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Copper oxide as a sintering agent for barium titanate based ceramics

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The purpose of this work was to study the effect of CuO as a versatile sintering agent for $BaTiO_3$ based ceramics. The response is shown to exist in three directions. Firstly, as liquid-phase former at comparatively low temperatures. Hence, the influence of various CuO-based flux formers on the shrinkage behaviour and the microstructure development of the ceramics was investigated. Secondly, the aptitude as an internal susceptor for secondary phase initiated microwave sintering. The use of CuO as a lossy secondary phase leads to an accelerated microwave heating of the ceramics. Thirdly, the addition of CuO to $BaTiO_3$ powders with Ba-excess results in a phase transition cubic → hexagonal at about 1300°C, which is a indication for the incorporation of Cu^{2+} ions into the $BaTiO_3$ lattice at Ti sites under this conditions.

1. Introduction

Barium titanate based ceramics have an acknowledged position in the set of advanced ceramics because of their unique electric/dielectric and electromechanic properties. These can be controlled mainly by varying the sintering conditions and by using externally preformed secondary phases in the sense of microchemical designing. Normally barium titanate green powders contain diverse additives because of two reasons:

1. to influence the sintering behaviour (densification and grain growth)
2. to develop desired electrical properties.

In order to lower the sintering temperature for $BaTiO_3$ ceramics, besides an excess of TiO_2 (eutectic melt $Ba_6Ti_{17}O_{40}$-$BaTiO_3$ at about 1330°C) [1] many oxides, such as B_2O_3, Bi_2O_3, LiF and SiO_2 [2–5] are added as low melting flux former.

The adjustment of special electrical properties can be achieved for example by doping with rare earth metals to create a semiconductor with PTCR behaviour or by substitution of Ti^{4+} by isovalent cations like Zr^{4+}, Sn^{4+} and/or Ba^{2+} by Pb^{2+}, Mg^{2+}, Sr^{2+} [6, 7] to shift the Curie point. In the set of sintering additives for $BaTiO_3$ ceramics, CuO seems to be a multi-purpose secondary phase which is usable as

1. low melting flux former
2. internal susceptor for microwave sintering
3. acceptor substituent at Ti-sites.

The aim of this study was the investigation of the above mentioned properties of CuO.

2. Experimental procedures

The $BaTiO_3$-based powders were synthesized by the conventional mixed-oxide method using TiO_2 (Merck, Charge 808), $BaCO_3$ (Feinchemikalien GmbH Bad Liebenstein, Charge 3018) and CuO (Merck, GR for analysis) as raw materials and deionised water as milling liquid. The $BaTiO_3$-starting powder was prepared by mixing/milling stoichiometric amounts of $BaCO_3$ and TiO_2 (agate balls, water), followed by calcination at 1100°C for 2 hours. The additives or mixtures of the additives used were added to the calcined barium titanate by mixing (zirconia balls, water) in a planetary mill.

Thermal analysis runs were carried out with the 92-multi-modul thermo-analysis system (SETARAM).

Wetting experiments were carried out in a heating microscope MHO 2 (Carl-Zeiss-Jena) using the sessile drop method. The heights of the eutectic powder tips on $BaTiO_3$ substrates were measured and analysed by video equipment. Detailed informations are described in [8]. A CAMEBAX (CAMECA) device was used for electron-probe microanalysis (EPMA). The samples were moulded in epoxy resin and were then ground down to the centre of the drop and polished.

The crystalline structure of the sintered samples was examined by X-ray diffraction analysis (URD 63; Freiberger Präzisionsmechanik GmbH; Cu-K_α radiation; Ni filter).

The ceramics were microwave (mw) sintered in a multi-mode cavity (2.45 GHz, 1 kW) equipped with a black body sensor for temperature measurement.

3. Results and discussion

3.1. CuO as a flux former

To attain lower firing temperatures without scarifying high densities several sintering aids have been studied in the past and CuO has been found to be an effective sintering aid for $BaTiO_3$ ceramics [9–14]. CuO can create various melting phases [15–17] and the systems of interest are shown in Table I.

To proof the effect of the above-mentioned flux formers on the densification behaviour of the $BaTiO_3$ ceramic, systems with the following nominal composition were prepared and investigated:

system 1: $BaTiO_3 + 1$ mol% $(BaCO_3 + 2\ CuO)$
system 2: $BaTiO_3 + 1$ mol% $(TiO_2 + CuO)$
system 3: $BaTiO_3 + 1$ mol% CuO

Compared to the system $BaTiO_3 + 1$ mol% TiO_2 (eutectic melt $Ba_6Ti_{17}O_{40}$-$BaTiO_3$ at about 1330°C) the effect of CuO on the densification is clearly seen (Fig. 1). However, in case of system 1 there is no immediate response with the expected formation of the CuO-based liquid phases at about 890°C on the densification process rather the complete densification was observed not until distinct higher temperatures. Similar results were published by other authors too [9–14].

In the presence of a liquid phase the densification behaviour and grain growth depend certainly on the properties of the liquid phase as a high wettability and solubility of the solid matrix material in the liquid. The sessile-drop method was used to evaluate the wetting behaviour of the Cu-containing liquid phases.

At first the expected formation of the corresponding melts were proofed by DTA-measurements (Fig. 2). The observed endothermic peaks only partly correspond with the known melting temperatures (see Table I). The main reason for this disagreement should be the inaccurate stoichiometry of the $BaTiO_3$ powders used. Abicht *et al.* [18] found that during the wet-milling process with H_2O Ba^{2+} ions are leached out of the $BaTiO_3$ structure and consequently a Ti-rich surface layer results. Even using a stoichiometric ratio of $BaCO_3$ and TiO_2, after the fine-milling process with water as milling liquid a 1–2 mol% excess of TiO_2 has to be taken into consideration.

TABLE I Melting points of different CuO-based flux former

System	BaO-CuO [15]	TiO_2-CuO [16]	CuO [17]
Melting phase	$BaCuO_2$-CuO (formation of $BaCuO_2$ at 830°C)	Cu_3TiO_4 (formation at 980°C)	CuO-Cu_2O
Melting point [°C]	890	1020	1075

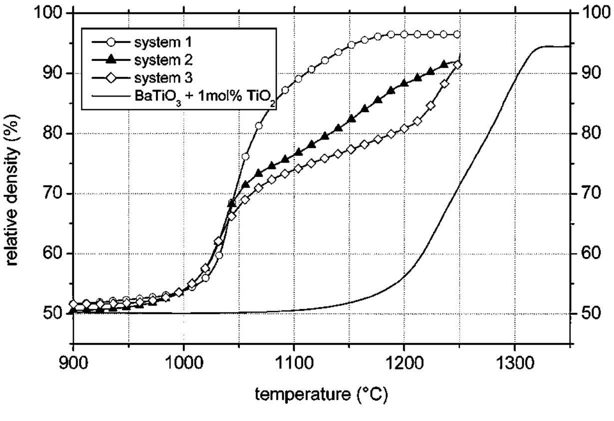

Figure 1 Dilatometric measurements of the systems 1–3 and $BaTi_{1.01}O_{3.02}$: system 1: $BaTiO_3 + 1$ mol% $(BaCO_3 + 2\ CuO)$ system 2: $BaTiO_3 + 1$ mol% $(TiO_2 + CuO)$ system 3: $BaTiO_3 + 1$ mol% CuO.

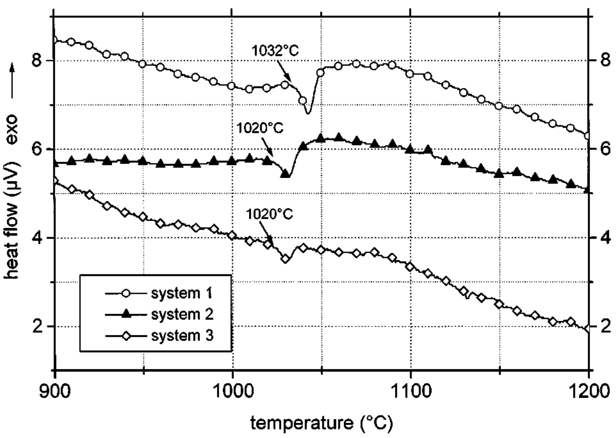

Figure 2 DTA measurements of the systems 1–3: system 1: $BaTiO_3 + 1$ mol% $(BaCO_3 + 2\ CuO)$ system 2: $BaTiO_3 + 1$ mol% $(TiO_2 + CuO)$ system 3: $BaTiO_3 + 1$ mol% CuO.

Thus, the formation of the observed melts (Fig. 2) are probably influenced by this a priori presence of the TiO_2 excess.

In the case of system 3 ($BaTiO_3 + 1$ mol% CuO) this TiO_2 excess apparently leads to the formation of Cu_3TiO_4, which melts at 1020°C instead of the expected eutectic melt of CuO-CuO_2 at 1075°C. Similar results were published by Yang [12], but he explained the identical melting temperatures of the above mentioned systems not with the presence of the TiO_2 excess rather than with a eutectic melt between CuO and $BaTiO_3$ at about 1000°C. Our own DTA measurements of both pure CuO and CuO-containing $BaTiO_3$ showed, that there is no influence of $BaTiO_3$ on the eutectic temperature of the system CuO-Cu_2O.

In order to find out the reasons for the observed melting point of the system $BaTiO_3 + 1$ mol% CuO, wetting experiments were carried out using the sessile-drop method.

A small quantity of CuO powder was tipped onto a $BaTiO_3$ compact (both sintered ceramic and single crystal) and heated in a defined manner under video recording. In order to get an overall view of the process the height of the tip was continuously measured and plotted against the temperature (height curve). Every change in the height of the tip indicates a reaction of the CuO itself or with the $BaTiO_3$ compact.

The height curve of the system CuO powder/$BaTiO_3$ single crystal is shown in Fig. 3. The increase of the height at about 1050°C corresponds with the release of oxygen during the reaction $2CuO \rightarrow Cu_2O + \frac{1}{2} O_2$. This is followed by a slight decrease of the height, which corresponds with the beginning of the eutectic melt (also seen in the video as the formation of a drop shape). At about 1125°C the formation of the eutectic

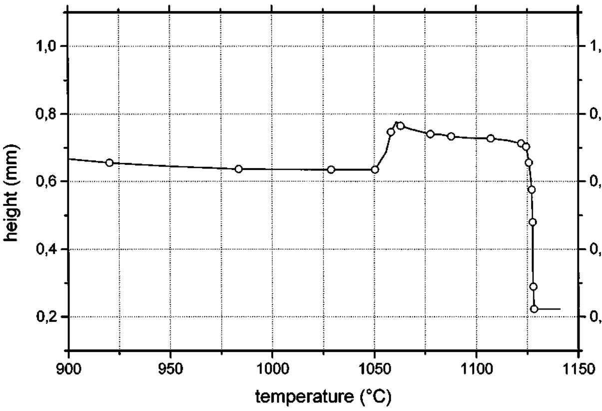

Figure 3 Height vs. temperature plot of CuO on a $BaTiO_3$ single crystal.

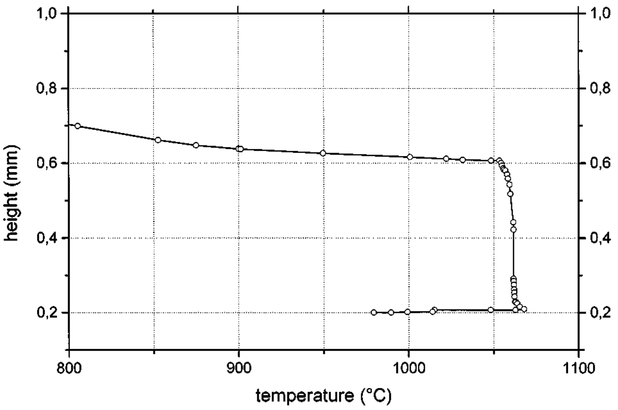

Figure 5 Height vs. temperature plot of CuO on a sintered $BaTiO_3$ (TiO_2 excess).

melt is completed, resulting in a distinct decrease of the height.

In order to detect possible boundary reactions between the CuO powder and the surface of the $BaTiO_3$ single crystal, the cross section of an as-fired specimen was investigated by EPMA measurements (Fig. 4). No migration between CuO and $BaTiO_3$ was found according to the element distribution images. Consequently, there is no reaction between CuO and $BaTiO_3$ until 1125°.

Furthermore, we used sintered $BaTiO_3$, prepared with an excess of TiO_2, as a compact. Compared to the single crystal we found a distinct decrease of the height only at about 1050°C, which indicates a reaction between the CuO and the TiO_2 rich phases at the grain boundaries of the $BaTiO_3$ compact (Fig. 5).

This assumption could be confirmed by EPMA investigations (Fig. 6). In the area of the CuO drop we found distinct Ti-enrichments, which establish the formation and melt of Cu_3TiO_4. Therefore, the observed endothermic peaks (ref. Fig. 2) in systems 2 and 3 can be attributed to the formation of the flux former Cu_3TiO_4.

However, the greatest disagreement between the observed and expected formation of the liquid phase we found in system 1 ($BaTiO_3 + 1$ mol% ($BaCO_3 + 2$ CuO)).

In the phase diagram BaO-CuO, published by Zhang *et al.* [15], there should be an eutectic melt between $BaCuO_2$ and CuO at about 890°C, which admittedly requires the formation of $BaCuO_2$ at lower temperatures. The formation of $BaCuO_2$ occurs at lower temperatures (800°C) only in the presence of BaO ($BaO + CuO \rightarrow BaCuO_2$). In case of $BaCO_3$ as a starting reagent, the decarbonization to BaO takes place at distinct higher temperatures. This leads to a delayed formation of $BaCuO_2$ and consequently to a "delayed" formation of the eutectic melt ($BaCuO_2$/CuO). This could be confirmed by DTA measurements (with 2 heat up cycles) of the system ($2CuO + BaCO_3$). Whereas during the first heat up cycle a delayed formation of the liquid phase was observed, during the second cycle the endothermic peak appeared at the expected eutectic temperature (890°C), since the formation of the $BaCuO_2$ already was completed (Fig. 7).

Another reason for the suppression of the eutectic melt seems to be the possible reaction of $BaCO_3$(BaO) with TiO_2 : $BaO + TiO_2 \rightarrow BaTiO_3$. This leads to a decrease of the BaO concentration or the BaO disappears completely. In the case of system 1 the strong endothermic peak (Fig. 2) should be attributed to the eutectic melt of CuO-Cu_2O.

The active flux formers of the investigated systems 1, 2 and 3 are shown in Table II. Although CuO creates a liquid phase at comparatively high temperatures, it seems to be the more suitable flux former. Compared to Cu_3TiO_4 the complete densification and grain growth occurs at lower temperatures.

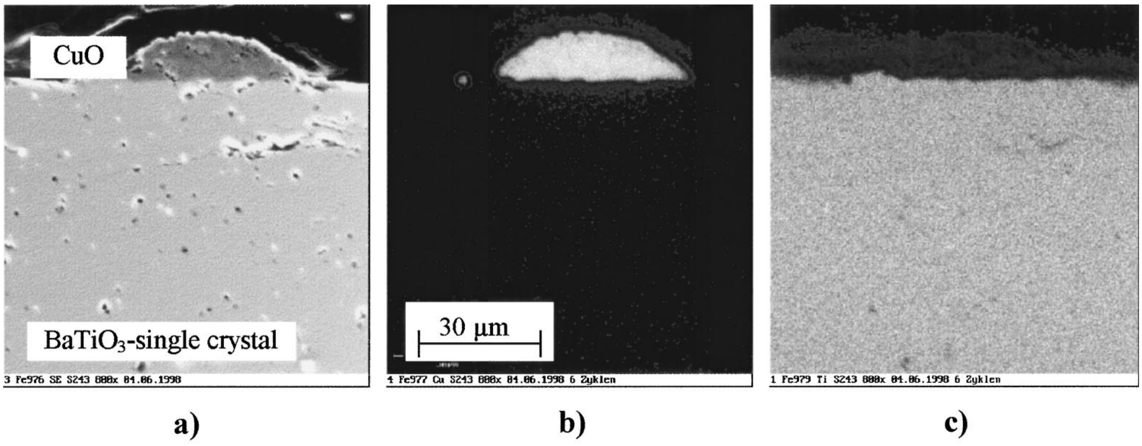

Figure 4 EPMA measurements of the system CuO/$BaTiO_3$ single crystal a) SE image b) Cu distribution c) Ti distribution.

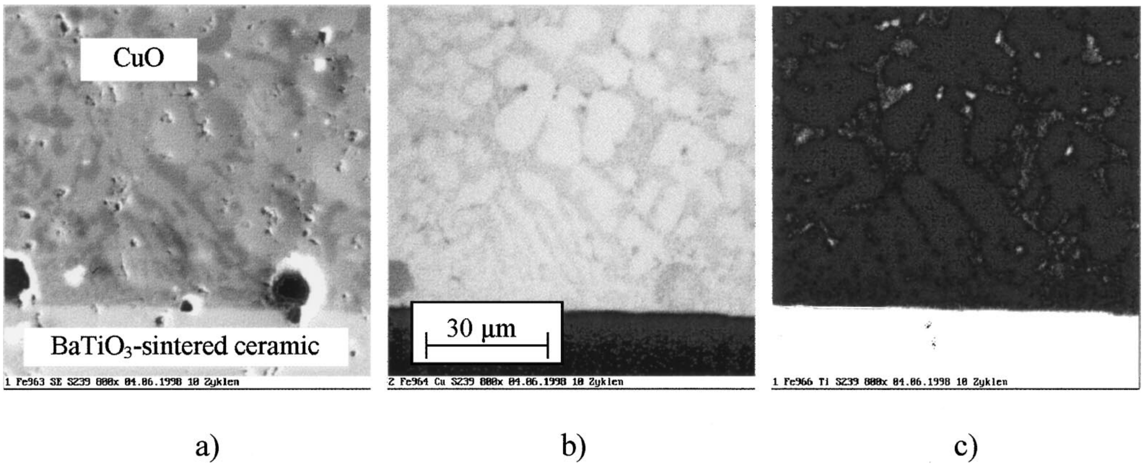

Figure 6 EPMA measurements of the system CuO/BaTiO$_3$-sintered ceramic a) SE image b) Cu distribution c) Ti distribution.

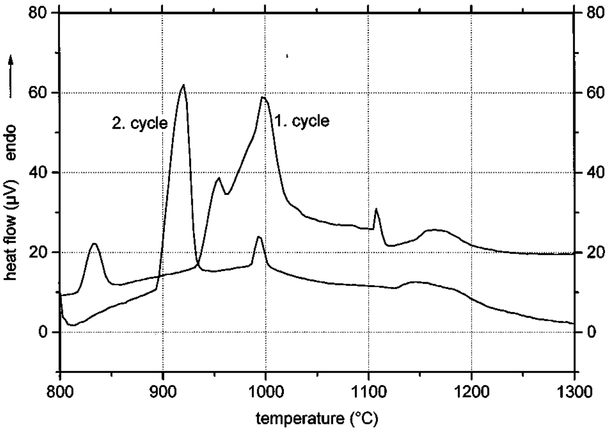

Figure 7 DTA measurements (2 heat up cycles) of the system (BaCO$_3$ + 2CuO).

TABLE II Active flux formers of the systems 1–3 and sintering temperature for a complete microstructure development (heating rate: 10 K/min; dwell time: 60 min)

Added Flux former	1 mol% (BaCO$_3$ + 2 CuO)	1 mol% (TiO$_2$ + CuO)	1 mol% CuO
Active Flux former	CuO-Cu$_2$O	Cu$_3$TiO$_4$	Cu$_3$TiO$_4$
Sintering temperature [°C]	1200	1250	1250

From Table II is also evident that in case of CuO-based flux former there is no immediate connection with the formation of a liquid phase and grain growth as it is known from the eutectic BaTiO$_3$/Ba$_6$Ti$_{17}$O$_{40}$. The densification behaviour and grain growth depend certainly on the properties of the liquid phase as high wettability and good solubility of the matrix material in the liquid [19]. Wetting experiments were carried out using the sessile-drop method to evaluate the CuO-based liquid phases in this direction. In Fig. 8 a video image of the melted drop (BaCuO$_2$-CuO) on BaTiO$_3$ at 1030°C is seen. The wetting angle is with 42° initially relatively high, compared with that of the eutectic BaTiO$_3$/Ba$_6$Ti$_{17}$O$_{40}$ with 8°. For the secondary phases CuO and CuO-TiO$_2$ a similar behaviour was observed.

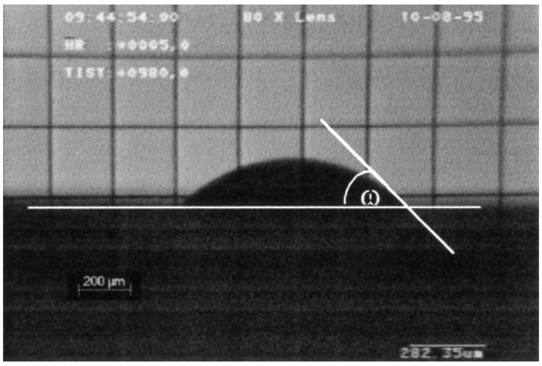

Figure 8 Video image of a melted drop of (BaCO$_3$ + 2CuO) for the determination of the wetting angle $\omega = 42°$ (1030°C).

3.2. CuO as an internal susceptor for microwave heating

The possibility to use microwaves as an alternative source for the sintering of ceramic materials is strongly dependent on the ability of the material to absorb mw energy. The magnitude of energy dissipation in a material (absorbed power per unit volume) is determined by both device and material parameters, as seen in Equation 1.

$$P_{abs} = \underbrace{|E|^2}_{\text{device parameter}} \omega\, \varepsilon_0\, \underbrace{\varepsilon_r''}_{\text{material parameter}} \qquad (1)$$

P_{abs}: absorbed power per unit volume; E: electric field strength; ω: frequency; ε_0: permittivity of free space; ε_r'': dielectric loss

An efficient mw heating requires sufficient power of the incident mw field and a minimum dielectric loss of the ceramic, respectively. Unfortunately, BaTiO$_3$ has a very small dielectric loss especially in the lower temperature range.

Beside the increase of the mw power, an alternative way to achieve an efficient mw heating is the use of so-called susceptors. These are materials with sufficiently dielectric loss over a wide temperature range which can be used as internal (secondary phases of the ceramic) or external susceptors (positioned around the ceramic) to improve the heat up in the lower temperature range. In the set of internal susceptors for $BaTiO_3$ ceramics CuO seems to be a suitable material in a twofold manner:

1. CuO has sufficient dielectric loss also in the lower temperature range.
2. CuO can be used as a flux former and, hence, as an appropriate sintering aid, as discussed above.

The dielectric properties of CuO [20] are shown in Fig. 9. Compared to $BaTiO_3$ [21] the distinctly higher dielectric loss of CuO is clearly seen.

In order to investigate the effect of CuO as an internal susceptor, following systems were mw heated from room temperature:

i) CuO
ii) $BaTiO_3 + 10$ mol% CuO
iii) $BaTiO_3 + 1$ mol% CuO

The heat up behaviour of the above mentioned systems are seen in Fig. 10, which shows the strong mw absorption of pure CuO and so its ability as internal susceptor.

On the other hand, with additions up to 10 mol% of CuO to $BaTiO_3$, a heat up of this specimen from room temperature up to sintering temperature could not be achieved by pure mw irradiation because of the limited power of the equipment. Nevertheless the effect of CuO as internal susceptor was demonstrated at least at higher temperatures preheating the sample until 700°C in a conventional furnace. Fig. 11 shows the action of CuO on the mw-initiated heating behaviour compared to that of pure $BaTiO_3$ under these conditions.

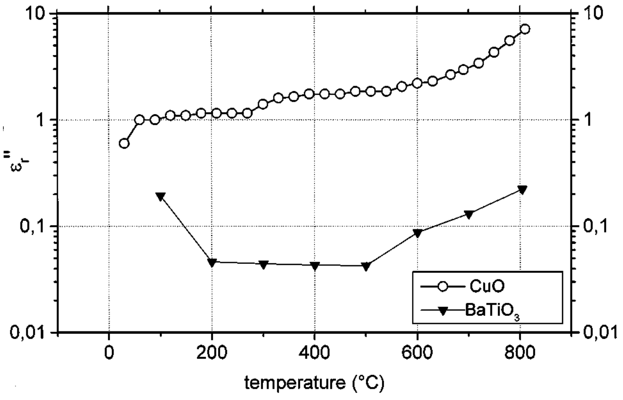

Figure 9 Dielectric properties vs. temperature of $BaTiO_3$ and CuO at 2.45 GHz [20, 21].

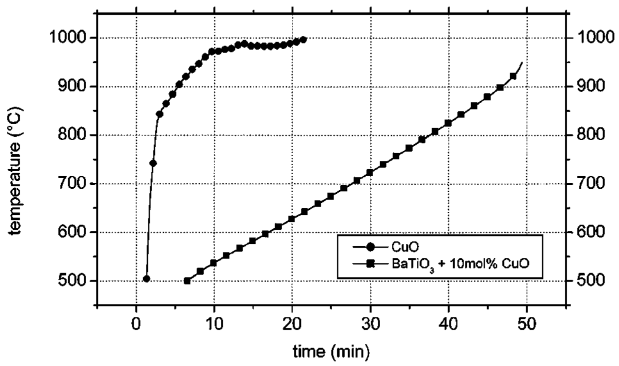

Figure 10 Heat up behaviour of CuO and ($BaTiO_3 + 1$ mol% CuO).

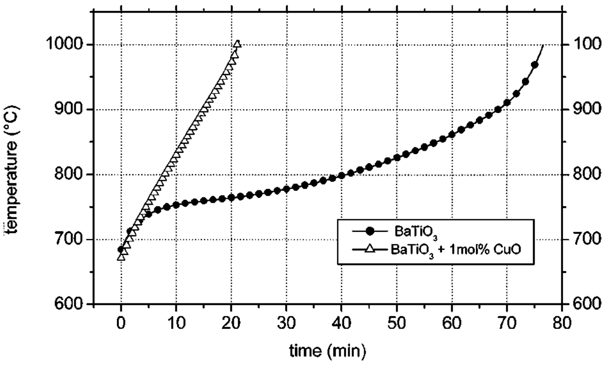

Figure 11 Heat up behaviour of $BaTiO_3$ and ($BaTiO_3 + 1$ mol% CuO) in the mw cavity at constant mw power (700 W) (preheated in a classical furnace until 700°C).

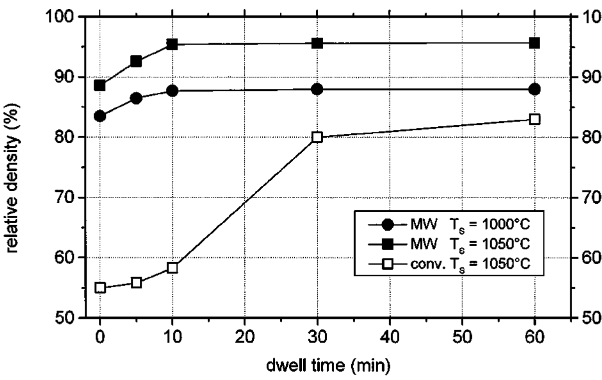

Figure 12 Isothermal shrinkage of the system ($BaTiO_3 + 1$ mol% CuO).

Beside the effect of CuO as lossy secondary phase, we could observe a specific mw effect of the CuO-containing $BaTiO_3$ ceramics. In opposite to systems with TiO_2 excess, the complete densification of the mw-sintered CuO-containing ceramics is achieved at distinctly lower temperatures. Additionally, in the case of isothermal shrinkage the specific mw effect of CuO is documented in Fig. 12. A possible reason for the accelerated shrinkage of the ceramic could be the influence of the microwaves on the properties (e.g.wettability) of the liquid phase [22].

3.3. Cu^{2+} as B-site substituent in $BaTiO_3$

Although CuO is mainly known as low melting flux former for $BaTiO_3$ ceramics, various authors reported on the influence of copper on the electric (dielectric) properties of the ceramics [11, 23]. However, the question remains still open wether the electrical properties are influenced by incorporation of Cu^{2+} into the $BaTiO_3$ structure or by the Cu-enriched intergranular phase.

Only a few is reported on the incorporation of Cu^{2+} into Ti sites of $BaTiO_3$ connected with the change of the properties of the final ceramics [24, 25].

Our own investigations showed that under certain conditions (Ba excess → Ba/Ti ratio > 1) the Cu^{2+} is incorporated into the $BaTiO_3$ structure. Because of its small ionic radius it substitutes for Ti^{4+}, which is commonly accepted in the literature. The stabilisation of the hexagonal phase, accompanied by a change in the microstructure, supports this findings. After sintering samples at 1300°C with a composition ($BaTiO_3 + 2$ mol% $BaO + 2$ mol% CuO) we observed a microstructure with a lot of exaggerated plate-like grains surrounded by small globular grains (Fig. 13). By X-ray diffraction measurements hexagonal $BaTiO_3$ was detected (Fig. 14). In the case of the sintering temperature 1300°C (dwell time 1 h) a content of hexagonal phase of about 27% was detected, determined by analysing the intensity ratios $(103)_h/(111)_t$ and $(103)_h/(200)_t$. Normally in the case of $BaTiO_3$ the phase transition cubic → hexagonal occurs at about 1460°C [1]. The Cu doping gives rise to the stabilisation of the hexagonal phase at room temperature. In analogy to the effect of incorporated Mn^{3+} ions, the incorporation of copper as an acceptor dopant into Ti sites results in the formation of additional oxygen vacancies. This leads in combination with the Jahn-Teller distortion to the formation of the hexagonal structure as discussed in detail elsewhere [26].

An excess of barium is necessary to incorporate a significant amount of Cu at Ti sites, but a certain amount remains as a part of the intergrannular phase. E.g., in case of a specimen, sintered at 1400°C for 1 h, at least 1 mol% Cu is incorporated. A paper, dealing with the incorporation of Cu into $BaTiO_3$, is in preparation.

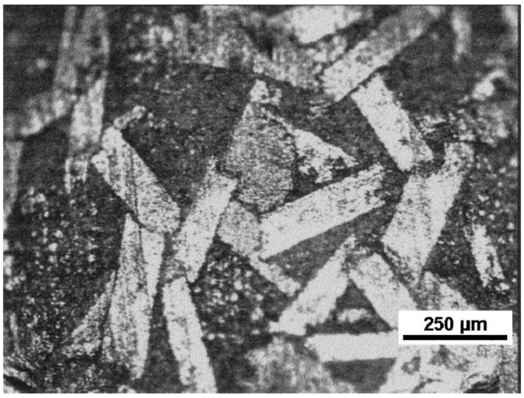

Figure 13 Microstructure (optical micrograph) of ceramics with the nominal composition ($BaTiO_3 + 2$mol% $BaO + 2$mol% CuO) sintered at 1300°C.

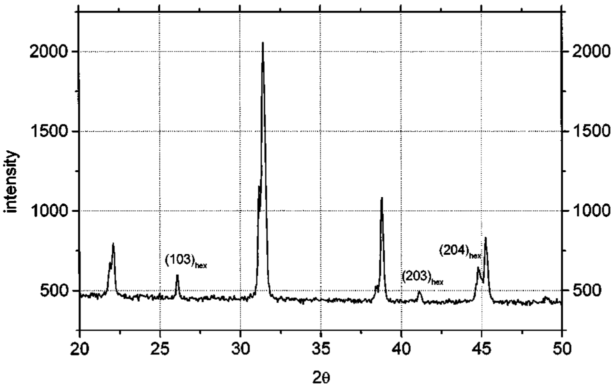

Figure 14 X-ray diffraction pattern of ceramics with the nominal composition ($BaTiO_3 + 2$mol% $BaO + 2$mol% CuO) sintered at 1300°C.

4. Conclusions

CuO can be used as an effective sintering agent for $BaTiO_3$ based ceramics both as low melting flux former and as internal susceptor for microwave sintering.

Various CuO-based liquid phases were investigated and the pure CuO seems to be the most effective flux former for the achievement of a complete shrinkage and grain growth at lower temperatures. However, at all CuO-based flux formers we observed no immediate response with the formation of the liquid phases and grain growth and a slightly delayed shrinkage. One reason for that should be the poor wettability of $BaTiO_3$ by the Cu-containing liquid phases.

In the case of mw sintering, the use of CuO leads to an increased mw absorption of the $BaTiO_3$ ceramics. Beside the effect of CuO as lossy secondary phase we could observe a specific mw effect of the CuO-containing $BaTiO_3$ ceramics. In opposite to systems with TiO_2 excess, the complete densification of the mw-sintered CuO-contained ceramics was achieved at distinctly lower temperatures.

In the case of systems with a Ba/Ti ratio > 1, the addition of CuO results in a stabilisation of the h-$BaTiO_3$ at room temperature, which is a strong indication for the incorporation of Cu^{2+} ions into the $BaTiO_3$ structure at Ti sites.

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