DSC Investigations of the CuO-BaO System

Ž. Živković[1]*, N. Štrbac[1], D. Živković[1], D. Grujičić[2]

[1]University of Belgrade, Technical Faculty VJ 12, 19210 Bor, Serbia and Montenegro;
*Phone/Fax: ++381 30 424 547; E-mail: jmm@eunet.yu
[2]University of Idaho, Department of Materials, Metallurgical, Mining and Geological Engineering, Moscow, USA

Abstract: Numerous data obtained by methods of thermal analysis are of the great importance for the determination and identification of the superconducting phases in the system Y-Ba-Cu-O. As a contribution, results of DSC investigations in the copper-based oxide CuO-BaO are presented in this work. Dependencies of specific heat on temperature are determined and values for heat effects at characteristic temperatures are given for investigated binary systems.

Keywords: thermal analysis, DSC, CuO-BaO system, superconductors

Received: December 14, 2004 **Accepted:** September 15, 2005

Introduction

Discovery of the high-temperature superconducting oxide ceramics in the middle eighties announced the beginning of a new era in the materials science, as well as in many different areas of high-temperature superconductors application. All this lead to increased scientific activity, aimed at characterization of these materials and development of new materials with similar or even better characteristics [1].

Especially, the discovery of superconductivity in the system Y-Ba-Cu-O has triggered a great interest in the copper-based oxides [1,2]. One of these activities is focused on thermal properties research of these ceramic materials, for they can provide a substantial insight into the theoretical aspect of superconducting transitions [2-4].

Considering the specific heat measurements and heat effects values determination, the literature data are numerous: Costa et al. [3,5] measured heat capacities of the high T_c superconductor $YBa_2Cu_3O_{7-}g$ by calorimetric measurements performed in a computer controlled continuous heating adiabatic calorimeter; Kishi et al. [6] investigated the specific heat anomaly of high T_c superconducting ceramics by AC calorimetry, while Niinisto and Karppinen [7] and Živković et al. [8] presented experimental results obtained by DTA and DSC for the study of the $YBa_2Cu_3O_{7-}g$ superconductor.

Since a larger number of works in this field is done on the superconducting phase $YBa_2Cu_3O_{7-}g$, we focused our research on DSC investigations of the copper-based oxide of CuO-BaO type as one of the main constituents of high-temperature superconducting Y-Ba-Cu-O ceramics.

Short scientific paper

EXPERIMENTAL

DSC technique was used in the experimental investigation of the CuO-BaO system. All experiments were performed on DSC 404 apparatus, by NETZCH, Germany.

Samples were synthesized by solid phase sintering of CuO and $BaCO_3$, in an oxygen atmosphere. Sample mass was 5mg. The samples were placed in Al_2O_3 crucibles. Sapphire was used as a standard for c_p evaluation.

RESULTS AND DISCUSSION

Composition of the investigated samples in the system CuO-BaO are presented in Table 1.

Results obtained by DSC measuring in the temperature interval up to 1000 °C, which include dependencies of specific heat on temperature and determined values for heat effects at characteristic temperatures, are given in Fig.1.

Table 1. Composition of the investigated samples in CuO-BaO system.

Sample	%wt CuO	%wt BaO	x_{CuO}	x_{BaO}
1	20	80	0.32	0.68
2	40	60	0.56	0.44
3	60	40	0.74	0.26
4	80	20	0.89	0.11

First, endothermic peak occurs in the temperature interval 810-812 °C and the enthalpy value is relatively constant. This can be explained by the phase transformation of $BaCO_3$, used in the preparation of mixture, from rhombic to hexagonal structure.

Endothermic peaks at higher temperatures, in the interval 920-935 °C, should be considered together with the known phase diagram of the investigated CuO-BaO system [9] (Fig. 2).

According to the literature data [10-12], eutectic line between barium cuprate and CuO is not yet fully estimated. WONG ET AL. [10] determined the eutectic slightly above 900 °C at about $x_{BaO} = 0.38$, while NEVRIVA ET AL. [11] and LICCI ET AL. [12] found the eutectic point at 925 °C with $x_{BaO} = 0.28$. Having these facts in mind, one can conclude that endothermic peaks at higher temperatures obtained in this work by using the DSC technique, correspond to the eutectic line in the CuO-BaO system, while the dicsrepancy between reported values and our results can possibly be caused by various materials used as sample holder, presumably due to the formation of an intermediate phase Ba_4PtO_6 [11].

Furthermore, the enthalpy dependencies on the composition, given in Fig. 3, show that the maximal enthalpy value corresponds to the eutectic composition. Moving left or right related to this value show on the enthalpy value decreasing, because of the less quantity of melted phase.

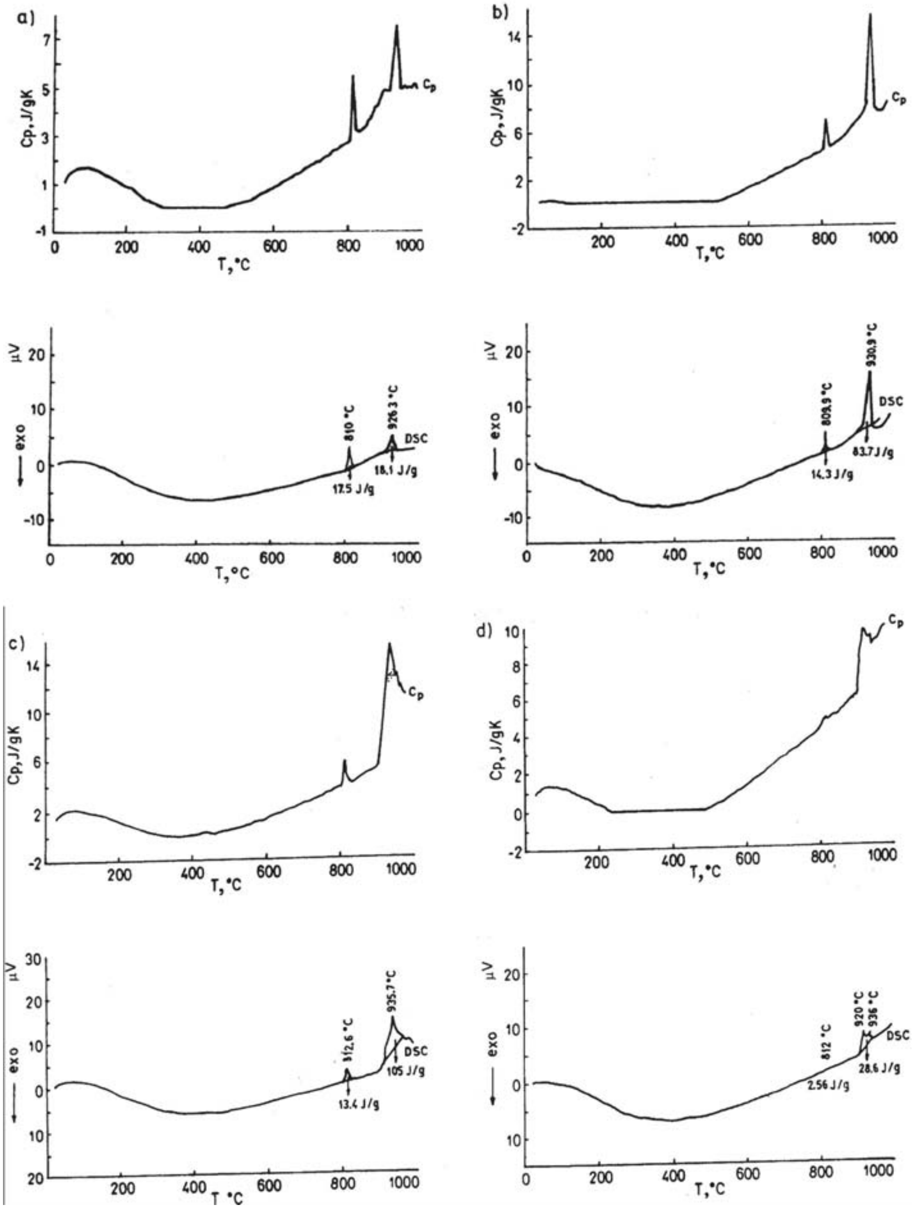
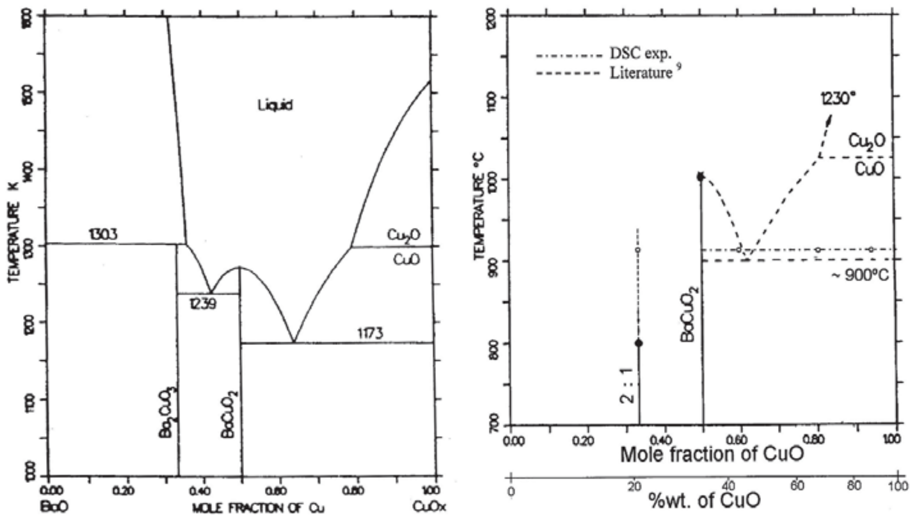


Figure 1. DSC and specific heat dependencies on temperature for investigated samples CuO-BaO (a - 20 % wt CuO; b - 40 % wt CuO; c - 60 % wt CuO; d - 80 % wt CuO)



a) Phase diagram according to [9]

b) Part of the phase diagram confirmed by DSC ex periments in this work

Figure 2. CuO-BaO phase diagram.

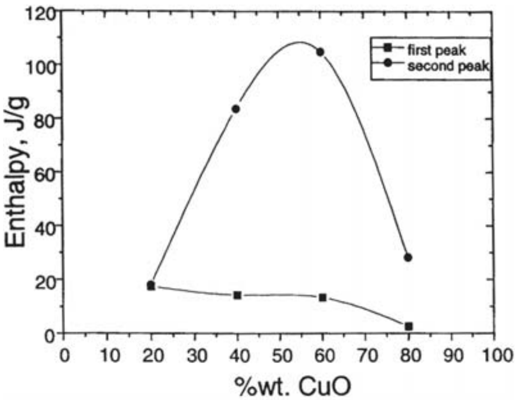


Figure 3. Enthalpy dependence on composition.

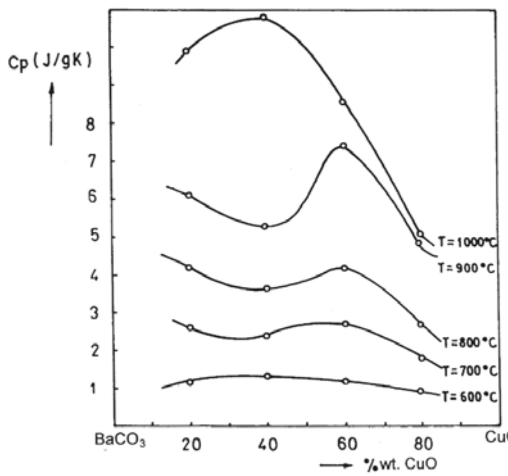


Figure 4. Specific heat dependence on composition.

The analysis of c_p variation with temperature and composition, shown in Figure 4., also confirmed mentioned assumption, because a peak on the curve is noted at the eutectic temperature and composition.

So, the obtained DSC results for the CuO-BaO system gave us not only the values of the specific heat and enthalpies of the characteristic peaks, but can also be used in the interpretation of the CuO-BaO phase diagram, in the investigated temperature interval up to 1000 °C.

Acknowledgement

The authors express their thanks to Prof. Jaroslav Šestak, Institute for Physics, Czech Academy of Sciences (Prague, Czech Republic) for his help and recommendations.

References

[1] Šestak, J. (1989): *Thermochim. Acta* 148, pp. 235-248.

[2] Bednorz, J.G., Muller, K.A. (1986): *Z. Phys.* 64B, p. 189.

[3] Costa, G.A., Ferretti, M., Olcese, G.L. (1988): *Thermochim. Acta* 137, pp. 65-70.

[4] Nevitt, M.V., Crabtree, G.W., Klippert, T.E. (1987): *Phys. Rev.* 36B, pp. 2398-2400.

[5] Costa, G.A., Ferretti, M., Fornasini, M.L., Giordani, M., Olcese, G.L. (1988): *Thermochim. Acta*, 133, pp. 49-54.

[6] Kishi, A., Kato, R., Azumi, T., Okamoto, H., Maesono, A., Ishikawa, M., Hatta, I., Ikushima, A. (1988): *Thermochim. Acta* 133, pp. 39-42.

[7] Niinisto, L., Karppinen, M. (1989): *J.Therm. Anal.* 35, pp. 319-327.

[8] Živković, Ž., Živković, D., Štrbac, N. (1992): *Mining and Metallurgy Quarterly* 39(1-2), pp. 69-82.

[9] Lee, B.J., Lee, D.N. (1989): *J. Am. Ceram. Soc.* 72(2), pp. 314-319.

[10] Wong-Ng, W.K., Davis, K.L., Roth, R.S. (1988): *J. Am. Ceram. Soc.* 71, p. 64.

[11] Nevriva, M., Pollert, E., Matejkova, L., Triska, A. (1988): *J. Crystal Growth* 91, p. 434.

[12] Licci, F., Scheel, H.J., Besagni, T. (1988): *Physica C* 153-155, pp. 431.