



Thermodynamic properties of $Y_2Cu_2O_5$ compound

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Abstract

Enthalpy of formation of $Y_2Cu_2O_5$ (Y is Yttrium) was calculated by solution calorimetry with the help of high-temperature Calvet calorimeter ($T < 1400$ K). Dissolution experiments were performed in molten bismuth borate at 1033 K. The heat content of $Y_2Cu_2O_5$ was also measured in temperature range 298 and 1033 K. The equation for the enthalpy of formation of $Y_2Cu_2O_5$ versus the temperature was established. A coherent agreement was observed with all our measures in this work and with the literature values.

Keywords: Enthalpy of formation, $Y_2Cu_2O_5$, solution calorimetry, heat content.

1. Introduction

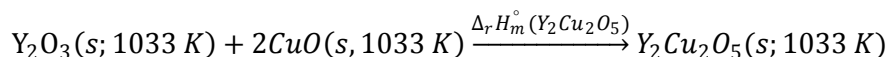
Phase diagram of Y_2O_3 - CuO_x system seems to be relatively simple; nevertheless, the existence of some compound is still being discussed. According to Konetzki *et al.* [1] and Watson *et al.* [2], this phase diagram (Figure 1) exhibits only one stoichiometric compound $Y_2Cu_2O_5$ which seems to be unstable at room temperature. Several temperatures of formation were proposed between 640 and 955 K. According to Kale *et al.* [3], $Y_2Cu_2O_5$ is transformed, at 1388 K, into $YCuO_2$ which decomposes peritectically at 1400 K. This transition is not observed by most authors who propose a melting temperature of Y_2CuO_5 close to that of $YCuO_2$.

The thermodynamic properties of $Y_2Cu_2O_5$ (202) have been determined by potentiometric methods [3-16] in the range 850-1340 K and by calorimetric measurements. The enthalpy of formation was determined by solution calorimetry in different acid baths at 298, 15K such as HCl (1M) [17]; HClO₄ (1.53M) [18]; HCl (6M) [19]; HCl(6M) [20] at 323 K; HNO₃ (4M) [21] and by drop solution calorimetry in molten lead borate at 975 K [22] and at 977 K [23]. In our previous work [22], at room temperature, the enthalpy of formation of compound 202 was determined from the enthalpies of solution in HNO₃ (4M) using the Calsol calorimeter [24]. The obtained formation enthalpy value (15.3 ± 6.5 kJ/mol) of $Y_2Cu_2O_5$ at room temperature is in good agreement with those determined in baths of different acids [18, 20]. This value is also in good agreement with that deduced by drop solution calorimetry [22; 23]. Some authors [17, 19] suggest a negative enthalpy that may be explained by incomplete dissolution in acid bath.

2. Apparatus and method

Several samples of the compound of 202 were prepared by solid state reaction and pelletization of the pure constituents in the L.M.P.G. –Grenoble –France.

The molar enthalpy of reaction of compound $Y_2Cu_2O_5$ was measured by solution calorimetry with the help of high-temperature Calvet calorimeter ($T < 1400$ K). It was deduced from the molar enthalpy of dissolution of compound, in suitable bath of oxide $0.6B_2O_3$ - $0.4Bi_2O_3$, following chemical equation described below:



The molar enthalpy of formation $\Delta_r H_m^\circ(A_a B_b)$ is given by the following relation:

$$\Delta_r H_m^\circ(Y_2Cu_2O_5; 1033 K) = \Delta_{sol} H_m^\circ(Y_2O_3) + 2\Delta_{sol} H_m^\circ(CuO) - \Delta_{sol} H_m^\circ(Y_2Cu_2O_5)$$

where $\Delta_{sol} H_m^\circ$ represent the molar enthalpy of solution at infinite dilution.

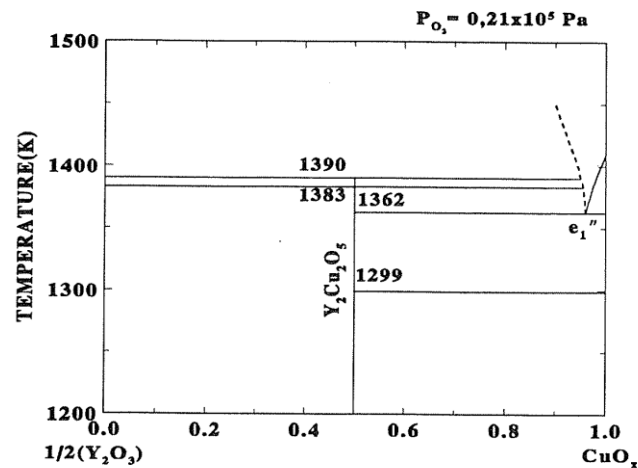
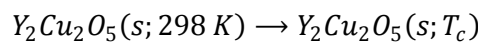


Figure 1: Phase Diagram of the Y_2O_3 - CuO_x System ($T > 1200K$) [1-2]

The heat content of the compound 202 was measured with respect to temperature from 298 to 1033 K. The heat enthalpy was deduced from the heat effects corresponding to the drop of small quantities of $Y_2Cu_2O_5$ at room temperature ($T_0 = 298 K$) in alumina crucible at the bottom of calorimeter cell at temperature T_c :



The measurement of heat content was made at four temperatures (413, 701, 838 and 1032 K). Then, this measurement was repeated about ten times for each temperature. At each temperature, the calorimeter was calibrated from the heat effects which produce the heating of small pieces of α -alumina from T_0 to T_c . The

corresponding enthalpy is well known [25].

3. Results and discussion

3.1. Enthalpy of formation of $Y_2Cu_2O_5$ at 1033 K

The enthalpy of formation of the compound 202 at 1033 K was determined in two manners: first by measuring the heat of dissolution of both oxides, Y_2O_3 and CuO , separately, then dissolving a mixture of both oxide in the proportion 1:2 corresponding to the $Y_2Cu_2O_5$ compound. In the case of dissolution of a mixture of both oxides, the analysis X, shows that the compound 202 does not appear during the annealing of the mixture in 1033 K during four hours corresponding to the time required for the stabilization of the calorimeter. The compounds Y_2O_3 ; CuO and $Y_2Cu_2O_5$ and the mixing ($Y_2O_3 + 2CuO$) were dissolved separately in the bath of oxide $0.6B_2O_3-0.4Bi_2O_3$ at 1033 K for various dilutions. Optical measurements showed that CuO oxide dissolves in the bath without stirring. For Y_2O_3 compound the agitation is imperative; its dissolution is difficult and becomes complete when it is dried and finely ground. The $Y_2Cu_2O_5$ compound dissolves quickly, however the agitation is necessary.

For each compound and each composition, four measurements of solution enthalpy were performed. The average value of the measures was carried according to the molar fraction as illustrated in figures 2, 3, 4 and 5. The enthalpy of solution at infinite dilution of compounds is deduced by extrapolation at zero molar fraction of the enthalpy of solution curve. The uncertainty attributed is obtained by extrapolation, at zero concentration, of fitted curves of the upper and lower points of uncertainty segments.

The results of the enthalpy of solution of compounds at 1033 K in $0.6B_2O_3-0.4Bi_2O_3$ bath and the enthalpy of formation ($\Delta_r H_m^\circ$) of $Y_2Cu_2O_5$ deduced are listed in table 1.

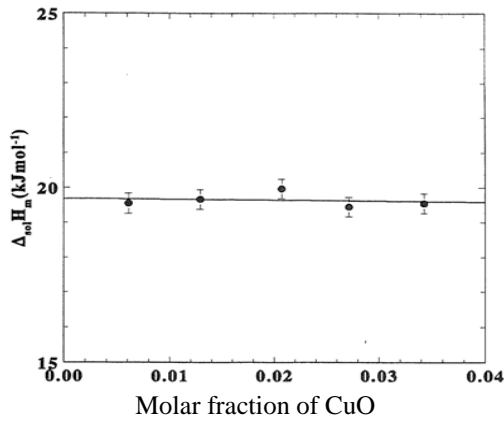


Figure 2: Enthalpy of solution in 0.6B₂O₃-0.4Bi₂O₃ at 1033 K versus molar fraction CuO

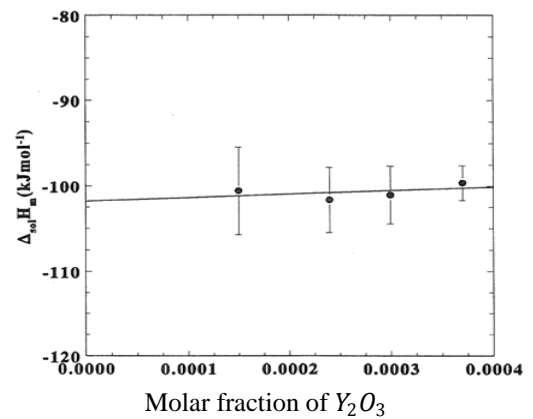


Figure 3: Enthalpy of solution in 0.6B₂O₃-0.4Bi₂O₃ at 1033 K versus molar fraction Y₂O₃

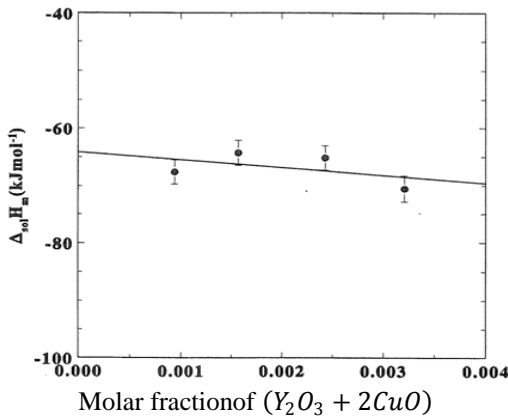


Figure 4: Enthalpy of solution in 0.6B₂O₃-0.4Bi₂O₃ at 1033 K versus molar fraction Y₂O₃ + 2CuO

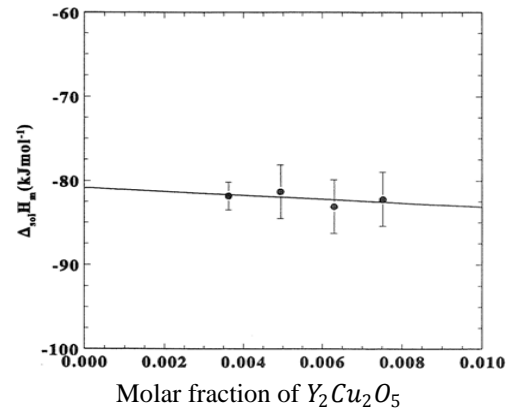


Figure 5: Enthalpy of solution in 0.6B₂O₃-0.4Bi₂O₃ at 1033 K versus molar fraction of Y₂Cu₂O₅

Table 1: Enthalpy of solution at 1033 K in 0.6B₂O₃-0.4Bi₂O₃ and enthalpy of formation of Y₂Cu₂O₅

^(a) Calculated by considering the different dissolutions made on simple oxides Y₂O₃ and CuO.

^(b) Calculated by using the enthalpy of solution of the mixture (Y₂O₃ + 2 CuO).

Compound	$\Delta_{sol}H_m^\infty$ (kJ/mol)	$\Delta_f H_m^\circ$ (kJ/mol)
CuO	19.69 ± 0.29	
Y ₂ O ₃	-101.83 ± 7.15	
Y ₂ O ₃ +2 CuO	-64.17 ± 2.08	
Y ₂ Cu ₂ O ₅	-80.84 ± 0.8	$18.40 \pm 8.5^{(a)}$ $16.70 \pm 2.9^{(b)}$

The value of enthalpy calculated according to (b) is included in the field of precision of that calculated according to (a) with a three times lesser uncertainty. The enthalpy value calculated in the manner (b) is more accurate as we consider only two measurement uncertainties. The calculation of the enthalpy of formation, using Y₂O₃ dissolution enthalpy which has a very important uncertainty was then avoided. The positive value of the enthalpy of formation shows that this compound is stabilized by entropic effect.

3.2. Heat content of Y₂Cu₂O₅ between 298 K and 1033 K

The heat content data of the compound Y₂Cu₂O₅ are consigned in table 2 and shown in Figure 6. This result agrees well with the literature data of heat content of Y₂Cu₂O₅ at 975 K [22] and 977 K [23] and calorific capacity measurements [26-27]. The heat enthalpy of Y₂Cu₂O₅ between 298 K and 1033 K can be fitted according to the following equation:

$$\Delta_{T_0}^T H(\text{kJ/mol}) = -50.29(\pm 1.01) + 0.154 (\pm 0.003)T + 5 \cdot 10^{-5}T^2$$

Table 2: Heat content of $\text{Y}_2\text{Cu}_2\text{O}_5$ versus temperature

TEMPERATURE (K)	$\Delta_{T_0}^T H(\text{kJ/mol})$
413	22.4 ± 0.4
701	79.4 ± 2.1
838	115.5 ± 1.9
1032	159.6 ± 3.5

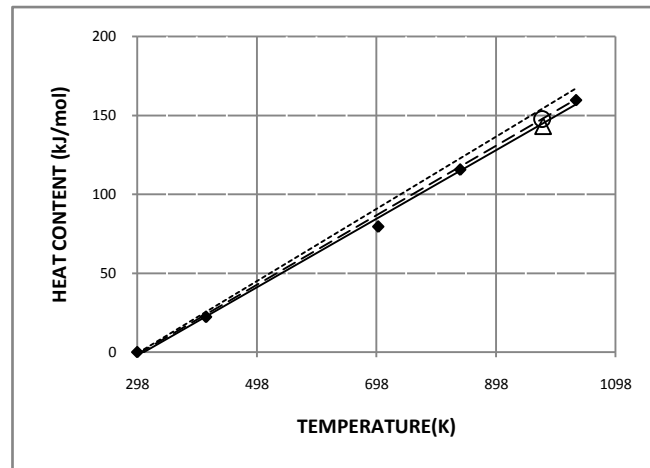


Figure 6: Variation of heat content of $\text{Y}_2\text{Cu}_2\text{O}_5$ versus the temperature

◆ : This study, [22], [23], [26], [27]

3.3. Variation of the enthalpy of formation of $\text{Y}_2\text{Cu}_2\text{O}_5$ versus the temperature

The expression of the enthalpy of formation of 202 according to the temperature can be thus, established from the results of heat content (Equation 1) and the value obtained from the enthalpy of formation of 202 at 298.15 K in our previous work [21].

The enthalpy of formation of 202 according to the temperature between 298 and 1033 K can be represented by the following equation:

$$\Delta_r H_{202}(\text{kJ/mol}) = 22.29(\pm 7.01) - 0.029(\pm 0.003)T + 2 \cdot 10^{-5}T^2$$

All results obtained for the compound $\text{Y}_2\text{Cu}_2\text{O}_5$ at 298,15K in the previous work; and at high temperature are consigned in table 3 and represented in figure 7.

Table 3: Enthalpy of formation of $\text{Y}_2\text{Cu}_2\text{O}_5$ with reference to oxides

T (K)	$\Delta_r H_m^\circ (\text{kJ/mol})$	Reference
298	15.4 ± 6.5	[21]
1033	$16.7 \pm 2.9^{(a)}$	This study
	$18.4 \pm 8.5^{(b)}$	This study
	13.8 ± 8 (equation (2))	This study
975	6.6 ± 2.9	[22]
977	5.1 ± 2.7	[23]

By taking into account the uncertainty of each measure, a good agreement exists between our three independent measures: enthalpy of formation at 298.15K and 1033K and the heat content obtained in the case of 202 compound.

Values of enthalpy of 202 established by Navrotsky and *et al.* at 975K [22] and Zhou *et al.* at 977 K [23] belong to the domain of uncertainty obtained in this study.

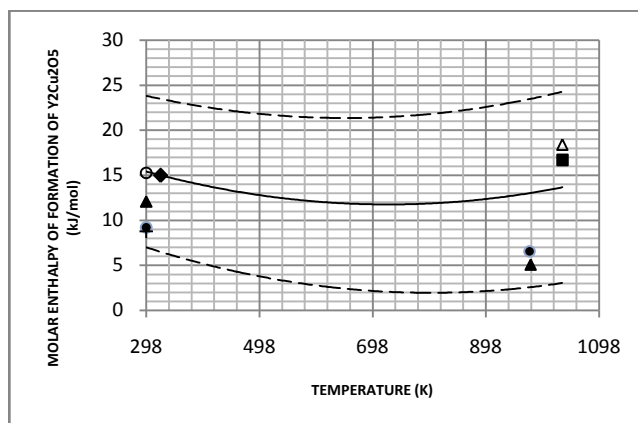


Figure 7: The enthalpy of formation of $Y_2Cu_2O_5$ versus the temperature

Δ : This work^a, \square : this work^b, O: [21],
 \bullet : [22], \blacktriangle : [23], + : [18], \blacklozenge : [19]
 — : Variation the enthalpy of formation versus temperature (this work)
 - - - - : Uncertainty of measure.

Conclusion

The enthalpy of formation and the heat enthalpy of $Y_2Cu_2O_5$ have been determined using a high-temperature Calvet calorimeter ($T < 1400$ K). The measurements performed in this work agree with those of literature. The positive value of the enthalpy of formation shows that this compound is stabilized by entropic effect.

References

- Konetzki R., R. Schmid-Fetzer; Technische University Clausthal, Brite/EuramProjet BREU0203C (1991).
- Watson A., B. B. Argent, Sheffield University, Brite /Euram project BREU0203C (1991).
- Kale G. M., K. T. Jacob, *Chem. Mater.*, 1 (1989) 515.
- Idemoto Y., K. Fueki, I. Ohyagi, *Physica C*, 199, (1992) 207.
- Glate F., H. Oppermann, W. Reichelt, *Z. Anorg. Allg. Chem.*, 606, (1991) 41.
- Azad A. M., O. M. Sreedharan, *Supercond.Sci. Technol.*, 3 (1990) 159.
- Borowiec K., K. Kolbrecka, *J. Less-Common Met.*, 163 (1990) 143.
- Fan Z., C. Ji, Z. Zhao, *J. Less-Comm. Metals*, 161 (1990) 49.
- Shimpo R., Y. Nakamura, *J. Jpn. Inst. Metals*, 54, N°5 (1990) 549.
- Suzuki R. O., S. Okada, T. Onishi, K. Ono., *Mat. Trans. JIM*, 31, N°10, (1990) 1078.
- Voronin G. F., S. A. Degterov, Y. Y. Skolis, Proc. 3rd German-Soviet Bilat. Seminar on High Temperature Supercond. Karlsruhe (1990) 562.
- Borowiec K., K. Kolbrecka, *Jpn. J. Appl. Phys.* 28 (1989) L1963.
- Skolis Y. Y., S. V. Kitsenko, *Russian J. Phys. Chem.*, 63 N°4 (1989) 632.
- Wiesner F., G. Krabbes, M. Ritschel, *Mat. Res. Bull.*, 24 (1989) 1261.
- Pankajavalli R., O. M. Sreedharan, *J. Mater. Sci. Lett.*, 8 (1989) 225.
- Tretyakov Y. D., A. R. Kauli, N. V. Makukhin, *J. Solid State Chem.*, (1976) 183.
- Grunin V. S., M. M. Pivovarov, I. B. Patrina, M. Rasumeenko, R. A. Bubnova, M. I. Domnina, M. M. Schultz, Dokl. Akad. Nauk. SSSR, 307 (1989) 143.
- Idemoto Y., J. Takahaschi, K. Fueki, I. Ohyagi, *Physica C*, 194, (1992) 177.
- Konkova T. S., J. N. Matyushin, J. H. Greenberg, V. B. Lazarev, I. S. Shapligni, *J. Chem. Thermodyn.*, 24 (1992) 225.
- Matskevich N. I., *J. Chem. Siberia*, 2 (1993) 119.
- Rais A., M. Ganteaume, M. Decressac, J. Rogez, J-C. Mathieu, *Ann. Chim. Fr.*, 20 (1995), 9.
- Navrotsky A., NIST Special Publication 804 (1990) 379.
- Zhou Z., A. Navrotsky, *J. Mat. Res.*, 7 N°11 (1992) 2920.
- Ganteaume M., M. Coten et M. Decressac, *Thermochem. Acta*, (1991) 178, 81.
- Standard Reference Materials 720, Synthetic Sapphire, Nat. Bur, U. S. Dept. Commerce Washington DC, (1982).
- Sharpataya G. A., A. D. Fedoseev, G. E. Nikiforovo, *Inorg. Mater.* 29 N°12 (1993) 1525.
- Pisch A., Thèse Doct. Institut Nationa Polytechnique de Grenoble, 22 Novembre 1994.

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