( $S_v$ ) vs temperature.

affecting the volatilizability of other constituent oxides especially at high temperatures, above 800°C.

Temperature dependences of  $S_v$  and  $S_p$  are shown in figures 3 and 4 respectively. In case of both  $S_v$  and  $S_p$ , higher the ratio, lesser the relative stability of the constituent oxide compared to that of the reference oxide of the particular system. In  $Y_2O_3$ -BaO-CuO system, CuO is the least stable oxide followed by  $Cu_2O$ , BaO and  $Y_2O_3$ . In BaO- $K_2O$ - $Bi_2O_3$  system,  $Bi_2O_3$  is the least stable oxide closely followed by BiO and then by  $K_2O$  and BaO. In  $La_2O_3$ -SrO-NiO system, NiO is the least stable oxide followed by SrO and  $La_2O_3$ . Thermodynamically, the reference oxide, CuO,  $Bi_2O_3$  or NiO, is found to be the least stable oxide amongst constituent oxides in these three systems  $Y_2O_3$ -BaO-CuO, BaO- $K_2O$ - $Bi_2O_3$  and  $La_2O_3$ -SrO-NiO

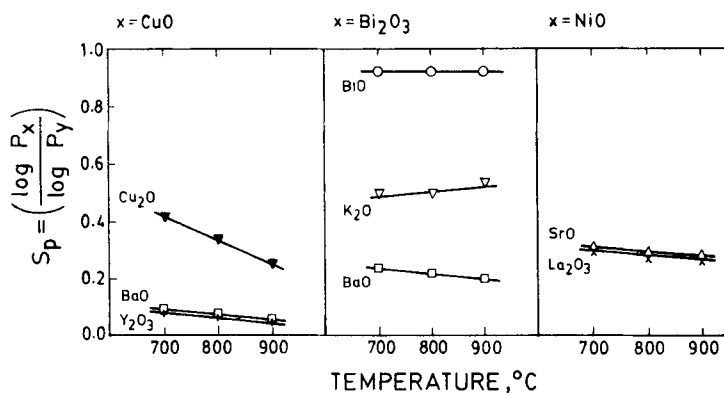


Figure 4. Relative stability ( $S_p$ ) vs temperature.

respectively. It is important to note that the relative stability of  $\text{Cu}_2\text{O}$  has a steep temperature dependence while that of  $\text{BiO}$  is almost insensitive to temperature.

#### 4. Conclusions

The stability of constituent oxides needs to be considered for effective processing of high  $T_c$  superconductor compositions. Thermodynamically, the reference oxide is the least stable amongst the constituent oxides in each of these systems.

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