



Short communication

## Mechanochemical synthesis of tetrahedrite materials using mixtures of synthetic and ore samples collected in the Portuguese zone of the Iberian Pyrite Belt

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### ABSTRACT

Considering that the synthesis of tetrahedrite-based materials usually uses high purity elements, the evaluation of the direct application of ore samples as raw materials for their synthesis is a pertinent issue. In the present study, multiphase synthetic tetrahedrite samples were mixed with tetrahedrite-tennantite ore samples (in weight ratios of 0.8/0.2, 0.5/0.5 and 0.2/0.8) to produce tetrahedrite-based materials by solid-state mechanochemical synthesis. The ore samples were obtained from the abandoned Barrigão mine dumps and from the Neves Corvo mine, both located in the Portuguese zone of the Iberian Pyrite Belt, whose main constituents were found to be As-rich tetrahedrite and tennantite-(Fe), respectively. Depending on the ore sample and on the mixture ratios, the displacement reactions occurring during the synthesis process gave rise to different phase transformation paths. For the ratios of 0.5/0.5 and 0.2/0.8, the mixtures with the Barrigão ore were found to consist of a single sulfide phase, tetrahedrite-tennantite-(Fe), plus quartz, while famatinite was also observed in the 0.8/0.2 mixture. Tetrahedrite-tennantite-(Fe) phase was the main constituent of all mixtures with the Neves Corvo ore, but in all of them other sulfide phases, famatinite-luzonite and pyrite, were also present in addition to quartz. Despite being dissimilar, these results are very promising and encouraging, by confirming the possible direct usage of ore samples and of dump material for the synthesis of tetrahedrite-based materials with all the potential environmental-economic gains that can be obtained.

### 1. Introduction

Tetrahedrite is a class of copper antimony sulfosalt mineral ( $\text{Cu}_6[\text{Cu}_4(\text{TM})_2]\text{Sb}_4\text{S}_{13}$  (TM = transition metal)) consisting of earth-abundant and relatively non-toxic elements (George et al., 2017). The substitution of antimony (Sb) by arsenic (As) gives rise to tetrahedrite-tennantite endmembers of the solid solution. Recently, synthetic tetrahedrite-based materials have demonstrated exceptional semi-conducting and photoconductivity properties that allows potential applications in solar energy conversion and thermoelectric devices (Candolfi et al., 2016; Heo et al., 2015).

The development of a cost-effective and high yield sustainable technology to synthesize tetrahedrites is still a major and relevant issue

(Candolfi et al., 2016). Mechanochemical synthesis (MCS) is considered an efficient and suitable route for the synthesis of different types of chalcogenides materials (Baláz et al., 2017). Furthermore, the possibility of the direct use of ore samples to produce tetrahedrite-based materials has been recently reported (Lu and Morelli, 2013). Although this approach proved to be feasible it has received little attention so far. Probably, this is due to ore chemical heterogeneities since every deposit has its own mineralogical characteristics with significant compositional variations (Levinsky et al., 2016).

Approximately half of one of the most important volcanogenic massive sulfide districts in the world, the Iberian Pyrite Belt (IPB), is located in southern Portugal, where tetrahedrite-tennantite mineral series is one of the naturally occurring compounds (de Oliveira et al.,

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