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### Rapid Synthesis of Zinc and Nickel Co-Doped Tetrahedrite Thermoelectrics by Reactive Spark Plasma Sintering and Mechanical Alloying

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#### Abstract

Tetrahedrite offers advantages over state-of-the-art thermoelectrics, such as lead telluride, because of its low cost and environmentally friendly composition. However, typical sealed-tube synthesis of tetrahedrite can require multiple days or weeks. In this study, tetrahedrite co-doped with nickel and zinc was synthesized by two different approaches which both require significantly less time than the conventional furnace-ampoule technique. The first technique utilizes a short ball milling step followed by reactive spark plasma sintering to form tetrahedrite, and the entire process requires less than two hours of total synthesis time. The second method involves mechanical alloying to obtain single-phase tetrahedrite, combined with spark plasma sintering (SPS) for densification. Thermoelectric properties were measured and compared for samples of composition  $Cu_{10}Ni_2x_Zn_xSb_4S_{13}$  (x=0, 0.5, 1, 1.5) made by both techniques. Peak *ZT* values were obtained for  $Cu_{10}Ni_2Sb_4S_{13}$  with *ZT*=0.66 at 673 K for SPS reacted and mechanically alloyed samples. Transport properties are comparable between the two techniques, and this provides evidence that supports reactive spark plasma sintering as a viable synthetic technique for tetrahedrite thermoelectric materials.

**Keywords:** Thermoelectric Materials, Tetrahedrite, Reactive Spark Plasma Sintering, Mechanical Alloying

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