Processing-property relationship for solid-state synthesized $CuAlO_2$ ceramic

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Copper aluminate ($CuAlO_2$) is the most extensively studied cuprous delafossite (general formula: $A^+B^{3+}O_2$, group: R-3m) p-type semiconductor, whose exceptional electrical, optical, magnetic and catalytic properties found many applications in catalysis and (opto)electronic technology, e.g. as field electron emitters, light-emitting diodes, functional windows or solar cells. While the processing-property correlations have been well explored for many materials with perovskite or spinel structure, the investigations of the mentioned relationship for delafosittes are still eliciting the attention of scientists. In order to attain the optimized $CuAlO_2$ material for a specific application, for example, as ceramic targets for further physical vapour deposition of thin films, the preparation routes should be precisely designed. The adequate synthesis parameters should allow the formation of pure $CuAlO_2$ and disable its disproportionation to CuO and detrimental spinel $CuAl_2O_4$. For the spinel $CuAl_2O_4$ phase is known that can notably influence the final product properties, since it is an n-type material and insulator.

Concerning the synthesis of $CuAlO_2$ sputtering targets, our approach to process single-phase delafossite $CuAlO_2$ has been to enhance the solid-state synthesis by milling of nano-boehmite $AlOOH.xH_2O$ and pre-milled Cu_2O powders mixture, and to control the atmosphere both during the synthesis and sintering steps. The pure delafossite $CuAlO_2$ powder was prepared by the double heating of the above mentioned powder mixture for 10 h at 1100 ^oC in argon atmosphere. A short sintering time of 2 h at 1100 ^oC in air atmosphere was essential to obtain single phase and dense $CuAlO_2$ ceramic with 86 % of theoretical density. In contrast to X-ray analysis, which confirmed the single phase composition of the sintered sample, the BEI/EDXS analysis revealed the presence of traces of Cu-rich impurities at the surface of the pellet, while the bulk of the sample was single phase delafossite with uniformly distributed porosity.

For further use, the sintered samples were cut and polished to remove the CuO from the surface. Beside the strong modes at 418 cm^{-1} and 767 cm^{-1}, typical for delafossite structured $CuAlO_2$, the low intensity features were also observed in the Raman spectrum of the sintered sample and could be mainly related to the leaning delafossite or 2H-$CuAlO_2$ hexagonal polytype. Nominally pure $CuAlO_2$ sample was analysed by electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectroscopy to get

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microscopic insight into composition of the sintered sample, i.e. presence of impurities within the bulk network.

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. Furthermore, the temperature dependence of the Hall parameters (resistivity-ρ, carrier concentration-N_D, mobility-μ) of the $CuAlO_2$ ceramic was analysed. The resistivity of the samples decreased with increasing temperature from 830 Ωcm at 230 K to 11 Ωcm at 350 K, due to the increase in both the number of charge carriers and their mobility. Also, room temperature Hall measurements revealed a positive Hall coefficient $R_H = 33.8\ cm^{-3}C^{-1}$, which confirmed the p-type conduction of the material.

Within this contribution the relationship between processing, composition and properties of the $CuAlO_2$ ceramic is discussed.