

Mechanochemically Assisted Synthesis of Kesterite $\text{Cu}_2\text{ZnSnS}_4$ Nano Powders for Photovoltaic Applications via Copper Alloys Formation

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The mechanochemical synthesis dwells on reactions induced in substrate mixtures under high energy ball milling conditions such as up to 900-1000 rpm speeds of planetary ball mills and use of extremely hard grinding balls. Starting from suitable mixtures of all four elements, we have successfully explored such a process for the preparation of nano powders of semiconducting kesterite $\text{Cu}_2\text{ZnSnS}_4$ – prospective material for photovoltaics. Herein, described is a modification of the process in which, first, the Cu, Zn, and Sn metal powders are wet milled at 900 rpm forming the well mixed copper binary nanocrystalline alloys, i.e., Cu/Sn (1:1) and Cu/Zn (5:8). Stoichiometric amount of natural sulfur S is then included, and response processing is proceeded for a predetermined timeframe to bring about one clean quaternary item that is likely called a pre-kesterite. It is a cubic polytype with normal crystallite sizes of 8-12 nm (XRD), attractive (EPR), shows no ^{65}Cu and ^{119}Sn MAS NMR spectra, and needs semiconducting properties (UV-vis), albeit artificially and basically is like the semiconducting tetragonal kesterite. In the subsequent advance, the pre-kesterite is thermally tempered, ideally, at 500°C, 6 h, under argon to bear the cost of the objective semiconducting kesterite nano powders. There are a few points of interest of such a two-advance processing process, i.e., metals first to shape the copper compounds followed by sulfur expansion and sulfurization responses, contrasted and a high vitality ball processing of each of the four components on the double. the mechanochemically helped amalgamation of kesterite $\text{Cu}_2\text{ZnSnS}_4$ from the components for photovoltaic applications. Beginning use of high vitality ball processing under chosen conditions, including the most elevated attainable revolution accelerates to 1000 rpm, manages an unadulterated cubic nanophase with the ostensible kesterite structure. The stage is probably called a pre-kesterite and it is appeared by EPR to be attractive. Accordingly, it does not produce either ^{65}Cu or ^{119}Sn MAS NMR spectra. Also, the material shows no well-defined absorption in the UV-vis range and, based on this, does not exhibit definite semiconducting properties. The highly disordered and defected structure with random metal site occupation originated in the mechanochemical synthesis step is proposed to account for the observed properties of pre-kesterite. Upon subsequent pyrolysis under argon at temperatures above 300 °C, preferably at around 500 °C, the cubic phase is converted to the tetragonal phase of kesterite, apparently, by metal site reconfiguration. The annealed nano powders show the expected ^{65}Cu and ^{119}Sn MAS NMR characteristics. The Raman spectra support similar bonding environment and lattice phonon characteristics for both related phases as well as the eventual formation

of kesterite nano powders whereas their UV-vis spectra provide the direct band gap in the range of 1.35–1.48 eV, typical for semiconducting kesterite. Kesterite-type $\text{Cu}_2\text{ZnSnS}_4$ was integrated from the comparing paired sulfides by a mechanochemical course in a planetary ball plant. The response progress during this processing step was followed inside a period scope of 10–180 min by powder X-beam diffraction. In addition, the crystallization of the milled material was studied in situ by high-temperature X-ray diffraction methods in the temperature range of 300–500 °C. Significant disorder (cation distribution) was observed at 500 °C, strongly decreasing during cooling down to ambient temperature with a rate of 60 K/h. The quaternary metal sulfide $\text{Cu}_2\text{ZnSnS}_4$, referred to as kesterite or CZTS, and the related stannite $\text{Cu}_2\text{FeSnS}_4$ have been in recent years a subject of an intensive upfront research encompassing both synthesis/characterization and utilization trials in inexpensive, highly efficient, and environmental-friendly photovoltaic devices. It gives the idea that in kesterite sulfur S can be in part or completely supplanted by selenium Se and zinc Zn by iron Fe prompting expanded cell efficiencies. For device applications, thin film formation including vacuum-based techniques (sputtering) or nanoparticle ink applications (electrodeposition, powder metallurgy) is usually applied. In the latter, kesterite nano powders may be used as the inorganic part of nano-contacts of the inorganic organic photovoltaic cell. For elucidation of fundamental properties, single crystals or micro- and nanocrystalline powders are preferably synthesized. In this regard, there are still some challenging research targets to be revisited and explored to name such issues as development of a simple, reproducible, and cost-effective synthesis method(s) including the preparation of nano powders, clarification of the interplay between the structure/lattice disorder/composition features and optical properties as well as, on the application side, a need for increased kesterite-based cell efficiencies. There are published somewhat confusing reports on kesterite composition and crystal structure/lattice order-disorder issues. The problem has been addressed both theoretically and experimentally. It appears that kesterite can tolerate a certain degree of lattice defects and metal position disorder, which impacts cell point group symmetry and, consequently, the macroscopic crystal structure. Because of comparable mass/size attributes of the metal places Cu(I) and Zn (II), the powder XRD judgments can furnish with just constrained data on point by point basic highlights. Despite this, there are accessible many XRD examines revealing kesterite materials as orthorhombic, hexagonal, or tetragonal of kesterite-or stannite-type, the last including the synchrotron radiation X-beam diffraction report. On account of the

kesterite period of numerous as prepared materials, it isn't exceptional, particularly, for little particles with sizes beneath somewhere in the range of 10 nm to regard it as tetragonal in spite of the evident cubic appearance of the XRD designs. In this regard, not easily available neutron scattering measurements can in principle shed more light into the structural details and order-disorder of site occupation of the evolving kesterite in multistep reaction pathways with an essential thermal annealing step. Similarly, the TEM/SAED/CBED case-study examination of both the as-prepared and thermally annealed kesterite samples pointed out to complex structure characteristics of the

basically tetragonal phase that may include extensive lamellar twinning and associated local hexagonal domains. EXAFS estimations for the kesterite $\text{Cu}_2\text{ZnSnS}_4$ e stannite $\text{Cu}_2\text{FeSnS}_4$ strong arrangements empowered assurance of the overall oxidation condition of iron as Fe (II) though for unadulterated powders of kesterite the oxidation condition of tin was affirmed to be Sn (IV). All in all, uncommon synchrotron spectroscopies seem crucial when coordination evenness and compound condition of particles are of worry as unquestionably is the situation of the compositionally/fundamentally complex kesterite.