Solid state synthesis of $CuAlO_2$: From a nano-boehmite - cuprous oxide powder mixture to the single phase ceramics

Vojisavljević Katarina (1), Malič Barbara (1), Senna Mamoru (1, 2), Drnovšek Silvo (1), Kosec Marija (1)

(1) Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

(2) Keio University, Yokohama 223, Japan

katarina.vojisavljevic@ijs.si

Recently, a considerable effort has been devoted to research and development of n- and p-type transparent conducting oxides (TCO), where the improvement of their properties will give an added impetus in the field of invisible electronics for production of different optoelectronic devices. Due to the lack of p-type oxide semiconductors, with high enough conductivity and transparency across the visible spectrum, special attention has been paid to synthesis of p-type delafossite $CuMO_2$ (M = Al, Cr or Y) materials. Copper aluminate ($CuAlO_2$) thin films prepared by physical vapour deposition from multicomponent sputtering targets exhibit the p-type behaviour and have already been used in various applications in optoelectronics. Besides, the $CuAlO_2$ can be used as a catalyst for the conversion of solar power to hydrogen energy, thermoelectric converter or ozone sensor.

The first step in production of high quality sputtering targets is related to preparation of phase pure powders and dense ceramics.A delafossite $CuAlO_2$ has been usually prepared by conventional solid state synthesis from CuO or Cu_2O and Al_2O_3 powders, where milling in different liquid media with long milling times were at first used to achieve homogeneous reagent mixtures, and then multiple calcinations at high temperatures with intermediate wet-milling steps were applied. However, secondary phases and low relative densities are yet to be improved for the solid-state synthesized delafossite $CuAlO_2$, even when high processing temperatures (1200 – 1350 ^oC) and extremely long periods have been used.

The main idea of this work was to promote the reaction of the delafossite $CuAlO_2$ formation during solid state synthesis by changing the usually used Al_2O_3 with more reactive Al- compounds, such as boehmite (AlOOH). Its exothermic decomposition at low temperatures is expected to improve the conventional solid state synthesis route. The well-mixed powder mixture, consisting of the 1 μm sized Cu_2O particles fully covered with fine nano-boehmite rod-like particles, and decomposition of the nano-boehmite powder upon heating have contributed to acceleration of the inherently slow solid state reaction during the double calcination of the powder mixture for 10 h at 1100 ^oC. The secondary spinel-$CuAl_2O_4$ phase has been avoided by calcining the powder mixture in argon atmosphere, where the oxidation of cuprous ions has been precluded. A short sintering time of 2 h at 1100 ^oC in air atmosphere was essential to obtain single phase $CuAlO_2$ 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 remained as a single phase delafossite with uniformly distributed porosity. 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.