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Preparation of copper niobates by thermal decomposition of freeze-dried complex oxalate solutions

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Abstract

Freeze-dried complex oxalates of copper and niobium are reactive precursors for ternary copper niobium oxides. The thermal decomposition of the amorphous precursors has been investigated by DTA, TG and mass spectroscopy. The gaseous decomposition products are assigned to steps in the TG graph. Above 500°C, crystallization of complex oxides takes place. In the temperature range up to 900°C, only the ternary phases $CuNb_2O_6$ and $Cu_3Nb_2O_8$ can be synthesized. The thermal decomposition of the oxalate precursor is advantageous with regard to the preparation of pure monoclinic $CuNb_2O_6$. The transformation between monoclinic and orthorhombic $CuNb_2O_6$ is reversible with a high activation energy of transformation.

Keywords: Copper niobates; Cu–Nb-oxalate precursor; Mass spectrometry; Phase analysis; Thermal analysis

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1. Introduction

The solid state reaction of CuO with Nb_2O_5 results in the formation of two compounds, $CuNb_2O_6$ [1, 2] and $Cu_3Nb_2O_8$ [3]. In addition, Krumreich and Gruehn [4] have obtained $Cu_{2/3}Nb_{34/3}O_{29}$ and $Cu_{1/3}Nb_{44/3}O_{37}$ by chemical transport of CuO from $CuNb_2O_6$ with gaseous $HgCl_2$, as metastable intermediates with block structures. However, experiments to achieve these metastable compounds by solid state reaction failed.

As well as the columbite-type phase of $CuNb_2O_6$ with orthorhombic symmetry, a monoclinic form has been observed [3]. The columbite-type phase is formed

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preferentially at temperatures above 900°C. The monoclinic form was obtained by decomposition of $CuNbO_3$ in air at 700°C followed by removal of the simultaneously formed CuO by aqueous acid . Norwig et al. [5] determined refined structural parameters of monoclinic $CuNb_2O_6$ using neutron powder diffraction and Rietveld refinement. The authors observed a stress-induced phase transition from monoclinic to orthorhombic $CuNb_2O_6$. According to Ref. [6], $CuNb_2O_6$ can be prepared in either the monoclinic ($\theta = 680$–$740°C$) or orthorhombic ($\theta > 740°C$) modification by heating equimolecular mixtures of CuO and Nb_2O_5 in air. In most cases, the two phases are found side by side.

To get more information concerning the existence and thermodynamic stability of crystalline phases in the system CuO–Nb_2O_5, we investigated the thermal decomposition of freeze-dried complex oxalates of Nb and Cu by varying the composition systematically. We were particularly interested in the nature of the phases formed after the thermal decomposition of the reactive precursor.

2. Experimental

Complex oxalate solutions were prepared by dissolving freshly precipitated niobium oxide hydrate or ammonium-oxo-tris-oxalato-niobate and copper oxalate in ammonium oxalate solution (systematic variation of composition from a pure Nb-containing solution to the solution of the copper-oxalato complex in steps of 10%, with a metal:oxalate ratio of 1:3, and total metal concentration 0.13 mol l^{-1}). After freeze-drying these solutions, fine-grained, soft agglomerated powders were obtained. The thermal decomposition was investigated by means of a Netzsch thermal analyser STA 409, coupled with a mass spectrometer QMS 125 (Balzers). X-ray diffraction was performed using a powder diffractometer URD 63 (Carl Zeiss Jena).

3. Results

As an example, Fig. 1 shows the TG, DTG and DTA curves of a freeze-dried complex oxalate with a Cu:Nb ratio of 1:2. Fig. 2 a and b illustrate the corresponding mass spectroscopic analysis of some gaseous products. The decomposition occurs in two clearly separated endothermic steps (Ar atmosphere). First, hydrate water is eliminated below 200°C ($m = 18$, 17). Further decomposition takes place between 220 and 320°C, eliminating CO ($m = 28$), CO_2 ($m = 44$), H_2O ($m = 18$, 17), NH_3 ($m = 17$), HCOOH ($m = 46$) and HCN ($m = 27$). In air, the decomposition process above 220°C is exothermic because of the CO oxidation. From the investigation of single oxalates, it is known that after dehydration the decomposition process starts with the niobium complex ($\theta > 200°C$) followed by the superimposed decomposition of the copper complex ($\theta > 250°C$). The endothermic peak at 300°C is connected with the decomposition of the intermediately formed oxamide, eliminating HCN in addition to the decomposition products already expected. Above 400°C, crystallization processes take place. The

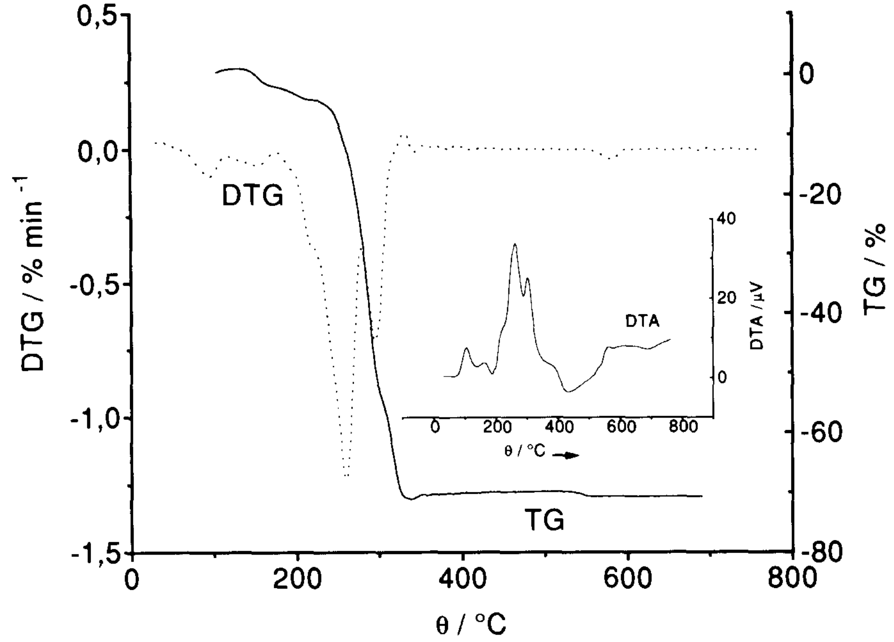

Fig. 1. Thermal analysis of the $CuNb_2O_6$-oxalate precursor. Heating rate, 5 K min^{-1}; atmosphere, argon.

small mass loss at 600°C is connected with the oxidation of pyrolytic carbon by traces of oxygen in the argon atmosphere.

The X-ray powder diffractograms of the solid decomposition products of the freeze-dried oxalate precursor with a Cu:Nb ratio of 1:2 are shown in Fig. 3. After decomposition at 300°C (3 h), an amorphous product is formed. Thermal treatment of this powder at 600°C (3 h) leads to an X-ray diffractogram characteristic for the pure monoclinic form of $CuNb_2O_6$ (Fig. 3a). Subsequent annealing at 800 or 900°C brings about a partial conversion into the orthorhombic columbite structure (Fig. 3b). Complete conversion into the orthorhombic form needs a long annealing time at $\theta > 900$°C. Orthorhombic $CuNb_2O_6$ can be synthesized by the solid state reaction of CuO with Nb_2O_5 at 900°C [4]. In accordance with this, the direct decomposition of the freeze-dried precursor at 900°C (3 h) leads to the formation of the pure orthorhombic form (Fig. 3c). According to Norwig et al. [5], orthorhombic $CuNb_2O_6$ also seems to be the more stable form at room temperature. The authors did not observe a retransformation from orthorhombic to monoclinic $CuNb_2O_6$ despite experimental efforts. To get more information on the reversibility of the conversion, the product 3c was annealed at 700°C (3 h). The annealing process results in the partial retransformation into the monoclinic form (3d). Subsequent annealing at 600°C provides a further transformation into the monoclinic form but even after a very long annealing time (72 h), the transformation remains incomplete. In this way, the results documented in Fig. 3 correspond to a thermodynamically stable monoclinic form of $CuNb_2O_6$ below

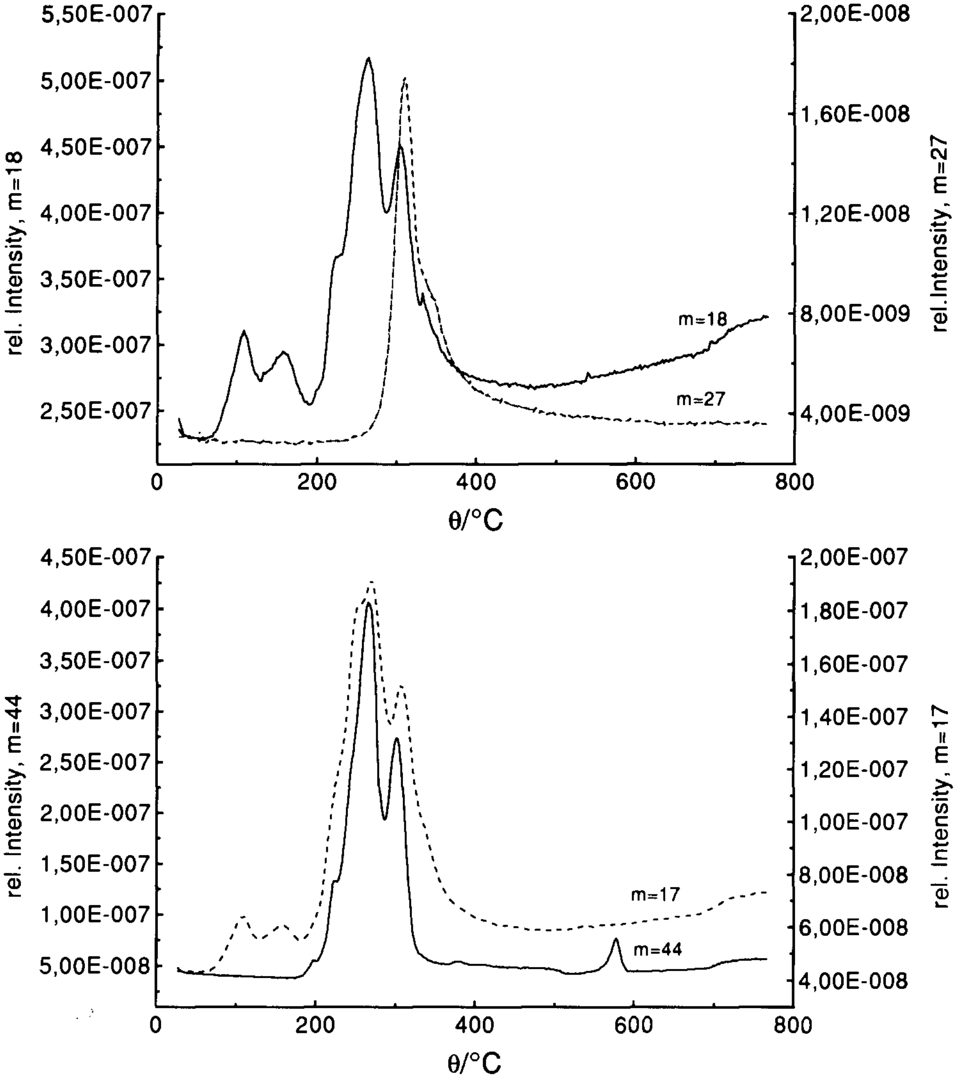

Fig. 2. Observation of several mass numbers during the decomposition of the $CuNb_2O_6$–oxalate precursor. a. $m = 18$, H_2O; $m = 27$, HCN. b. $m = 17$, NH_3 and OH from H_2O; $m = 44$, CO_2.

700°C and a thermodynamically stable orthorhombic form above 700°C with a large activation barrier to the interconversion.

The thermal decomposition of freeze-dried oxalate precursor of composition Cu:Nb = 3:2 at 300°C also results in an amorphous product. On annealing at 600°C (3 h), monoclinic $CuNb_2O_6$ crystallizes in addition to CuO. The solid state reaction between the two compounds begins between 700 and 800°C and leads to $Cu_3Nb_2O_8$. The reaction is completed after annealing for about 8 h at 900°C, and single-phase

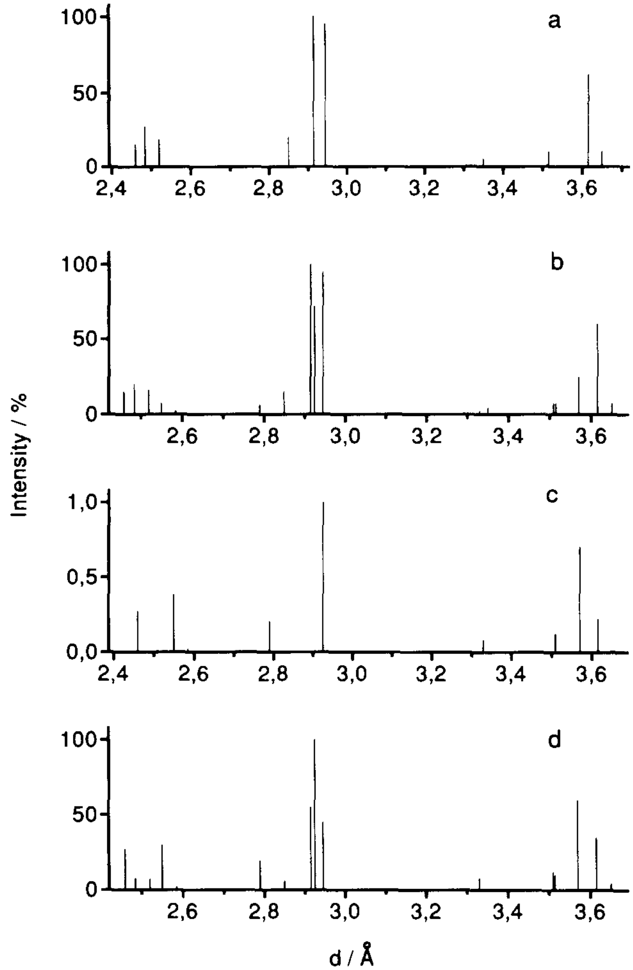

Fig. 3. X-ray powder diffractograms of solid decomposition products of the $CuNb_2O_6$–oxalate precursor. a. 3 h at 600°C. b. 3 h at 900°C, after a. c. 3 h at 900°C, immediately. d. 3 h at 700°C after c.

$Cu_3Nb_2O_8$ results. During this process, orthorhombic $CuNb_2O_6$ can appear as a further intermediate.

The thermal decomposition of all other precursor compositions at 300°C also results in amorphous products. The results of the annealing at 600 and 900°C (Table 1) can be interpreted as follows. In Nb-rich compositions, TT-Nb_2O_5 crystallizes first. There is some evidence that TT-Nb_2O_5 forms solid solutions with a low CuO content ($< 10\%$). After annealing at 900°C all compositions between Nb_2O_5 and $CuNb_2O_6$ contain only $CuNb_2O_6$ and H(M)-Nb_2O_5 in the appropriate quantities. The Cu-rich compositions are characterized by the crystallization of $CuNb_2O_6$, $Cu_3Nb_2O_8$ and CuO in the way discussed above for $Cu_3Nb_2O_8$. No other phases apart from CuO and $Cu_3Nb_2O_8$ can

Table 1
Crystalline phases after thermal decomposition of Nb–Cu-oxalate precursors of different compositions at 600 and 900°C

Composition Cu:Nb	600°C	900°C
0:10	**TT-Nb_2O_5**	**H(M)-Nb_2O_5**
1:9	**TT-Nb_2O_5**	**H(M)-Nb_2O_5**, $CuNb_2O_6$(m,o)
2:8	**TT-Nb_2O_5**, $CuNb_2O_6$(m)	**H(M)-Nb_2O_5, $CuNb_2O_6$(m,o)**
5:5	**$CuNb_2O_6$(m), CuO**	$CuNb_2O_6$(o,m), **$Cu_3Nb_2O_8$**
8:2	**$CuNb_2O_6$(m), CuO**	**$Cu_3Nb_2O_8$, CuO**
10:0	**CuO**	**CuO**

be observed between these borders after adjustment of the thermodynamical equilibrium.

4. Conclusions

Freeze-dried complex oxalates of copper and niobium are reactive precursors for ternary copper niobium oxides. By thermal decomposition of the oxalate precursors, amorphous intermediates are obtained. Above 500°C, crystallization of the amorphous intermediates takes place. The experimental results described above lead to the conclusion that in the system CuO–Nb_2O_5, only the ternary phases $CuNb_2O_6$ and $Cu_3Nb_2O_8$ can be synthesized in the temperature range up to 900°C. The block structures synthesized by Krumreich and Gruehn [4] cannot be achieved by unconventional synthesis at relatively low temperatures.

The thermal decomposition of freeze-dried complex oxalates is particularly advantageous with regard to the preparation of pure monoclinic $CuNb_2O_6$. The experiments have shown that the transformation between the monoclinic and orthorhombic phases of $CuNb_2O_6$ is reversible. However, after crystallization, the monoclinic form shows a remarkable kinetic stability above the transition temperature of about 700°C, and the transformation into the orthorhombic high-temperature phase is characterized by a high activation barrier. Concerning the preparation of the single-phase orthorhombic form, it is advantageous to avoid primary crystallization of monoclinic $CuNb_2O_6$.

Concerning the kinetics, the crystallization of $CuNb_2O_6$ from copper niobium oxide amorphous intermediates is favoured, regardless of their composition.

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