

# Experimental determination of the eutectic temperature in air of the CuO–TiO<sub>2</sub> pseudobinary system

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## Abstract

Eutectic temperature and composition in the CuO–TiO<sub>2</sub> pseudobinary system have been experimentally determined in air by means differential thermal analysis (DTA), thermogravimetry (TG) and hot-stage microscopy (HSM). Samples of the new eutectic composition treated at different temperatures have been characterized by X-ray diffraction (XRD) and X-ray absorption near-edge structural spectroscopy (XANES) to identify phases and to determine the Cu valence state, respectively. The results show that the eutectic temperature in air is higher by 100 °C (~1000 °C) for a Ti-richer composition ( $X_{\text{TiO}_2} = 25$  mol%) than the one calculated in the literature. The reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> takes places at about 1030 °C. The existence of Cu<sub>2</sub>TiO<sub>3</sub> and Cu<sub>3</sub>TiO<sub>4</sub> has been confirmed by XRD in the temperature range between 1045 and 1200 °C. © 2011 Elsevier Ltd. All rights reserved.

*Keywords:* Powder-solid state reaction; Firing; TiO<sub>2</sub>; Transition metal oxides; Eutectic

## 1. Introduction

The eutectic reaction in the CuO–TiO<sub>2</sub> system has recently gained attention due to its relevance in several applications. The eutectic liquid can aid to improve the sinterability by means of a reactive liquid-phase sintering mechanism.<sup>1,2</sup> CuO is known to be the most effective additive for promoting the anatase–rutile phase transformation. The lower valence of the Cu<sup>2+</sup> ion compared to the Ti<sup>4+</sup> ion is compensated by an increase in the oxygen vacancy concentration which facilitates the phase transformation.<sup>3</sup> The addition of 2 wt% CuO to TiO<sub>2</sub> anatase decreases the sintering temperature from 1350 to 900 °C.<sup>4</sup> Al<sub>2</sub>O<sub>3</sub> ceramics can also sintered with low CuO and TiO<sub>2</sub> amounts that decrease sintering temperature from 1600 to 1360 °C.<sup>5</sup> Another application of the CuO–TiO<sub>2</sub> eutectic reaction is to enhance the metal Cu oxidation. A small amount of TiO<sub>2</sub> is added to metal Cu for the formation of large CuO crystals.<sup>5</sup> Novel materials based in the CaO–CuO–TiO<sub>2</sub> system, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> (CCTO) has recently attracted much interest due to its giant dielectric constant (up to 10<sup>5</sup>) which is almost frequency independent and

shows good temperature stability in the range between 100 and 400 K.<sup>6</sup>

Recently Jacob et al.<sup>7,8</sup> have determined the heat capacity of CCTO and the phase diagram for the pseudoternary system CaO–TiO<sub>2</sub>–CuO/Cu<sub>2</sub>O at 1000 °C as a function of oxygen partial pressure, without point to the presence of liquid phase except when the CCTO decomposed at ~1167 °C in TiO<sub>2</sub>, CaTiO<sub>3</sub> and a liquid phase rich in Cu<sub>2</sub>O. Veith et al.<sup>9</sup> have determined the phase relationship in the ternary system CuO–TiO<sub>2</sub>–CaO at 950 °C in air where the copper oxide transforms into a liquid phase during the sintering treatment and leads to anomalous grain growth. It is necessary to emphasize, that the synthesis and sintering of CCTO is always carried out in air and the microstructure always present in rest of a liquid phase that assist the sintering process. That liquid phase is attributed to the eutectic point in the CuO–TiO<sub>2</sub> system. The eutectic temperature of the CuO–TiO<sub>2</sub> binary phase diagram is calculated at 919 °C for  $X_{\text{TiO}_2} = 16.7$  mol% at PO<sub>2</sub> = 1 atm,<sup>10</sup> although the authors indicate that the eutectic reaction in air would take place at lower temperature than 900 °C. According to previous data, there are discrepancies about the eutectic point at temperatures lower than 1000 °C in ternary systems when CuO and TiO<sub>2</sub> are involved. If there are stable phases formed below the binary eutectic temperature the liquid phase would appear due to the presence of unreacted CuO and TiO<sub>2</sub>.

Besides the unknown eutectic temperature in air for the CuO–TiO<sub>2</sub> system there exist large discrepancies in the literature about the Cu<sup>2+</sup> to Cu<sup>+</sup> reduction temperature. Guillemet-Fritsch et al.<sup>11</sup> point out that Cu<sup>2+</sup> cations are reduced to Cu<sup>+</sup> at  $T \sim 1000$  °C and affirm that due to a possible liquidus temperature below 1000 °C in CuO-rich region, pure CuO cannot be treated higher than 1000 °C. Lu et al.<sup>10</sup> proposed that in air CuO would not melt but decomposes at 1031 °C into Cu<sub>2</sub>O. Tsang et al.<sup>12</sup> point to that CuO is the stable copper oxide phase up to  $1061 \pm 3$  °C at the copper-rich end of the system and Cu<sub>2</sub>O is stable until the liquidus is reached at 1121 °C at 1 atm of oxygen. Other authors proposed that Cu<sub>2</sub>O melts incongruently at 1134 °C.<sup>13</sup> Anyway, Jeong and Cho<sup>14</sup> assumed that the boundary between CuO and Cu<sub>2</sub>O is close to 1000 °C. Both Cu<sub>2</sub>O and CuO are nonstoichiometric oxides, with copper vacancies, Cu<sub>2- $\delta$</sub> O and Cu<sub>1- $\gamma$</sub> O, respectively and both are p-type semiconductor.<sup>14,15</sup> According to these discrepancies about the Cu valence, the CuO–TiO<sub>2</sub> binary is a very complex system.

This binary eutectic, depending on the reactivity of the different oxides involved, allows controlling the presence of liquid phase and therefore the microstructural development. Materials in which CuO and TiO<sub>2</sub> are involved as for example, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> ceramics, the giant dielectric constant is consequence of the final microstructure. The experimental procedure carried out to avoid the contamination of the samples with the Pt substrate according to the literature<sup>16</sup> does not allow reach equilibrium conditions and therefore the identified phases at high temperature could be metastables.

The aim of this study is to determine the eutectic temperature and the composition in the CuO–TiO<sub>2</sub> system in air related to the reduction temperature of Cu<sup>2+</sup> to Cu<sup>+</sup>. The eutectic temperature is a useful tool for designing new sintering strategies of materials which contain both CuO and TiO<sub>2</sub> and other oxides.

## 2. Experimental procedure

High purity raw materials were used: CuO (99%, Sigma–Aldrich) with an average particle size of 1.10  $\mu$ m and anatase TiO<sub>2</sub> (99.5%, Merck) with an average particle size of 0.74  $\mu$ m. Corresponding amounts of components (in mol%) were attrition milled by using zirconia balls for 3 h in water and then dried at 60 °C.

Thermal treatments of the samples at temperatures over 1000 °C have been carried out in air atmosphere for 15 min in Pt crucibles, since the crucibles are not inert in respect to Cu compositions. Pt diffuses in to Cu-rich compositions, with the contamination advancing from the contact with the capsule to the interior. After 2 h of thermal treatment, 10% of the sample was affected.<sup>16</sup> In all the cases the heating rate was 10 °C/min and samples were rapidly cooled by quenching in liquid nitrogen in order to retain the high temperature phase.

Thermal characterization of the samples was studied by differential thermal analysis and thermogravimetry in air atmosphere at 10 °C/min (DTA–TG, Setsys Evolution 1750 °C of SETARAM Instruments, France). Hot Stage Microscope (Axel Hesse Instruments, Germany), was carried out from RT to 1200 °C in air atmosphere with a heating rate of 10 °C/min on

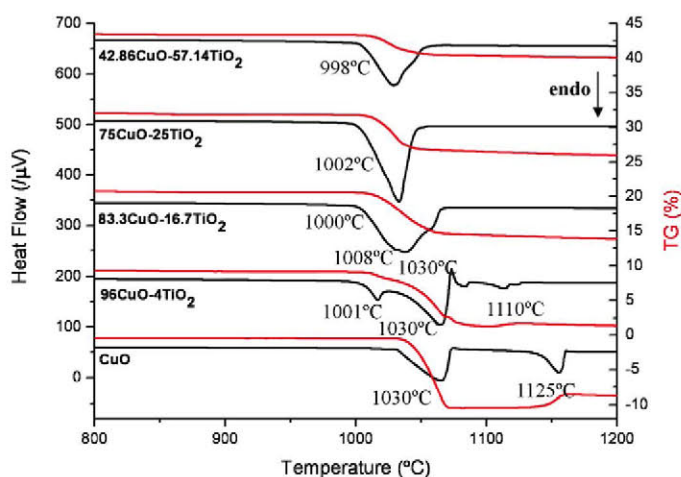


Fig. 1. DTA–TG analysis in air of pure CuO and experimental compositions prepared (in mol%).

platinum substrate. X-ray diffraction analysis was performed on a diffractometer X’Pert PRO of Panalytical using CuK $\alpha$ 1 radiation. Microstructural characterization was carried out by a SEM Hitachi T-1000. Room temperature XANES spectra were measured at the SPLINE line of ESRF at Cu K-edge in transmission. Beam energy was calibrated by the adsorption edge of the Cu foil at energy of 8979 eV.

## 3. Results and discussion

Fig. 1 shows the DTA–TG curve of pure CuO where two sharp endothermic peaks are observed. The onset of the first peak at 1030 °C corresponds to the reduction of CuO to Cu<sub>2</sub>O, with a weight loss of 10.5 wt% according to TG. This temperature is lower than the temperature established by Tsang et al.<sup>12</sup> at  $1061 \pm 3$  °C, although at PO<sub>2</sub> = 1 atm. The onset of the peak of DTA indicates the first measurable sign of the process. Point to that DTA–TG profiles and therefore the temperature for any process can be significantly affected by the heating rate and the transformation kinetics. According to this, higher or lower heating rates give place to displacement in both the onset and the peak temperatures. Second peak at 1125 °C corresponds to the congruent melting of Cu<sub>2</sub>O. This temperature is slightly lower than to the one observed in Hot Stage Microscope analysis (Fig. 2). Hot stage microscopy data are in agreement with the peak temperature in the DTA analysis that usually indicates the end of the process and that it can overestimate by up to 30–40 °C the transformation temperature.

This liquidus temperature measured in the present work is in agreement with the one previously reported by Tsang et al.<sup>12</sup> for the congruently melting of Cu<sub>2</sub>O (1121 °C) at an oxygen partial pressure of 1 atm. Massalski<sup>13</sup> proposed that Cu<sub>2</sub>O melts incongruently at 1134 °C although Hot Stage Microscope analysis presented here confirms the congruent melting. The congruently melting of Cu<sub>2</sub>O is accompanied by a weight gain of 2 wt% approximately. Different authors point to the existence of non-stoichiometries phases in CuO and Cu<sub>2</sub>O, as well indicate that copper vacancy generation is unfavoured with increasing temperature and the important defects in Cu<sub>2- $\delta$</sub> O at high oxygen

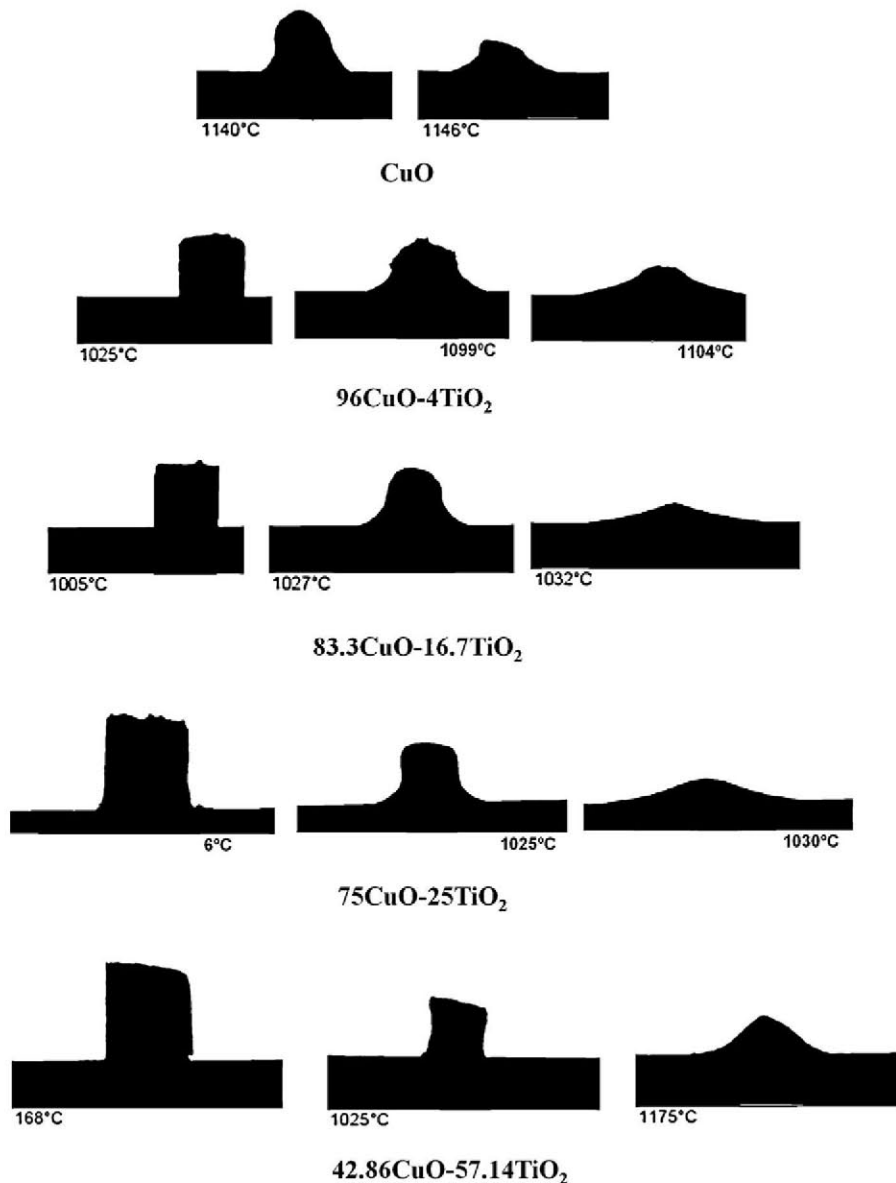


Fig. 2. Hot stage microscopy images in air of pure CuO and experimental compositions prepared (molar ratio).

activities are neutral interstitial oxygen ions (oxygen traces diffusion).<sup>14,15</sup> The weight gain during the congruently melting of  $\text{Cu}_2\text{O}$  would be related to the oxygen enrichment favoured in liquid phase, giving rise to a nonstoichiometric oxygen-rich phase or a sorption phenomena which can yield partial re-oxidation of  $\text{Cu}_2\text{O}$ .<sup>2</sup>

The DTA–TG results for the different CuO/TiO<sub>2</sub> mixtures studied in this work are also presented in Fig. 1, while the hot stage microscopy data are shown in Fig. 2. Point to that the endothermic peaks corresponding to the eutectic melts and the reduction temperature of CuO to  $\text{Cu}_2\text{O}$  are asymmetric, indicating a kinetic control of both reactions due to the high speed of the thermal treatment.

Composition 1 corresponds to the Cu-rich intergranular secondary phase determined by EDX in sintered CCTO samples

by Leret et al.<sup>17</sup> DTA analysis of this composition shows three endothermic peaks. The onset of the first peak at 1000 °C corresponds to the eutectic temperature and the second peak, observed at 1030 °C, relates to the reduction of CuO to  $\text{Cu}_2\text{O}$  according to DTA of pure CuO (Fig. 1). The third endothermic peak at ~1090 °C is in fact composed of two overlapped peaks and indicates the liquidus temperature for the complete melting. This melting is accompanied by a slight gain of weight according to TG analysis related to the oxygen enrichment of the liquid phase. It is remarked that the presence of a small amount of TiO<sub>2</sub> reduces both the temperature and the amount of weight gain. Hot Stage Microscope analysis, Fig. 2, show negligible deformation at the eutectic temperature, 1025 °C, implying that the proportion of liquid phase is not meaningful. At higher temperature, ~1100 °C, takes place the deformation

of the sample and at slightly higher temperatures the flow point is reached.

The composition 2 corresponds to the eutectic composition proposed by Lu et al.<sup>10</sup> The DTA of this sample shows the onset of three overlapped endothermic peaks at temperatures of 1000, 1008 and 1030 °C, respectively (see Fig. 1). The presence of the two first peaks indicates that this composition cannot correspond to the eutectic composition. The peak at the lowest temperature represents the eutectic temperature and the one at 1008 °C corresponds to the complete melting of the material. According to this experimental result, this composition it is close to the eutectic one in the binary CuO–TiO<sub>2</sub> system but it is not in fact the eutectic one. The third overlapped peak observed at 1030 °C corresponds to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> according to Fig. 1. Hot stage microscopy analysis, Fig. 2, shows that the melting temperature is near to the deformation temperature, which highlights that this composition is close to the eutectic one. It is important to point out here that the eutectic temperature in air ( $P_{O_2} = 0.21$  atm) measured in our work (1000 °C) is much higher than the one calculated by Lu et al. in air (~900 °C) or at  $P_{O_2} = 1$  atm (919 °C).<sup>10</sup>

Composition 3 (75 CuO–25 TiO<sub>2</sub> mol%) corresponds to the stoichiometric compound “Cu<sub>3</sub>TiO<sub>4</sub>” proposed in the literature to exist in the CuO–TiO<sub>2</sub> system at  $P_{O_2} < 0.21$  atm and temperatures  $\leq 1000$  °C.<sup>8,18</sup> DTA of this composition (Fig. 1) shows only one endothermic peak with onset at 1000 °C. The asymmetry of the endothermic peak corresponding to the eutectic melting could be attributed to surface diffusion phenomena due to the size of particles and consequence of it, i.e. the melting takes place in a small temperature range. Hot Stage Microscope analysis shows that the deformation and flow points for this composition are 1025 °C and 1030 °C, respectively (Fig. 2) in good accordance with the peak temperature in DTA, which is higher by 25–30 °C than the onset of the peak. Therefore liquid phase appears at lower temperatures than 1025 °C. Hot stage microscopy results confirm that composition 3 would be the eutectic composition in the CuO–TiO<sub>2</sub> pseudobinary system. Cu<sup>2+</sup> to Cu<sup>+</sup> reduction reaction is overlapped with the melting and therefore this result could indicate that the reduction is favoured in liquid phase.

Composition 4 corresponds to the molar ratio of CuO and TiO<sub>2</sub> in stoichiometric CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> ceramics (42.86 mol% CuO–57.14 mol% TiO<sub>2</sub>). Thermal analysis shows two overlapped peaks with the onset of the peak at 998 °C. Around 1030 °C a second peak can be observed, corresponding to Cu<sup>2+</sup> to Cu<sup>+</sup> reduction. Hot Stage Microscope analysis of this composition confirms the presence of a lower proportion of liquid phase according to the pseudobinary phase diagram. The deformation point takes place around 1030 °C according to the eutectic peak temperature determined for composition 3, and this deformation evolves with temperature till the maximum measurement temperature before complete melting, as observed in Fig. 2.

According to the obtained results the eutectic reaction between CuO and TiO<sub>2</sub> in air corresponds to 75 CuO–25 TiO<sub>2</sub> mol%, with an eutectic temperature of ~1000 °C. This means that conventional synthesis of CCTO, which is generally carried out in air at temperatures lower than 1000 °C, does

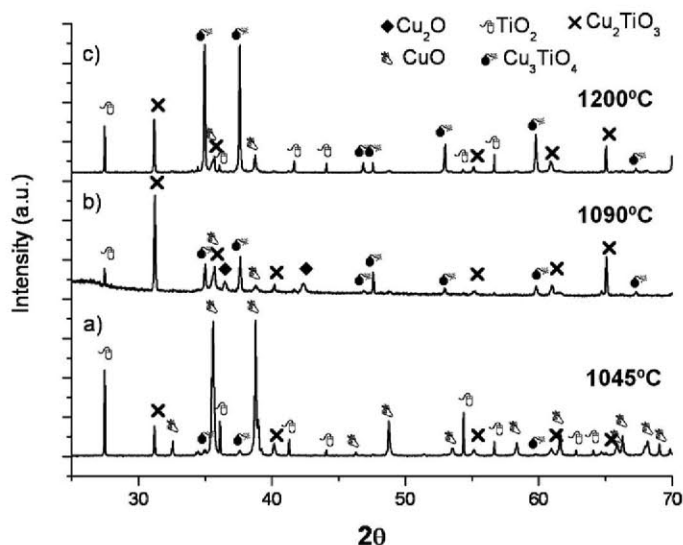


Fig. 3. XRD analysis of composition 3 (75% CuO–25% TiO<sub>2</sub> molar ratio, experimentally determined eutectic) at different temperatures for 15 min in air and fast cooled. (a) 1045 °C, (b) 1090 °C and (c) 1200 °C.

not take place in the presence of a liquid phase, as is commonly assumed.<sup>11,17</sup>

The determined eutectic composition has been thoroughly studied by XRD, SEM and XANES. Fig. 3 shows the XRD analysis of composition 3, with 75 CuO:25 TiO<sub>2</sub> molar ratio (proposed as eutectic) at different temperatures. It is important to emphasize that the objective of the XRD analysis is only to identify the phases present at different temperatures to clarify the oxidation state of Cu in these species and the experimental conditions does not allow carrying out some quantitative analysis. In any case this analysis corresponds to equilibrium phases taking into account the dwell time at high temperature of the composition studied. Three temperatures have been chosen to carry out thermal treatments according to DTA-HSM analysis. The first temperature is 1045 °C – 15 min, that is higher than the peak temperature of the eutectic one and close to the onset of the Cu<sup>2+</sup> to Cu<sup>+</sup> reduction reaction one. XRD analysis of this composition (Fig. 3a), shows unreacted raw materials as CuO tenorite (JPCDS 41-0254) and TiO<sub>2</sub> rutile (JPCDS 21-1276), and secondary phases as Cu<sub>2</sub>TiO<sub>3</sub> (JPCDS 17-0618) and Cu<sub>3</sub>TiO<sub>4</sub> (27-0199). These two last double oxides have been previously observed on the CuO/TiO<sub>2</sub> mixtures at this temperature.<sup>19,20</sup> Fig. 4 shows the polished surface of this composition thermally treated at 1045 °C – 15 min and cooled by quenching. The dark phase is unreacted CuO and the light one is the CuO–TiO<sub>2</sub> eutectic that, as consequence of the quenching, does not crystallize with the characteristic microstructure of a eutectic phase. The second studied temperature is 1090 °C – 15 min, a temperature that is over the Cu<sup>2+</sup> to Cu<sup>+</sup> reduction reaction temperature. The phases identified in this case on the XRD analysis (see Fig. 3b) are Cu<sub>2</sub>TiO<sub>3</sub> and Cu<sub>3</sub>TiO<sub>4</sub> (Cu<sub>2</sub>O·CuO·TiO<sub>2</sub>), accompanied by TiO<sub>2</sub> rutile, Cu<sub>2</sub>O cuprite (JPCDS 03-0892), and CuO as secondary phases.

The samples treated for 15 min at 1200 °C, over the melting temperature of Cu<sub>2</sub>O show the presence of four phases: Cu<sub>3</sub>TiO<sub>4</sub>, TiO<sub>2</sub> rutile and as secondary phases Cu<sub>2</sub>TiO<sub>3</sub> and

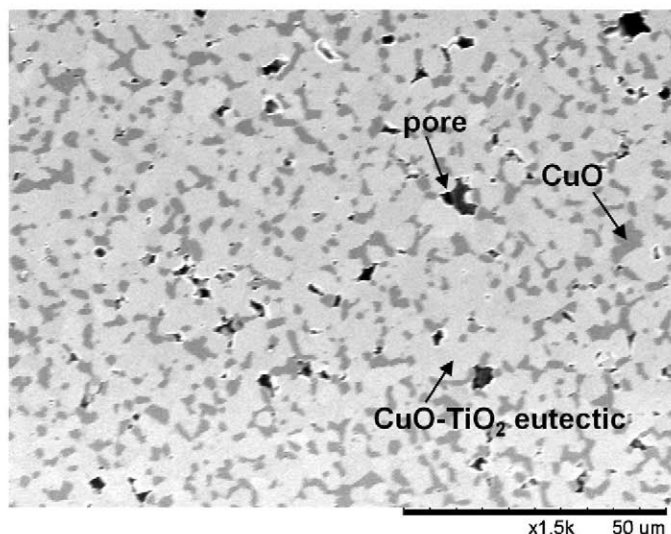


Fig. 4. Surface view by SEM of composition 3 (75% CuO–25% TiO<sub>2</sub>) thermally treated at 1045 °C in air. The dark phase is CuO and the light phase is the CuO–TiO<sub>2</sub> eutectic.

tenorite CuO (see Fig. 3c). At this temperature, a partial re-oxidation of Cu<sub>2</sub>O to CuO<sup>2</sup> occurs, explaining the disappearance of Cu<sub>2</sub>O and favouring the formation of Cu<sub>3</sub>TiO<sub>4</sub>.

Fig. 5 shows XANES spectra of the Cu K-edge on samples of composition 75 CuO–25 TiO<sub>2</sub> mol% calcined at different temperatures and reference compounds CuO, Cu<sub>2</sub>O and Cu as a metal foil. In this figure Cu K-edge, pre-edge, Cu (I) pre-edge peak, Cu (II) pre-edge shoulder and a band between 8990 and 9000 eV are labelled. Edge position and shape are sensitive to formal valence state. An application of XANES is to use the shifts on the edge position to determine the valence state. Heights and position of the pre-edge peaks can be used to empirically determine oxidation state.

Cu (I), in Cu<sub>2</sub>O, possesses a linear two coordinate structure and presents a sharp peak at 8977 eV. Cu (0) exhibits

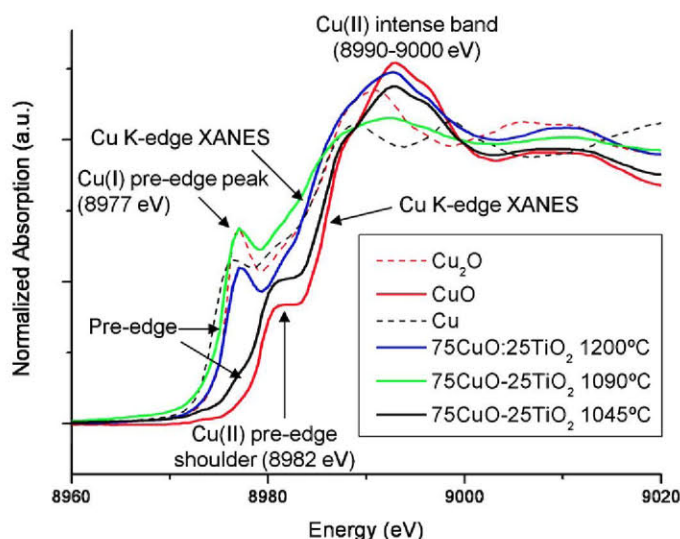


Fig. 5. XANES spectra at RT of Cu metal foil, Cu<sub>2</sub>O, CuO and composition 3 after annealing at 1045, 1090 and 1200 °C for 15 min in air.

also this peak in the pre-edge around 8977 eV although less intense, moreover the resonance features above the edge jump are clearly different from those of Cu<sub>2</sub>O, in agreement with the literature.<sup>21–23</sup> CuO shows a weak peak with difficulty to identify around 8974 eV. This peak corresponds to the dipole Cu (II) 1s–3d electronic transition forbidden by the selection rule of the perfect octahedral symmetry and it is characteristic of divalent Cu. An intense band attributed to the dipole-allowed Cu (II) 1s–4p transitions is located on the absorption edge at about 8992–8998 eV. In the case of tetragonal Cu(II) symmetry, as in CuO, the 1s–4p<sub>z</sub> transition shifts to lower energy, resulting in a clear shoulder at 8982 for CuO and an intense band between 8990 and 9000 eV. With the ATHENA program provided by ESRF it is possible to carry out a semi-quantitative analysis of the amount of Cu (0), Cu<sub>2</sub>O and CuO found in the samples analyzed from the normalized difference absorption edge for Cu K-edge.

The 75 CuO–25 TiO<sub>2</sub> mol% (composition 3) samples calcined at 1045 °C – 15 min show a spectrum that mainly resembles the CuO one. This fact indicates that the Cu ions in this case are in 2+ oxidation state with tetragonal symmetry. This sample was thermally treated at a temperature very close to the onset of the peak corresponding to the Cu<sup>2+</sup> reduction temperature for a very short time and consequence of it no valence change has been produced. This experimental result is in agreement with XRD analysis. The estimated quantities of Cu<sub>2</sub>O and CuO from the XANES spectra are 14% Cu<sub>2</sub>O and 86% CuO.

The samples of composition 3 thermally treated at 1090 °C – 15 min show a sharp peak at 8977 eV in the near-edge absorption, although the resonance features above the edge jump are similar to those of CuO, as can be seen in Fig. 5. The sharp peak at 8977 eV is very similar to the one in the XANES spectrum of Cu<sub>2</sub>O implying the presence of Cu<sup>1+</sup> in the material. This monovalent copper would be mainly present in Cu<sub>2</sub>TiO<sub>3</sub>, Cu<sub>3</sub>TiO<sub>4</sub> (Cu<sub>2</sub>O–CuO·TiO<sub>2</sub>) and as a Cu<sub>2</sub>O. Moreover, the post-edge features resemble the CuO spectrum, indicating the presence of divalent copper that should be present at Cu<sub>3</sub>TiO<sub>4</sub> and as CuO, according to XRD analysis. The estimated quantity of Cu (0), Cu<sub>2</sub>O and CuO from the XANES spectra corresponds to 6% Cu (0), 80% Cu<sub>2</sub>O and 14% CuO. The presence of Cu (0) may be attributed to the formation of a Pt–Cu alloy caused by the reaction between the Cu of the samples and the Pt crucible. Cu<sub>3</sub>Pt alloy (JPCDS 35-1358) would appear overlapped with the peak corresponding to the Cu<sub>2</sub>O phase at 2θ = 42.3.

The samples thermally treated at 1200 °C – 15 min show a XANES spectrum that resembles that of Cu<sub>2</sub>O with a peak at 8977 eV in the near-edge absorption, although there are some resemblances to the Cu K-edge XANES of CuO spectrum at energies over 8985 eV and the intense band between 8985 and 8995 eV. This suggests the existence of Cu<sup>1+</sup> and Cu<sup>2+</sup> oxidation states in this sample, in agreement with XRD analysis. Semi-quantitative analysis of XANES spectra allows quantifying the presence of Cu<sub>2</sub>O and CuO, 70 and 30%, respectively.

Experimental results obtained have allowed determining the eutectic temperature and composition in the CuO–TiO<sub>2</sub> binary system in air. These results are important to determine the presence or not of a liquid phase in different systems in which CuO

and TiO<sub>2</sub> are involved when the thermal treatment is carried out in air. The identified phases at high temperature must not be considered equilibrium phases according to the dwell time. The objective of this analysis at high temperature is to corroborate the Cu valence according to DTA and hot stage microscopy results minimizing the contamination of the samples with the Pt substrate.

#### 4. Conclusions

Eutectic temperature and composition have been experimentally determined in air for the pseudobinary CuO–TiO<sub>2</sub> system. Eutectic temperature (1000 °C) is much higher than the one calculated by Lu et al.,<sup>10</sup> both in air and at PO<sub>2</sub> = 1 atm (~900 and 919 °C, respectively) and it is displaced to Ti-rich composition (75 CuO–25 TiO<sub>2</sub> mol%) compared to the one proposed in literature (83.3 CuO–16.7 TiO<sub>2</sub> mol%). The reduction of CuO to Cu<sub>2</sub>O takes place at higher temperature than the eutectic one.

Samples prepared at different temperatures over the eutectic temperature and rapidly quenched show the presence of Cu<sub>2</sub>TiO<sub>3</sub> and Cu<sub>3</sub>TiO<sub>4</sub> with coexistence of Cu<sup>1+</sup> and Cu<sup>2+</sup> for those samples treated at temperatures over the Cu<sup>2+</sup> reduction temperature (1030 °C). The dwell time at high temperature does not allow considering these compounds as equilibrium phases.

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