Self-sustained combustion synthesis of the p-type nanocrystalline CuAlO₂ powder

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Recently, a considerable effort has been devoted to research and improvement of both dielectrics and wide band-gap semiconductors for the realization of fully transparent devices. Due to the lack of available p-type transparent conducting oxide (TCO) materials, special attention was paid to production of delafossite structured $CuMO_2$ (M = Al, Cr or Y), which exhibit sufficiently large energy gap, required for transparency across the full visible spectrum, and high enough concentration of holes with sufficiently large mobility. Those materials are considered to be good candidates for p-type TCOs. Among them, the $CuAlO_2$ seems to be the most promising candidate to fulfill the demands for technical application.

However, related studies on CuAlO₂ are interested not only in examination of the transparent conducting oxides properties, but also in exploring its applications as a catalyst for the conversion of solar power to hydrogen energy, catalysts for steam reforming process and exhaust gas purification, room temperature ozone sensors, or thermoelectric devices. The performance of CuAlO₂ in some of the mentioned applications could be optimized by increasing surface area and decreasing its particle size. Therefore, the synthesis of nanocrystalline CuAlO₂ has been a hot topic for material chemists.

The nanocrystalline delafossite CuAlO₂ powder was synthesised by a sol-gel nitrate-citrate self-sustained combustion route. Citric acid was introduced both as the chelating and reducing agent or fuel. The citric acid/metal ion ratio was adjusted to provide fuel-lean, stoichiometric or fuel-rich conditions of the redox reaction. Equimolar amounts of copper and aluminium nitrates and the citric acid were dissolved in deionized water. The solution was agitated at room temperature for 1 h, and then neutralized to increase the efficiency of chelating agent. After several hours of drying in temperature range 60 °C - 80 °C, the sol was turned to homogeneous viscous gel. During the rapid heating, the gels auto-ignited at approximately 250 °C (depending on the amount of the fuel) and underwent smouldering combustion spontaneously with the evolution of large amounts of gases, subsequently forming the grey-black voluminous precursor powders.

According to the X-ray diffraction analysis the phase pure delafossite was obtained only when the precursor powder was prepared from the stoichiometric redox reaction, and after the calcination at 920 °C for 4 h in Ar atmosphere. The field emission scanning electron micrographs revealed the cauliflower aspect of the calcined powder, where small primary particles formed the agglomerates. The formation of the phase pure CuAlO₂ powder was also confirmed by Fourier transformed infrared spectroscopy.

Compared with the solid state synthesis where high processing temperatures (1100 $^{\circ}$ C) and long reaction times (96 h) have been used to obtain single-phase delafossite CuAlO₂ [1, 2], both the calcination temperature and the dwell time are certainly lowered by the proposed citrate-nitrate combustion route.

References:

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