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Grivel, J. -C.

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Subsolidus Phase Relations of the CaO-WO₃-CuO System at 800 °C in Air

J.-C. Grivel

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The subsolidus phase relations of the CaO-WO₃-CuO system were investigated in air. The samples were equilibrated at 800 °C. Under these conditions, five binary oxide phases are stable: Ca₂CuO₃, Cu₃WO₆, CuWO₄, CaWO₄ and Ca₃WO₆. The pseudo-ternary section is characterised by 6 three-phase regions. No Ca equivalents to the Sr₂CuWO₆, Ba₂CuWO₆ or Sr₈CuW₃O₁₈ phases were formed.

Keywords CaO-WO₃-CuO, phase equilibria, X-ray diffraction

1. Introduction

The large potential of high temperature superconductors for power applications has initiated extensive research activities aiming at understanding the chemistry and physics of cuprates in view of unveiling the underlying mechanisms of high temperature superconductivity and discovering new compounds with higher transition temperatures. Due to these aspects, the sub-solidus phase equilibria of several ternary oxide systems including BaO and CuO have been studied. In contrast, whereas a few RE₂O₃-CaO-CuO (RE = rare earth) systems were explored,^[1,2] the pseudo-ternary systems including CaO, CuO and a transition element oxide have been poorly investigated. During a recent study of the SrO-WO₃-CuO system at 800 °C in air^[3] a new ternary oxide compound with Sr₈CuW₃O₁₈ composition was discovered besides the already known Sr₂WCuO₆.^[4] Since no Ca equivalent to these compounds are known, the phase equilibria of the CaO-WO₃-CuO system under similar conditions were determined in order to explore the possible occurrence of new cuprate compounds.

1.1 Earlier Studies

At ambient pressure, WO₃ adopts various structures depending on temperatures. In the 300-850 °C range, it crystallises in the P2₁/n space group (monoclinic).^[5]

Several studies^[6–11] have been devoted to the CaO-CuO system, in which only one binary oxide phase is known to

be stable at 800 °C in air: Ca₂CuO₃ (orthorhombic, space group *Immm*^[12]). Two other phases, Ca_{1-x}CuO₂ and CaCu₂O₃ are stable in air but only at lower and higher temperatures respectively.^[7,8,11] A CaCuO₂ “infinite-layer” phase with tetragonal structure can be stabilized under high pressure and temperature conditions (3-5 GPa, 1050-1200 °C) and transforms into a monoclinic form at higher pressure.^[13]

The WO₃-CuO system was first studied by Gebert and Kihlberg,^[14] who identified two intermediate phases after equilibrating reagent mixtures at 800 °C in sealed, evacuated platinum tubes. These phases are Cu₃WO₆ (cubic, space group *Pa3*^[15]) and CuWO_{4-x} (triclinic, space group *P1*^[14]). The stoichiometry of the latter phase, which might be Cu-deficient, was not completely elucidated in Ref 14. More recently, Kol'tsova and Nipan^[16] established the phase equilibria of the same system in air between 700 and 1000 °C. They reported the existence of two binary oxides: Cu₃WO₆ and CuWO₄ (triclinic, space group *P1*^[17]) that are stable at 800 °C. Another compound, Cu₂WO₄ was synthesised under reducing conditions.^[18] Its structure has been determined by Marinder et al.^[19] (triclinic, space group *P1*).

The phase equilibria in the CaO-WO₃ system were reported by Chang et al.^[20] According to this study, the CaWO₄ (tetragonal, space group *I4₁/a*^[21]) and Ca₃WO₆ (monoclinic, space group *P2₁*^[22]) phases are the only binary oxide phases present in the system at 800 °C.^[20] Nassau and Mills^[23] isolated a metastable Ca₆WO₉ phase formed during cooling of a CaO-Na₂WO₄-WO₃ melt. The synthesis of Ca_xWO₃ bronzes requires high pressures^[24] or a slow oxidation reaction of Ca₃N₂, Ca and W mixtures in an oxygen poor atmosphere.^[25]

No ternary oxide phase has been reported in the CaO-WO₃-CuO system until now.

2. Experimental Details

High purity WO₃, CaCO₃ and CuO, powders (all ≥99.9%) were thoroughly mixed in an agate mortar. In total, 46 samples with various nominal compositions were

J.-C. Grivel, Materials Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, 4000 Roskilde, Denmark. Contact e-mail: jean@risoe.dtu.dk.

studied. The powders were calcined at 800 °C for 60 h. After grinding, these pellets were pressed under a pressure of 1.8 kbar and sintered at least twice at 800 °C for 60 h with intermediate grinding and repressing. The samples were quenched in ambient air at the end of the sintering treatments. All heat treatments were performed in air.

The phase contents of the pellets were checked after each heat treatment by X-ray diffraction (XRD) in a STOE diffractometer using $\text{CuK}\alpha$ radiation. In some cases, additional heat treatments were performed in order to reach equilibrium. Equilibrium was considered as achieved if no difference was detectable in the XRD patterns performed after two consecutive sintering treatments. Silicon powder was added as an internal standard for lattice parameter determination for selected samples. In the cases of CaWO_4 and CuWO_4 , for which too severe overlap with the Si reflections takes place, annealed KCl powder was used as a standard instead of Si.

3. Results

3.1 CaO-CuO

Only one binary oxide phase was formed at 800 °C in air in this system. It is the Ca_2CuO_3 phase, as previously reported.^[6–11] Its lattice parameters are in agreement with those reported by Hazen et al.^[21] (Table 1). The CaCu_2O_2 and $\text{Ca}_{1-x}\text{CuO}_2$ phases were not found in the present study as a consequence of the lack of stability of these phases in air at 800 °C. As expected, the high-pressure phase CaCuO_2 ^[13] was not formed either.

3.2 WO_3 -CuO

Being in agreement with the results presented in Ref 16, CuWO_4 and Cu_3WO_6 are the only binary oxide phases stable at 800 °C in air in this system. The detection of

Table 1 Phases observed in selected samples after equilibration and crystallographic data for the major phases

Nominal cation ratio W:Ca:Cu	Phases (XRD) (a)	Space group (b)	Lattice parameters (c)					
			<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	α , °	β , °	γ , °
0:0:100	CuO	<i>C2/c</i>	4.663(8)	3.416(2)	5.136(11)	...	99.50(3)	...
1:0:99	$\text{CuO}(\text{Cu}_3\text{WO}_6)$	<i>C2/c</i>	4.661(8)	3.416(2)	5.138(11)	...	99.52(3)	...
24:0:76	$\text{Cu}_3\text{WO}_6(\text{CuO})$	<i>Pa-3</i>	9.776(2)
25:0:75	Cu_3WO_6	<i>Pa-3</i>	9.782(2)
26:0:74	$\text{Cu}_3\text{WO}_6(\text{CuWO}_4)$	<i>Pa-3</i>	9.800(2)
25:3:72	$\text{Cu}_3\text{WO}_6(\text{CuO}, \text{CaWO}_4)$	<i>Pa-3</i>	9.778(2)
49:0:51	$\text{CuWO}_4(\text{Cu}_3\text{WO}_6)$	<i>P-1</i>	4.706(3)	5.845(3)	4.881(3)	91.64(5)	92.43(6)	82.75(6)
50:0:50	CuWO_4	<i>P-1</i>	4.705(3)	5.843(3)	4.879(2)	91.65(4)	92.44(5)	82.78(5)
51:0:49	$\text{CuWO}_4(\text{WO}_3)$	<i>P-1</i>	4.706(3)	5.844(3)	4.881(2)	91.68(4)	92.41(5)	82.77(5)
50:2:48	$\text{CuWO}_4(\text{CaWO}_4)$	<i>P-1</i>	4.707(4)	5.845(3)	4.881(3)	91.64(5)	92.44(6)	82.76(6)
48:2:50	$\text{CuWO}_4(\text{CaWO}_4, \text{Cu}_3\text{WO}_6)$	<i>P-1</i>	4.707(4)	5.845(3)	4.880(3)	91.66(5)	92.42(6)	82.77(6)
99:0:1	$\text{WO}_3(\text{CuWO}_4)$	<i>P2₁/n</i>	7.289(3)	7.525(3)	7.669(5)	...	90.94(5)	...
100:0:0	WO_3	<i>P2₁/n</i>	7.293(3)	7.528(3)	7.669(5)	...	90.93(5)	...
99:1:0	$\text{WO}_3(\text{CaWO}_4)$	<i>P2₁/n</i>	7.285(4)	7.520(4)	7.662(7)	...	90.91(6)	...
51:49:0	$\text{CaWO}_4(\text{WO}_3)$	<i>I4₁/a</i>	5.244(1)	...	11.376(3)
50:50:0	CaWO_4	<i>I4₁/a</i>	5.244(2)	...	11.379(3)
49:51:0	$\text{CaWO}_4(\text{Ca}_3\text{WO}_6)$	<i>I4₁/a</i>	5.243(2)	...	11.373(4)
48:50:2	$\text{CaWO}_4(\text{Ca}_3\text{WO}_6, \text{CuO})$	<i>I4₁/a</i>	5.242(2)	...	11.374(4)
50:48:2	$\text{CaWO}_4(\text{CuWO}_4)$	<i>I4₁/a</i>	5.243(2)	...	11.372(4)
26:74:0	$\text{Ca}_3\text{WO}_6(\text{CaWO}_4)$	<i>P2₁</i>	5.791(3)	5.537(3)	7.978(12)	...	90.12(10)	...
25:75:0	Ca_3WO_6	<i>P2₁</i>	5.792(3)	5.536(3)	7.979(13)	...	90.12(10)	...
24:76:0	$\text{Ca}_3\text{WO}_6(\text{CaO})$	<i>P2₁</i>	5.788(2)	5.534(3)	7.970(11)	...	90.20(10)	...
23:75:2	$\text{Ca}_3\text{WO}_6(\text{CaO}, \text{Ca}_2\text{CuO}_3)$	<i>P2₁</i>	5.793(3)	5.536(3)	7.960(13)	...	90.24(11)	...
25:73:2	$\text{Ca}_3\text{WO}_6(\text{CaWO}_4, \text{CuO})$	<i>P2₁</i>	5.788(4)	5.537(4)	7.956(13)	...	90.23(17)	...
1.67:66.67:31.67	$\text{Ca}_2\text{CuO}_3(\text{Ca}_3\text{WO}_6, \text{CuO})$	<i>Immm</i>	12.218(1)	3.770(1)	3.252(1)
0.00:66.67:33.33	Ca_2CuO_3	<i>Immm</i>	12.217(3)	3.769(3)	3.251(2)
1.67:65.00:33.33	$\text{Ca}_2\text{CuO}_3(\text{Ca}_3\text{WO}_6, \text{CuO})$	<i>Immm</i>	12.218(1)	3.770(1)	3.252(1)
0:100:0	CaO	<i>Fm-3m</i>	4.802(10)
1:99:0	$\text{CaO}(\text{Ca}_3\text{WO}_6)$	<i>Fm-3m</i>	4.802(10)

(a) Phases between brackets are minority phases

(b) Space group of the majority phase

(c) The lattice parameters are those of the majority phase

Section I: Basic and Applied Research

Cu_3WO_6 in the sample with $\text{Cu}_{0.99}\text{W}_{0.01}\text{O}_x$ nominal composition, coupled with similar CuO lattice parameters (Table 1) allows concluding that no extended substitution of W occurs in CuO under the present experimental conditions. Similarly, the presence of CuWO_4 and equivalent lattice parameters (Table 1) show that Cu substitution in WO_3 is in any case limited to less than 1 at.%. Departing from the ideal CuWO_4 and Cu_3WO_6 compositions, results in equilibrium between the respective stoichiometric phases and other compounds as shown in Table 1. CuWO_4 and Cu_3WO_6 thus do not appear to form solid solutions, as previously reported in Ref 16, although the slight increase of the cubic lattice parameter of Cu_3WO_6 as the W content in the $\text{Cu}_{3-x}\text{W}_{1+x}\text{O}_{6+\delta}$ nominal composition suggests a limited solid solution range restricted to $-0.04 < x < 0.04$.

3.3 WO_3 -CaO

In this pseudo-binary system, we found two stable binary oxides with compositions CaWO_4 and Ca_3WO_6 . Excess CaO or WO_3 in the respective starting compositions of these phases systematically results in the appearance of impurities, while the cell parameters of the main phases are not affected. Similar considerations are valid for the WO_3 and CaO end compounds. None of these phases appears to form

an extended solid solution and our results are therefore in agreement with the data published in Ref 20.

3.4 CaO- WO_3 -CuO

The tie-line compatibilities of phases in the pseudo-ternary CaO- WO_3 -CuO phase diagram at 800 °C in air are shown in Fig. 1. There are 6 three-phase regions and five binary oxide phases, but no ternary oxide phases. Representative XRD patterns for nominal compositions situated in all three-phase regions are shown in Fig. 2. None of the binary oxide phases of the pseudo-binary systems appears to give rise to ternary solid solutions as can be deduced from the appearance of 2-phase or 3-phase equilibria when attempts were made to dope these compounds with the third element (Table 1). The CaO- WO_3 -CuO system thus differs from the SrO analogue due to the absence of ternary oxide compounds equivalent to Sr_2CuWO_6 and $\text{Sr}_8\text{CuW}_3\text{O}_{18}$. A Ca-analogue to the Sr_2WO_5 was not found either.

4. Conclusion

In air, at 800 °C, the CaO- WO_3 -CuO system contains 6 three-phase regions and five binary oxide phases (Ca_2CuO_3 , Cu_3WO_6 , CuWO_4 , CaWO_4 and Ca_3WO_6). No ternary oxide

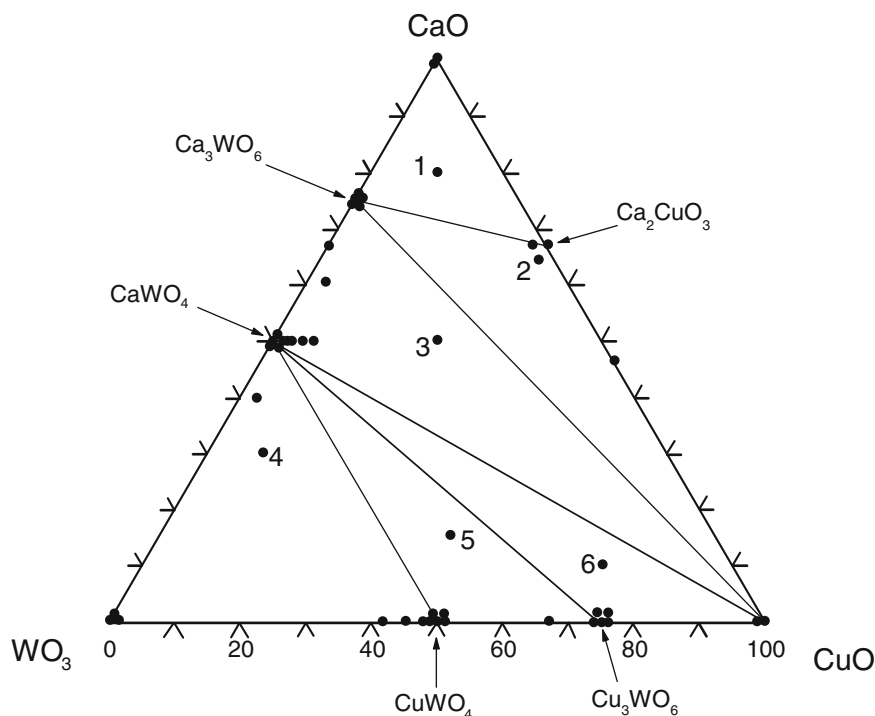


Fig. 1 Phase equilibria of the CaO- WO_3 -CuO system at 800 °C in air. Dots represent the studied compositions. Numbers 1-6 refer to the XRD patterns that are shown in Fig. 2

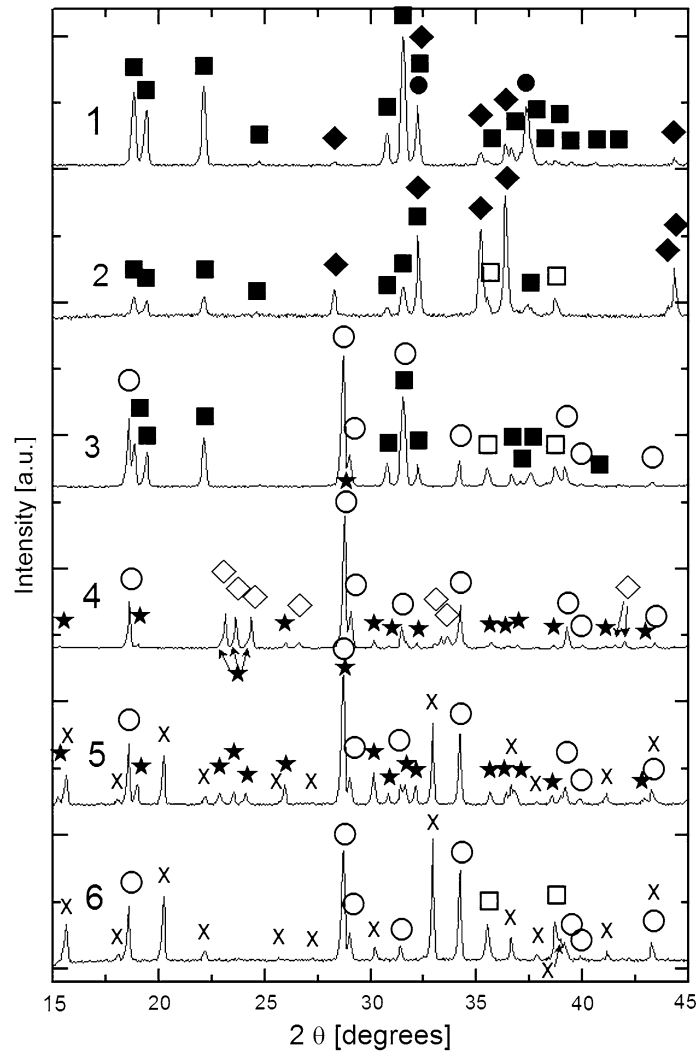


Fig. 2 Representative XRD patterns collected on samples with compositions lying in each of the three-phase regions of the pseudo-ternary sections. The pattern numbers refer to Fig. 1. Phases: ● CaO, ■ Ca_3WO_6 , ◆ Ca_2CuO_3 , □ CuO, ○ CaWO_4 , ◇ WO_3 , ★ CuWO_4 and × Cu_3WO_6

phases were formed under the present equilibrium conditions.

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