Journal of Alloys and Compounds, 195 (1993) 53–56
JALCOM 7413

Phase equilibria in the binary $TlO_{1.5}$-CuO, $TlO_{1.5}$-BaO and ternary $TlO_{1.5}$-BaO-CuO systems

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Revised version

Abstract

We present the phase diagrams of the $TlO_{1.5}$-CuO, $TlO_{1.5}$-BaO, and $TlO_{1.5}$-BaO-CuO systems under a pressure of 1 atm of oxygen which allowed us to prepare pure $Tl_2Ba_2CuO_{6\pm x}$ using $Tl_2Ba_2O_5$ as precursor and the properties of quasibinary sections. The stoichiometric thallium cuprate was found to have the orthorhombic-type structure and was not superconducting. Accurate thermogravimetric measurements showed that the tetragonal symetry is observed with at least 10% thallium deficiency.

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1. Introduction

In the study of the superconducting properties of the high T_c thallium-based cuprates $Tl_mBa_2Ca_{n-1}Cu_nO_y$, the preponderant role of the method for preparation emerges from a literature review [1] and reveals the importance of the phase formation and phase equilibria knowledge. In the present work we present the phase diagrams of the $TlO_{1.5}$-CuO, $TlO_{1.5}$-BaO and $Tl_{1.5}$-BaO-CuO systems. The congruent formation of the mixed oxide $Tl_2Ba_2O_5$ allows to consider the isopletic line with CuO as a quasibinary system. Thus $Tl_2Ba_2CuO_{6\pm x}$ may be prepared without trace of $BaCuO_2$, the main poisining impurity in this system. We have also inverstigated the transition from orthorhombic to tegragonal symetry in terms of phase equilibrium and the low temperature behaviour of the two compounds is reported.

2. Experimental details

Samples for the phase diagram studies were prepared by solid state reaction of Tl_2O_3 (99.9%), BaO_2 (99%) and CuO (99,9%) powders (Rhône-Poulenc). The temperature and duration of the base heat treatments were dependent on the system under investigation and are reported in table 1. $Tl_2Ba_2O_5$ with CuO additions was used as precursor for preparing $Tl_2Ba_2CuO_{6\pm x}$.

Differential Thermal Analysis coupled with thermogravimetric measurements (DTA/TG) was used to check for phase transition and weight losses. Assuming the latter to be essentially due to thallium oxide vaporization the thallium content in the samples could be precisely known. It has been controlled by plasma emission spectroscopy.

Phase identification and transition (in the case of $Tl_2Ba_2CuO_6$) was obtained by X-Ray diffractometry.

A.c. susceptibility was used for the measurements of the superconducting transition temperature T_c but also as analytical support for the detection of magnetic impurities at a few ppm level.

3. The binary systems

- $TlO_{1.5}$-CuO: Very little is known in this system excepted the work of Zhou et al [2] who reported 0.12% copper solubility in thallium oxide. In fact, we have found a simple eutectic system (fig. 1)

0925-8388/93/$06.00

Table 1: Summary of heat treatments in the thallium-based systems

$TlO_{1.5}$-BaO	$TlO_{1.5}$-CuO	$TlO_{1.5}$-BaO-CuO	Tl_2-Ba_2O_5-CuO
750°C/5min*	500°C/2H	750°C/5min*	630°C/24H
+775°C/12H	+700°C/1H	+775°C/12H	+840°C/15min
	+650°C/16H	+630°C/12H	+630°C/72H

* the heating rate was 1°C/min

with an eutectic temperature T_E=760°C. We could not confirm the existence of the thallium solid solution from the value of the Tl_2O_3 lattice parameter : a=10.551 (5) Å.

- $TlO_{1.5}$-BaO: The system is reported in figure 2 as it results from our previous study [3]. The main features are :

- a small region of the thallium oxide solid solution

- 4 intermediate compounds Tl_2BaO_4, $Tl_6Ba_4O_{13}$, $Tl_2Ba_2O_5$ and $Tl_2Ba_4O_7$.

- the congruent melting of $Tl_2Ba_2O_5$ which may be used as precursor for the formation of $Tl_2Ba_2CuO_6$ with controlled thallium content.

- BaO-CuO: in the literature we found informations about this system [4,5] which remains doubtful in the BaO-rich field. We did not yet investigate this system but our XRD patterns of samples containing mixed oxide of Ba and Cu could be indexed with the known $BaCuO_2$ and $Ba_2Cu_3O_5$ structures.

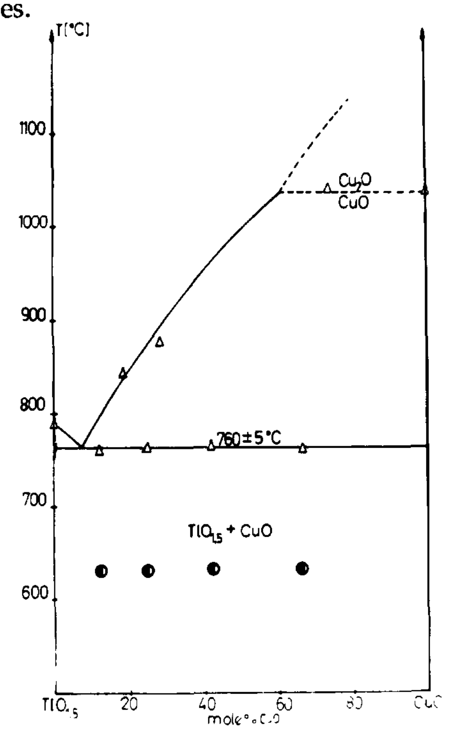

Fig. 1: $TlO_{1.5}$-CuO system

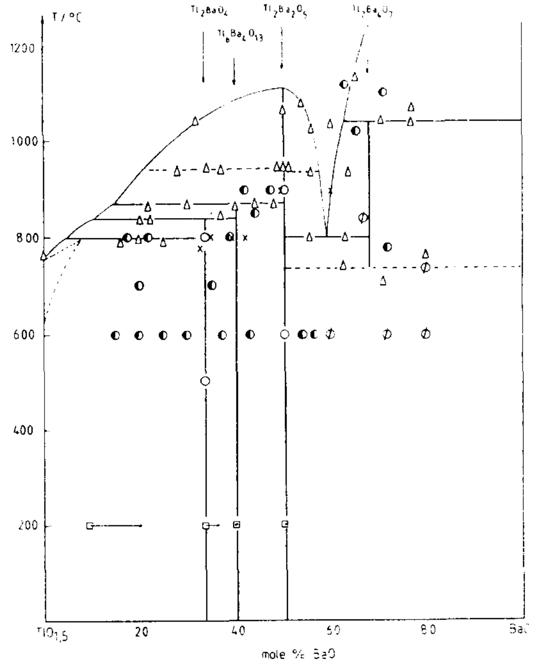

Fig. 2: $TlO_{1.5}$-BaO system

Δ DTA ; ◐ 2 phases ; ○ single phase

ɸ non equilibria ; □ plasma emission

4. The quasi-binary $Tl_2Ba_2O_5$-CuO system

As previously mentionned, the congruent melting of $Tl_2Ba_2O_5$ allows to consider the isopletic line $Tl_2Ba_2O_5$-CuO as a quasi binary section of the ternary $TlO_{1.5}$-BaO-CuO system. Consequently, only compounds corresponding to a combination of $Tl_2Ba_2O_5$ and CuO may be formed in this line, thus excluding for instance $BaCuO_2$. The system in figure 3 shows that $Tl_2Ba_2CuO_6$ is formed by peritectic reaction from $Tl_2Ba_2O_5$ and the liquid at 930 ± 5°C with reduced weight losses, namely less than 0.1 thallium/formulae unit. The resulting cuprate is orthorhombic and the lattice cell remains constant along the isopletic line suggesting a very limited homogeneity range. We have found [6] that the formation of the tetragonal $Tl_2Ba_2CuO_6$ from the orthorhombic material

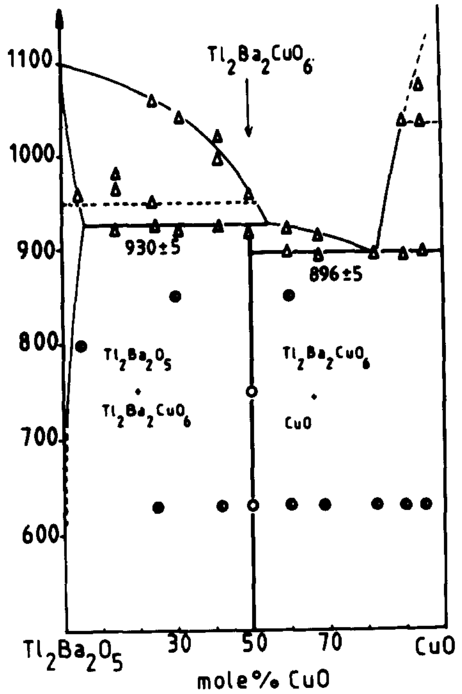

Fig. 3: $Tl_2Ba_2O_5$-CuO

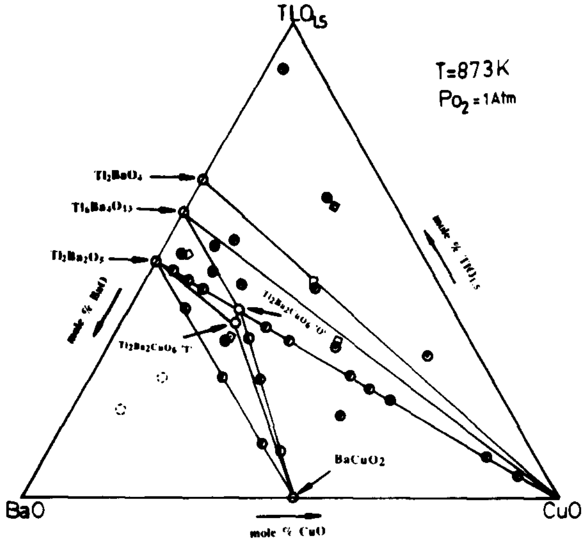

Fig. 4: $TlO_{1.5}$-BaO-CuO

implies thallium departure and actually the tetragonal compound should be better described as $Tl_{1.7}Ba_2CuO_{6\pm x}$, the inverse reaction occuring by thallium additions. It is noteworthy that all superconducting compounds in the double TlO series correspond in fact to a thallium stoichiometry of 1.7. This result may be drastically modified in samples prepared under high pressure (100 atm) of oxygen or argon. Companion papers in this Conference [7,8] indicate that the orthorhombic to tetragonal transition is influenced by the gaz nature. Under oxygen the orthorhombic $Tl_2Ba_2CuO_{6\pm x}$ is observed whereas the tetragonal structure is formed under argon without significant thallium losses suggesting a pressure dependence on the phase limits. The presence of $Ba_2Cu_3O_x$ and CuO as impurity phases after the high temperature-high pressure treatment producing tetragonal $Tl_2Ba_2CuO_6$ has to be compared with the presence of $BaCuO_2$ after the 1atm pressure elaboration which resulted in thallium losses.

From high temperature XRD in flowing helium, we observed the structural change, associated with formation of $BaCuO_2$ at 630°C. This result is in agreement with DTA/TG measurements performed in helium, argon or vacuum and revealing that the weight losses thus occur from 600°C. The formation of $BaCuO_2$ as impurity phase may be understood on the basis of the ternary phase diagram assuming thallium oxide vaporization.

5. The ternary $TlO_{1.5}$-BaO-CuO system at 600°C

The isothermal section at 600°C of the ternary $TlO_{1.5}$-BaO-CuO system is displayed in figure 4. In the field of interest surrounding the $Tl_2Ba_2CuO_{6\pm x}$ compounds, we observe that $Tl_6Ba_4O_{13}$, $Tl_2Ba_2O_5$, $BaCuO_2$ and CuO may be found in equilibrium with either orthorhombic or tetragonal $Tl_2Ba_2CuO_6$. Plasma emission analysis confirmed the compositions of the samples with an accuracy of ± 2 mole % for Tl. Studies of isopletic sections in order to localise the invariant equilibrium are under work.

6. A.C. Susceptibility

The a.c. susceptibility measurements in the range 10-150 K revealed a magnetic susceptibility of about 10^{-4} SI, in agreement with results of Junod et al. [9]. Our orthorhombic $Tl_2Ba_2CuO_6$ samples were not superconducting but a large lowering of the magnetic susceptibility was observed at about 50K (fig. 5), independent of an external applied field. A magnetic ordering is thus suspected. This behaviour may be an intrinsic property of the ortho

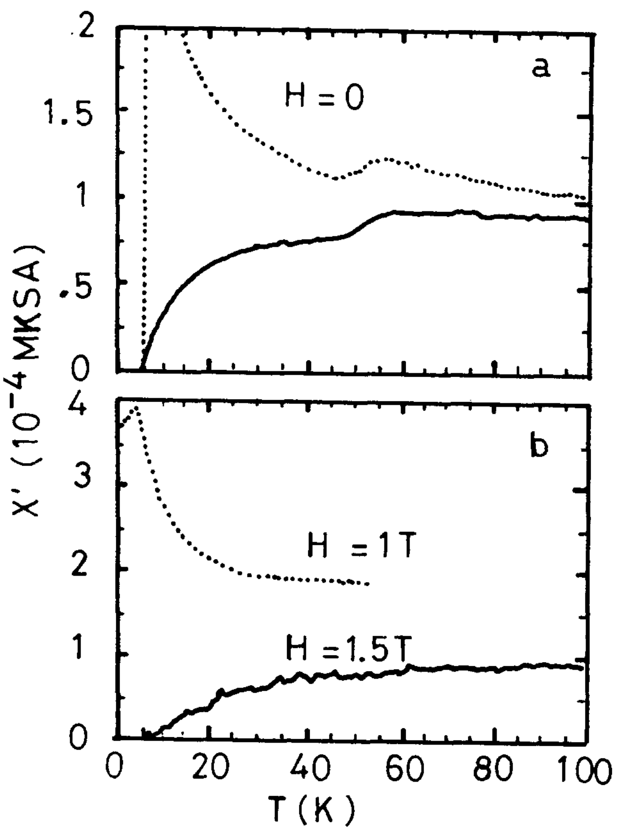

Fig. 5: A.c. susceptibility of ortho (-) and tetra (...) $Tl_2Ba_2CuO_6$
a : zero external field
b : non zero external field

rhombic structure and is counterbalanced by the presence of impurity phases ($BaCuO_2$, CuO...). For instance, we notice that samples prepared under high oxygen pressure show a Curie-like behaviour [8] similar to that observed for samples prepared under 1 atm and belonging to the $BaCuO_2$-CuO-$Tl_2Ba_2CuO_6$ (ortho), $Tl_2Ba_2CuO_6$ (ortho)-$Tl_{1.7}Ba_2CuO_6$ (tetra)-$BaCuO_2$, and $Tl_{1.7}Ba_2CuO_6$-$Tl_2Ba_2O_5$-$BaCuO_2$ ternary fields.

Tetragonal $Tl_{1.7}Ba_2CuO_6$ becomes superconducting at temperatures depending on the oxygen concentration. In figure 5, the transition temperature at 6K of a sample presenting poor superconductivity is preceded by a positive contribution characteristic of traces of $BaCuO_2$ [6], not observed by XRD. Thus, it appears that a.c. susceptibility, more than a superconducting sensor may be, with the ability to detect magnetic impureties at a ppm level, a powerful tool for materials characterization.

7. Conclusion

We have reported the phase equilibria at an oxygen pressure of 1 atm, in binary and ternary systems based on Tl_2O_3, CuO and BaO which allowed us to prepare the first member of the double TlO-cuprate $Tl_2Ba_2CuO_6$ by controlling the thallium content on the $Tl_2Ba_2O_5$-CuO line. We showed that formation of tetragonal, superconducting $Tl_{1.7}Ba_2CuO_6$ is not a simple allotropic transition from the orthorhombic $Tl_2Ba_2CuO_6$ but implies both thallium and oxygen deficiency. Accurate a.c. susceptibility measurements have been used as a powerful sensor of magnetic impurities at a low level.

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