Electron Microscopy Study on Hydrothermally Synthesized (SnO₂)_x(ZnO)_{1-x} Powders

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Transparent conductive oxides are unusual materials that are both electrically conductive and visually transparent [1]. In recent years, TCO layers based on doped and undoped ZnO and SnO₂ are technologically important because of their high visible transparency and good electrical conductivity. SnO₂, an n-type semiconductor with a direct band gap of 3.6–4 eV and with high thermal stability [2], is capable of emitting light when excited with suitable input energy. ZnO, another versatile n-type semiconductor has direct band gap (3.37 eV) and large exciton binding energy (60 meV) [3]. It is a wellknown fact that the transparent conducting oxide (TCO) films have been widely used as transparent electrodes in various devices which include liquid crystal displays, solar cells, flat panel displays and LEDS. The role of cation concentration on particle formation mechanism during hydrothermal synthesis of nano sized SnO₂ has already studied by using HREM imaging technique [4]. Moreover Zn₂SnO₄ powders were synthesized successfully via hydrothermal method however formation mechanism has not explained yet [5]. Therefore, the research objectives of this study were to investigate the effect of process parameters on particle formation of (SnO₂)_x(ZnO)_{1-x} composite system by using electron microscopy techniques. Hydrothermally synthesized powders were characterized by using a field emission ZEISS SUPRA 50VP SEM and a field emission Jeol 2100F TEM, operating at 200 kV and equipped with a HAADF-STEM detector (Fishione), ADF and BF STEM detectors (Gatan STEM pack), an energy filter and EELS (Gatan GIF Tridiem).

Figure 1 (a-d) show the STEM-BF images of pure SnO_2 , ZnO powder and $(SnO_2)_x(ZnO)_{1-x}$ composite system with x=0,33 and x=0.29. According to SEM investigations x=0, 0,5M12h at 220 0 C ZnO particles are 10 μ m in size and they have flower like morphology (Fig. 1a). As it can be seen from the STEM-BF image in figure 1b it is really hard to determine the morphology and the size of the SnO_2 particles due to the agglomeration problem. Figure 1c shows that the size of the particles is around 25 nm and their morphology is cubic and round-cornered for x=0.33 and figure 1d shows that composite powders prepared with x=0,29 have cubic and angular shape and their size is around 40 nm. In terms of STEM-EDX (Fig.2a) analyses the rod-like shaped particles are SnO_2 (point 1) and the cubic shaped particles are Zn_2SnO_4 (point 2). Although XRD results showed that the powder is pure Zn_2SnO_4 ; STEM EDX analyses revealed that SnO_2 phase (Point 4) still exists between the Zn_2SnO_4 particles (Fig. 2b). [6]

References:

- [1] Wager, J. F., Transparent electronics. Science, **300** (2003), 1245-1246.
- [2] El-Etre, A. Y., and S. M. Reda., Applied Surface Science, **256** (2010), 6601-6606.
- [3] Saravanakumar, K., B. Sakthivel, and K. Ravichandran., Materials Letters, 65 (2011), 2278-2280.
- [4] Aciksari, C. et al., Journal of the Australian Ceramic Society, 52 (2016), 60-71.
- [5] Tuncolu, İ.G et.al., Journal of the European Ceramic Society, 35 (2015) 3885-3892.
- [6] The authors would like to thank to İ.Gözde Tuncolu, Cem Açıksarı, Emel Özel and Ender Suvaci for providing of the samples

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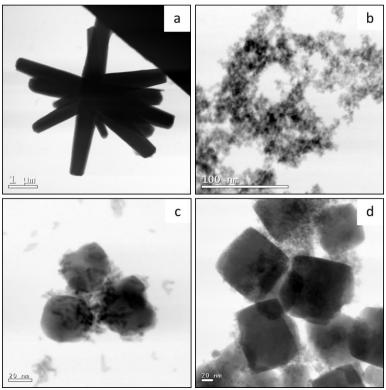


Figure 1. STEM-BF image of hydrothermally synthesized powders prepared at 220 $^{\circ}$ C with (a) x=0, 0.5M12h (b) x=1, 1.0 M4h (c) x=0.33 (d) x=0.29.

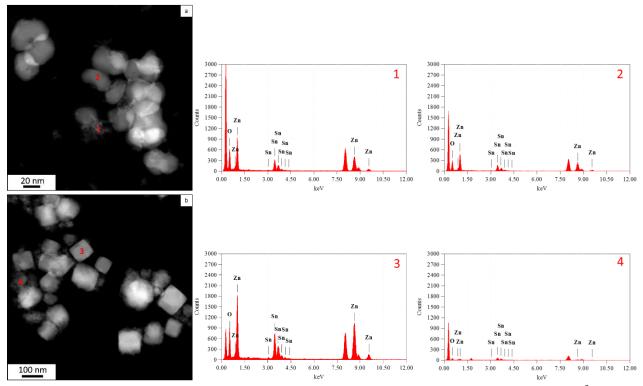


Figure 2. STEM-HAADF image of hydrothermally synthesized powders prepared at 220 0 C with (a) x=0.33 (b) x=0.29 and corresponding EDX spectra for the analyzed points.