Growth of $Cu_2ZnSnSe_4$ Monograin Powders in Molten Potassium Iodide

Master Thesis
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The quaternary Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ (CZTSe) are promising absorber materials in solar cells. They have gained a lot of research interest due to their suitable physical and electronic properties, utilization of earth-abundant and readily available elements and implementation by low-cost technology. However, the formation conditions of $Cu_2ZnSnSe_4$ monograin powders have not been studied thoroughly and better knowledge of crystal growth parameters could give higher material yield of useful crystal size.

The objective of this thesis is to study the formation mechanism and growth parameters of CZTSe crystals grown in molten potassium iodide (KI) and to understand how the synthesis duration and temperature affect the particle size and morphology of formed monograins. CZTSe powder materials with the chemical input formula of $Cu_{1.78}Zn_{1.12}Sn_{1.0}Se_{4.03}$ were synthesized from binary compounds (CuSe, ZnSe and SnSe) at temperatures 720-760°C and from elemental metal powders (Cu, Zn, Sn) and Se pellets at 700°C in the liquid phase of KI as a flux material in evacuated quartz ampoules. Annealing temperatures used in the experimental synthesis processes were 700°C, 720°C, 740°C and 760°C and durations 30 h, 60 h, 96 h, 168 h, 264 h and 336 h.

The results of EDX and Raman analyses indicated that in addition to the $Cu_2ZnSnSe_4$ phase, powders contained binary ZnSe in small quantities. Temperature and synthesis conditions had no remarkable influence to the chemical composition of produced powders. The sieving analysis showed that the increase in synthesis temperature and longer annealing duration resulted in increased medium crystal size. Scanning electron microscope (SEM) revealed that synthesized crystals had principally tetragonal shape with either sharp or rounded edges and longer annealing at higher temperatures caused numerous quantities of sintered grains. The activation energy of crystals' growth was calculated from the Arrhenius equation: $\Delta E_d = 0.59$ (±0.13) eV. The determined geometric factor values (n = ~ 4) for powders synthesized at temperatures 720°C and higher indicate that mass diffusion through the liquid phase and sintering of formed grains due to material's crystals surface diffusion together were dominating in the growth process of monograin powder crystals. However, the syntheses at 700°C starting from elemental precursors had unexpected growth parameter n = 1.2 (±0,1). The reason of the found different n value has to be clarified in the future.