Preparation and dielectric properties of $CuAlO_2$ ceramics

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***Abstract* – Within this work, the focus was on preparation of the delafossite $CuAlO_2$ single phase powder and ceramic with a high density by the solid state synthesis, and on dielectric properties of the as-synthesized ceramic. The reaction between the nanoboehmite γ-AlOOH, with a high specific surface area, and the Cu_2O, with the particles below 1 μm, was enhanced by comminution in a high energy mill, which resulted in reduction of the particle size and consequently shorter diffusion paths between constituent powders. The phase pure $CuAlO_2$ powder was synthesized upon heating the reagent powder mixture two times for 10 h at 1100°C in the inert argon atmosphere as confirmed by the X-ray analysis. The ceramic with 86% of theoretical density was obtained after sintering the $CuAlO_2$ powder compact at 1100°C for 2 h in air. According to the X-ray analysis the ceramic sample was single-phase. The bulk of the sample revealed a dense microstructure with a uniform distribution of porosity within the delafossite matrix. However, traces of Cu-rich impurities have been identified at the surface of the pellets by the EDXS analysis. The semiconducting nature of the ceramic sample was confirmed by the temperature dependent dielectric parameters measurements (ε and tgδ) in the 10 kHZ-1MHz frequency range between 297 and 473 K.**

1 INTRODUCTION

Recently, due to an increasing interest in the functional oxides for transparent electronic applications, a considerable effort has been devoted to the study and development of different n- and p-type oxide semiconductors. The p-type delafossite materials $CuMO_2$ (M = Al, Cr or Y) are of particular interest. Copper aluminate ($CuAlO_2$) films prepared by physical vapor deposition have been reported to exhibit the p-type behavior and have already been used in various applications in optoelectronics [1, 4]. Undoubtedly, the phase-pure targets with a high relative density are prerequisites for physical vapour deposition of high quality $CuAlO_2$ films. However, secondary phases and low relative densities have been reported for the solid-state synthesized delafossite $CuAlO_2$, although high processing temperatures and extremely long times have been used [5, 6]. The presence of secondary phases, especially as they are the result of degradation of the $CuAlO_2$ during the cooling cycle of the thermal treatment can drastically affect electrical and dielectric properties of material.

Within this work, the focus was on processing of $CuAlO_2$ single-phase powder and ceramic with a high relative density by the solid-state synthesis using the the nano-boehmite powder. For comparison, the delafossite powder was also synthesized from the mixture of oxides.

Dielectric properties of the as-prepared ceramic were analysed to confirm the semiconducting nature of material. The results shown in this work are a contribution to a better understanding of processes involved in the synthesis of single phase and dense ceramic targets for physical vapour deposition of thin films.

2 EXPERIMENTAL

2.1 Processing of $CuAlO_2$ powder and ceramic

The $CuAlO_2$ powder was prepared by the solid-state synthesis from the nano-boehmite $AlOOH.xH_2O$ (99.99%, expressed as the purity of the γ-Al_2O_3 phase at 600°C, d_{50} = 0.18 μm of the primary particles, SkySpring Nanomaterials, Houston, Texsas) and the milled Cu_2O (99.9%, d_{50} = 4.18 μm – the median particle size of starting powder, Alfa Aesar, Karlsruhe, Germany). The latter was obtained by wet high-energy milling in a planetary mill for 8 h (Retsch PM400, Retsch GmbH, Haan, Germany) using zirconia vials and balls, and isopropyl alcohol (IPA) as the liquid medium. The particle size of the as-milled Cu_2O powder was below 1 μm. Afterwards the powders were mixed in a stoichiometric molar ratio (Cu/Al = 1), homogenized in a planetary mill in IPA for 4 h and dried in a desiccator at 90°C. To optimize the calcination process of the as-prepared mixture with respect to the final phase, several calcination procedures were tested in different reactive atmospheres (oxidizing –air and inert -Ar) in a heating stage microscope (Leitz V.1A; Leitz, Wetzlar, Germany). The results of these analyses indicated that heating in inert –Ar atmosphere at temperatures above 1000°C could lead to the pure delafossite phase.

Consequently, the powder mixture was pressed into pellets and calcined twice at 1100°C for 10 h in

argon. To reduce the particle size and shorten the reaction paths between reacting species, the pellets were crushed between two calcination steps in a mortar and milled in a mixer mill for 30 min (Retsch MM400, Retsch GmbH, Haan, Germany) in IPA. The median particle size of final powder product was determined from the area distribution measured by a laser granulometer (Microtrac S3500 Particle Size Analyzer, Montgomeryville, PA).

The nano-boehmite derived $CuAlO_2$ powder was uniaxially pressed into pellets of 8 mm in diameter at 100 MPa and subsequently by cold isostatic pressing at 700 MPa, and sintered in air with a constant heating rate of 5^oC/min to 1100^oC, followed by a holding time of 2 h. The density of the sintered compact has been calculated from the measured mass and dimensions of the sample. The relative density was calculated using the theoretical value of 5.10 g/cm^3, given in the crystallographic card of $CuAlO_2$ (PDF 00-035-1401, R3-m) [7].

The $CuAlO_2$ powder was synthesized also from the α-Al_2O_3 (AKP -50, 99.5%, d_{50} = 0.36 μm, Sumitomo Chemical, Tokyo, Japan) and the pre-milled Cu_2O.

2.2 Characterization

The phase composition of the powder and ceramic were analyzed by PANalytical diffractometer (X'Pert PRO MPD, Almelo, Netherlands). The measurements were performed in Bragg-Brentano geometry using the CuKα radiation and X'Celerator detector configured in reflection geometry. The data acquisition was done in the step scan mode ($2\theta = 0.034^o$, integration time 100 s) in angular range $2\theta = 10 - 70^o$. The phases were identified with the X'Pert High Score package, using the PDF-2 reference patterns database.

The microstructure of the $CuAlO_2$ powder was examined by the field emission scanning electron microscope FE-SEM (JEOL JSM 7600F, Tokyo, Japan). The powder was ultrasonically dispersed in IPA and the suspension was spread at the surface of sample holder. After alcohol evaporation a 5 nm thick layer of carbon was deposited on the powder surface under the vacuum and analyzed. The microstructure and phase composition of sintered sample was analyzed on polished cross-section using the scanning electron microscope, SEM (JEOL JSM 5800, Tokyo, Japan) equipped with a LINK ISIS EDS 300 energy dispersive system (Oxford Instruments Analytical Ltd., Abington, UK).

For dielectric measurements, the sintered $CuAlO_2$ pellet was cut perpendicular to the cylindrical axis to form the 1mm thick parallel faces, which were polished and gold electrodes were deposited on them. The temperature dependence of the dielectric permittivity and losses (ε' and tanδ) were measured in the temperature range of 297 to 473 K, at three different frequencies (10, 100 and 1000 kHz).

3 RESULTS AND DISCUSSION

3.1 Phase composition and microstructure of the nano-boehmite derived $CuAlO_2$ powder and ceramic

The expected advantages of using the nano-boehmite powder instead of the α-Al_2O_3 in the solid state synthesis were: 1) the nano-boehmite should enable a good mixing with the Cu_2O and thus provide short reaction paths between the species, and 2) the higher reactivity of the boehmite as compared to the oxide was expected as a consequence of the thermal decomposition of the former (Hedvall effect, [8]), which can significantly promote the reaction. The morphologies of the $AlOOH.xH_2O$ and α-Al_2O_3 starting powders and $AlOOH.xH_2O\_Cu_2O$ and $Al_2O_3\_Cu_2O$ powder mixtures are presented in Fig. 1. The $AlOOH.xH_2O$ exhibited the granular morphology. The majorities of granules have a medium diameter of ~7 μm and can be easily crushed and dispersed in IPA by mechanical milling. The SEM micrograph taken at a higher magnification (see the inset in Fig. 1a)) reveals that the granules are built of nanorods as primary particles with lengths of 100-200 nm and diameters 10-20 nm. In contrast, the Al_2O_3 particles are equiaxed and larger, a few 100 nm. Depending on the powder used as an Al-source, the powder mixtures showed the considerably different morphologies (Fig. 1c) and d)). In the former case, the rod like nano-boehmite particles are well dispersed across the surfaces of the Cu_2O particles, providing shorter reaction paths then in the latter case.

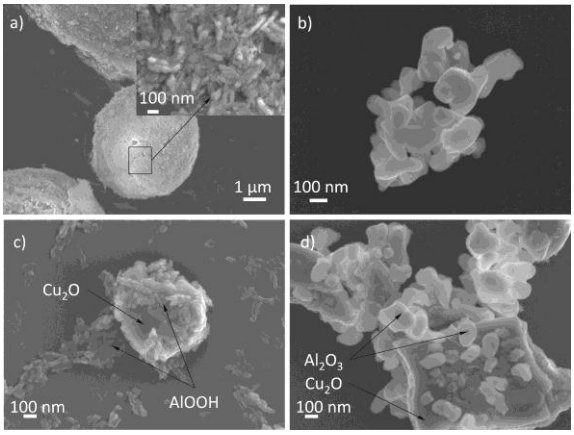

Figure 1: SEM micrographs of the a) $AlOOH.xH_2O$, b) Al_2O_3, c) $AlOOH.xH_2O\_Cu_2O$ and d) $Al_2O_3\_Cu_2O$ powder mixtures. The inset shows a higher magnification view of the boxed area.

A proper selection of the temperature, time and atmosphere of the solid-state reaction should be considered. Particularly, in the case of the $CuAlO_2$, the valence state of the Cu ions in the powder mixture during the heating and cooling cycles should be controlled. The cuprous Cu^{+1} ion can be easily oxidized to cupric Cu^{+2} ion during heating in air atmosphere at relatively low temperatures (200-500°C). The CuO reacts with the Al_2O_3 according to the equation (1) at temperatures below 1100°C:

$$CuO + Al_2O_3 \rightarrow CuAl_2O_4 \quad (1)$$

From the literature [9] it is inferred that the $CuAlO_2$ should be formed according to the following reaction (2), but only at the temperatures above 1100°C.

$$CuO + CuAl_2O_4 \leftrightarrow CuAlO_2 + 1/2O_2 \quad (2)$$

Only at high enough temperatures, there is enough energy for CuO and spinel $CuAl_2O_4$ to react. Furthermore, the CuO gradually decomposes and evaporates from the powder mixture upon heating above 1100°C. According to the Le Chatelier's principle, the equilibrium should be shifted toward the backward reaction in equation (2), leading to re-appearance of the spinel-$CuAl_2O_4$ in the calcined powder, after cooling cycle.

To avoid the formation of the undesired spinel-$CuAl_2O_4$ phase, it is necessary to preclude the oxidation of the cuprous ions during the heating cycle and in that way enable the formation of the delafossite-$CuAlO_2$ through the following reaction (3):

$$Cu_2O + Al_2O_3 \rightarrow CuAlO_2 \quad (3)$$

The inert atmosphere, such as N_2 or Ar, provides the best conditions for the completion of the reaction presented in equation (3), because almost all cuprous ions stay in +1 valence state.

The dynamic shrinkage vs. temperature curves have been recorded at a constant heating rate of 10°C/min to investigate the temperature behavior of the $AlOOH.xH_2O\_Cu_2O$ powder mixture during the heating stage of the calcination in air and argon atmospheres. The results are collected in Fig. 2, together with the XRD patterns of the powdered samples after heating in the microscope up to 1150°C in above mentioned atmospheres. Both shrinkage curves could be divided into three regions. At low temperatures, i.e. up to 450°C the shrinkage was not observed due to the lack of reaction between the reactants. The second region between 450°C and 800°C could be related to the removal of the chemisorbed water and decomposition of the γ-AlOOH [10], and partial reaction between the reactants, as verified by XRD analysis at different temperatures (results were not presented here). A steep slope was detected in both shrinkage curves, indicating the final reaction between the components. The shrinkage at the temperature of 1120°C was 15.2 % for the sample heated in air, while for the sample heated in Ar atmosphere it was only 4.57% at the temperature of 980°C. According to the XRD patterns, shown as insets in Fig. 2 a) and 2 b), almost pure delafossite $CuAlO_2$ was formed during heating in the inert atmosphere, indicating that the equilibrium under the mentioned conditions was shifted toward the forward reaction presented in equation (3). The observed decrease in the intensity of the $CuAlO_2$ diffraction peaks could be related to a slower crystallite growth in the inert than in the air atmosphere. The reaction in air atmosphere resulted in the formation of the spinel-$CuAl_2O_4$ phase (see the inset in Fig. 2 a)), therefore the powder obtained by calcination in Ar atmosphere was considered for further study.

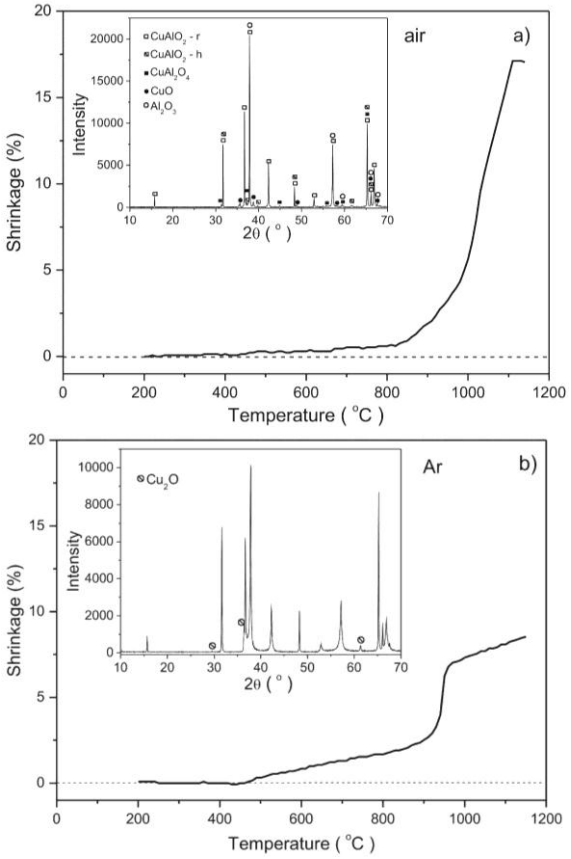

Figure 2: Shrinkage versus temperature of the $AlOOH.xH_2O\_Cu_2O$ powder compacts in a) air and b) argon atmospheres. The insets show the XRD patterns detected on the powdered samples after heating in the microscope to the final temperature.

According to the results obtained by the heating stage microscope, the temperature of 1000°C was selected for the calcination of the

$AlOOH.xH_2O\_Cu_2O$ powder mixture in argon. The reaction time of 10 h did not result in formation of the phase pure delafossite, as shown in Fig. 3 a). The temperature was increased to 1100°C, and after 10 h the $CuAlO_2$ phase with only a small amount of the Cu_2O was obtained (Fig. 3b). For comparison, the conventional solid state reaction with the nano-Al_2O_3 and Cu_2O was conducted. The mixture was heated in argon atmosphere at 1100°C for 10h, and the result is shown in Fig. 3c). Besides the $CuAlO_2$, both unreacted oxides in appreciable amounts were found in the powder. A similar phase composition was obtained even after the 24 h of heating in argon (XRD pattern was not presented here).

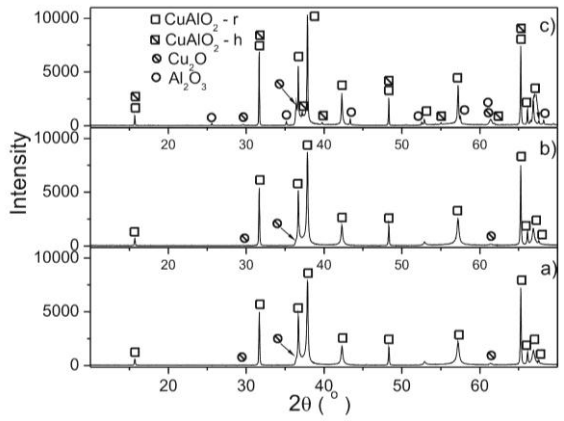

Figure 3: XRD patterns of the $AlOOH.xH_2O\_Cu_2O$ mixture calcined at a) 1000°C for 10h, b) 1100°C for 10h, and $Al_2O_3\_Cu_2O$ mixture calcined at c) 1100°C for 10 h in Ar atmosphere.

The phase pure delafossite powder was synthesized after a double calcination of the $AlOOH.xH_2O\_Cu_2O$ powder mixture at 1100°C for 10h in Ar atmosphere.

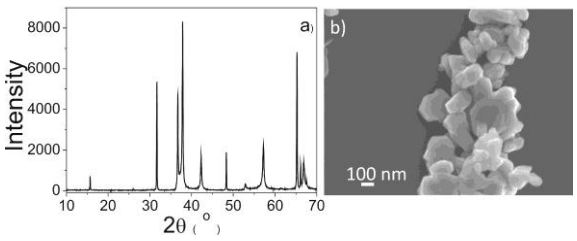

Figure 4: The $AlOOH.xH_2O\_Cu_2O$ powder mixture calcined 2 x 10h at 1100°C in Ar: a) XRD pattern and b) SE micrograph.

The XRD result, presented in Fig 4 a) confirmed that the traces of the Cu_2O, observed in the powder after the first calcination (compare with Fig. 3b) completely disappeared during the second calcining step. The powder consisted of loose agglomerates of plate-like particles of a few 100 nm in size (see Fig. 4 b). The median particle size of final powder product, determined by a laser granulometer was $d_{50} = 0.35$ μm.

The as-synthesized $CuAlO_2$ powder was uniaxially pressed into pellets by applying the pressure of 100 MPa and subsequently by cold isostatic pressing at 700 MPa. The green densities of the powder compacts were 60 % of the theoretical density. Afterwards, the compacts were sintered at 1100°C for 2 h in air and argon atmosphere. Sintering of the $CuAlO_2$ powder compacts in argon atmosphere resulted in almost no densification, the relative density was about 60 % TD, while the ceramic, sintered in air atmosphere reached 4.36 g/cm^3, or 86% of theoretical density. These experimental observations have shown that sintering of $CuAlO_2$ is not only temperature dependent, but it is also influenced by the surrounding gas atmosphere. Due to the fact that the shrinkage was not observed in the sample heated in argon atmosphere, it is possible to conclude that the material transport in inert atmosphere contributed to lowering of the driving force for densification.

In comparison with the literature data on the $CuAlO_2$ ceramics prepared by the solid state synthesis and conventional sintering or by the reaction-sintering process, the density of the material sintered in air, presented in this work is much higher. For example, Liou et al [6] obtained low densities of 2.53 – 2.68 g/cm^3 (49.7 – 52.6 % TD) of $CuAlO_2$ pellets prepared by reactive sintering process at 1200°C for 2-6 h in air. Slightly higher values of 2.83 – 3.04 g/cm^3 (55.6 – 59.7 % TD) were achieved after sintering at 1350°C.

Park and coworkers [9] obtained $CuAlO_2$ ceramic samples with the density of 3.74 g/cm^3 and 3.82 g/cm^3 (73.5 – 75 % TD) after two times for 20 h of sintering at 1160°C and 1200°C, respectively. Only a recent report from Dura and coworkers [11] sheds a new light on the production of dense $CuAlO_2$ ceramic. Using the conventional solid state synthesis proposed by Kawazoe et al. [1], after several repeated milling and calcining steps of the Cu_2O and Al_2O_3 powder mixture they prepared the powder, which was subsequently submitted to intensive mechanical milling for 36 h and sintering at 1100°C in air. The resulting $CuAlO_2$ ceramic sample with the density of 4.43 g/cm^3 (87 % TD) was obtained. However, the material contained a small amount of the undesired $CuAl_2O_4$ spinel phase [11].

It seems that some additional energy induced either by heating the powder mixture at temperatures higher than 1200°C or by the defects created during the highly-energetic milling, is needed for fabrication of dense $CuAlO_2$ ceramic. Both procedures suffer from

serious drawbacks, namely in the former the sintering temperature is close to the melting point of $CuAlO_2$, which is about 1238°C in air where it decomposes into Al_2O_3 and a liquid [12]. In the latter case, the obtained material was not a single phase, it contained traces of spinel [11].

The XRD pattern and the SEM / EDXS images of the interior and edge region of the sintered pellet are collected in Fig. 5.

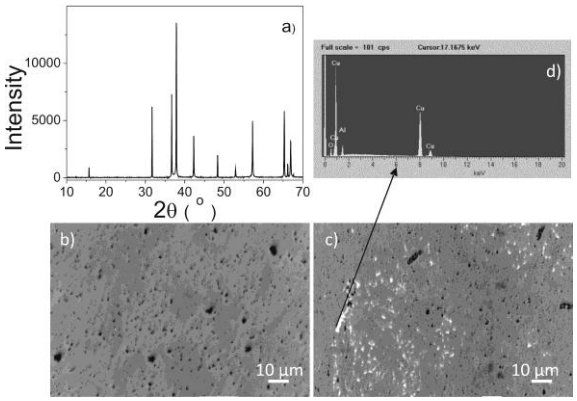

Figure 5: XRD a) and SEM micrographs of the $CuAlO_2$ ceramic, sintered at 1100°C for 2h in air: interior b) and edge c) regions of the pellet, and EDXS analysis d) performed at the edge region of the pellet.

The dense ceramic prepared by the solid state synthesis from the nano-boehmite and the Cu_2O powder mixture, reported in this work, is a phase pure delafossite $CuAlO_2$ according to the XRD. The analysis of the microstructure by SEM / EDXS revealed that the bulk of the sample had a dense microstructure with a uniform distribution of porosity within the delafossite matrix. However, traces of Cu-rich impurities could be identified at the surface of the pellet, as confirmed by EDXS.

3.2 Dielectric properties of the $CuAlO_2$ ceramic

The dielectric permittivity and losses (ε' and tgδ) of the $CuAlO_2$ ceramic sample were measured in the temperature range of 297 to 473 K, at three different frequencies (10, 100 and 1000 kHz). The results are shown in Fig. 6. The room temperature value of the dielectric permittivity at 100 kHz is 105. In the measured frequency and temperature range, the dielectric permittivity increases with increasing temperature, and it decreases with increasing frequency, which confirms the semiconducting nature of the $CuAlO_2$ ceramic sample. The temperature dependence of the dielectric loss factor shows the typical semiconducting behaviour - the apparent increase with increasing temperature.

It was reported in [13] that the decomposition of the $CuAlO_2$ into CuO and spinel-$CuAl_2O_4$ due to the intentional oxygen doping at high temperatures may hinder the charge transportation in the delafossite structure. In general, any process that could be responsible for degradation of the delafossite structure could be responsible for dramatic changes in electrical and dielectric properties of this material, which are important for possible applications. In our case, after 2 h of sintering in air atmosphere, the decomposition of the $CuAlO_2$ to CuO and spinel-$CuAl_2O_4$ was not observed.

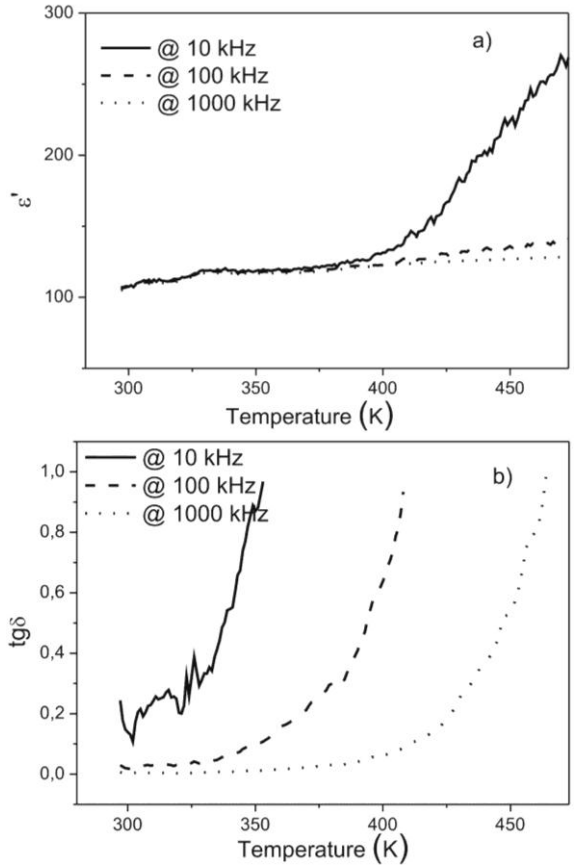

Figure 6: Temperature dependence of the a) permittivity ε' and b) dielectric loss tgδ for the $CuAlO_2$ ceramic, measured at three different frequencies.

The presence of the Cu-rich impurities at the surface of the sintered sample could be responsible for the slightly higher value of the dielectric constant measured at 10 kHz at room temperature compared to the one reported by Brahimi [14]. Nevertheless, the measured dielectric properties of the ceramic sample sintered at 1100 °C for 2 h in air support the conclusion that the ceramic is predominantly single phase delafossite.

4 CONCLUSIONS

In conclusion, the pure delafossite $CuAlO_2$ powder has been prepared from the nano-boehmite $AlOOH.xH_2O$ instead of the usually used Al_2O_3 powder, and pre-milled Cu_2O by the solid state synthesis by a double heating for 10 h at 1100°C in argon. The well-mixed powder mixture, consisting of the 1 μm sized Cu_2O particles fully covered with fine $AlOOH.xH_2O$ rod-like particles, and decomposition of the nano-boehmite powder upon heating have contributed to acceleration of the inherently slow solid state diffusion during the calcination step. A short sintering time of 2 h at 1100°C in air atmosphere was essential to obtain single phase and dense $CuAlO_2$ ceramic with 86 % of theoretical density. According to EDXS, traces of Cu-rich impurities were identified only at the surface of the pellet, while the bulk of the sample was single phase delafossite with uniformly distributed porosity.
The semiconducting nature of the sintered sample was confirmed by the apparent increase of both dielectric permittivity and dielectric loss factor with increasing temperature and decrease with increasing frequency.

Acknowledgments

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