Electronic Supplementary Information

Mechanically induced self-propagating reactions (MSRs) to instantly prepare binary metal chalcogenides: Assessing the influence of particle size, bulk modulus, melting temperature difference and thermodynamic constants on the ignition time

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Section S1: Characterization of the precursors

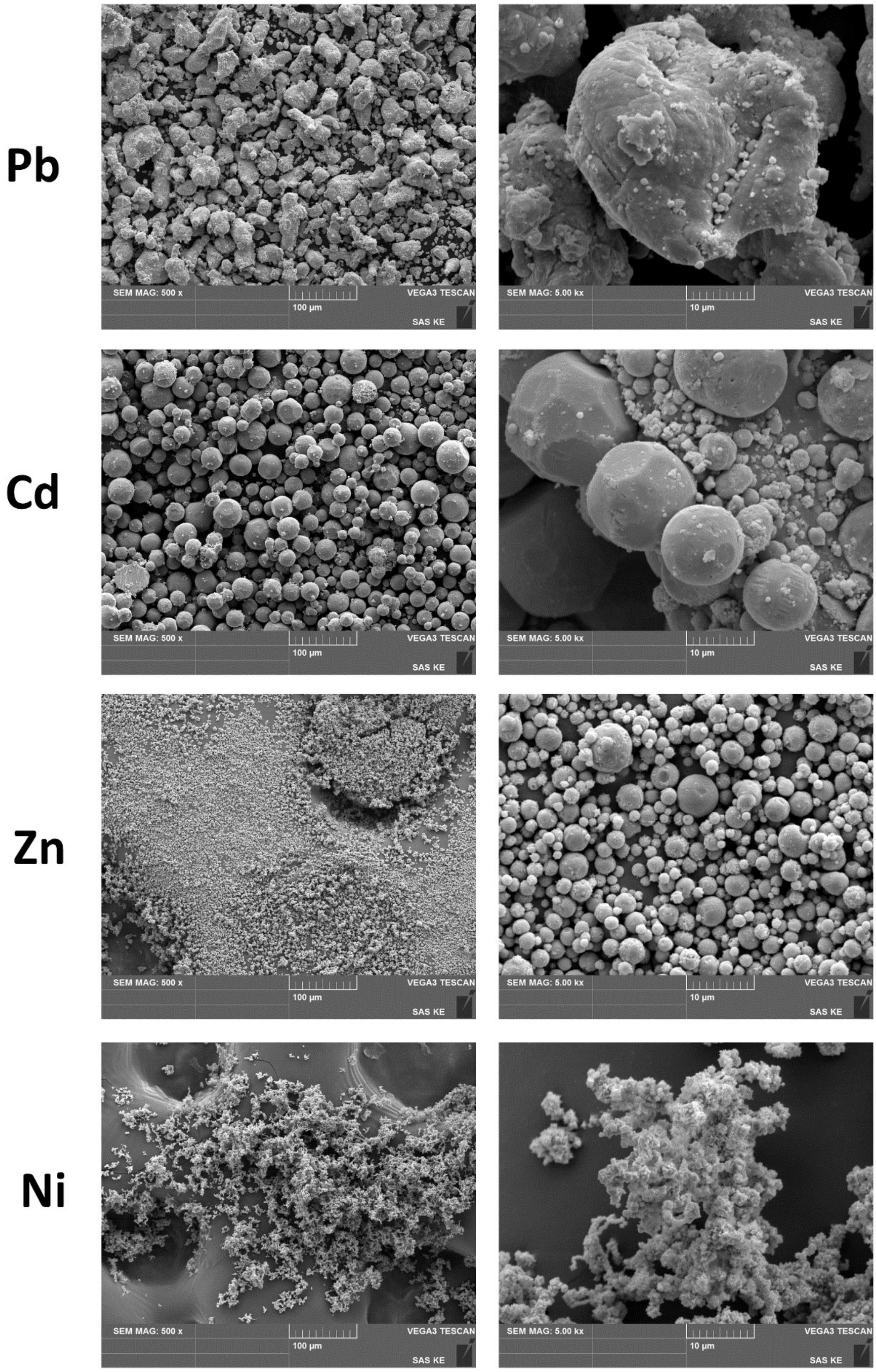

Fig. S1: SEM images of the used metallic Pb, Cd, Zn and Ni precursors at different magnifications: (a) 500 x, (b) 5 kx

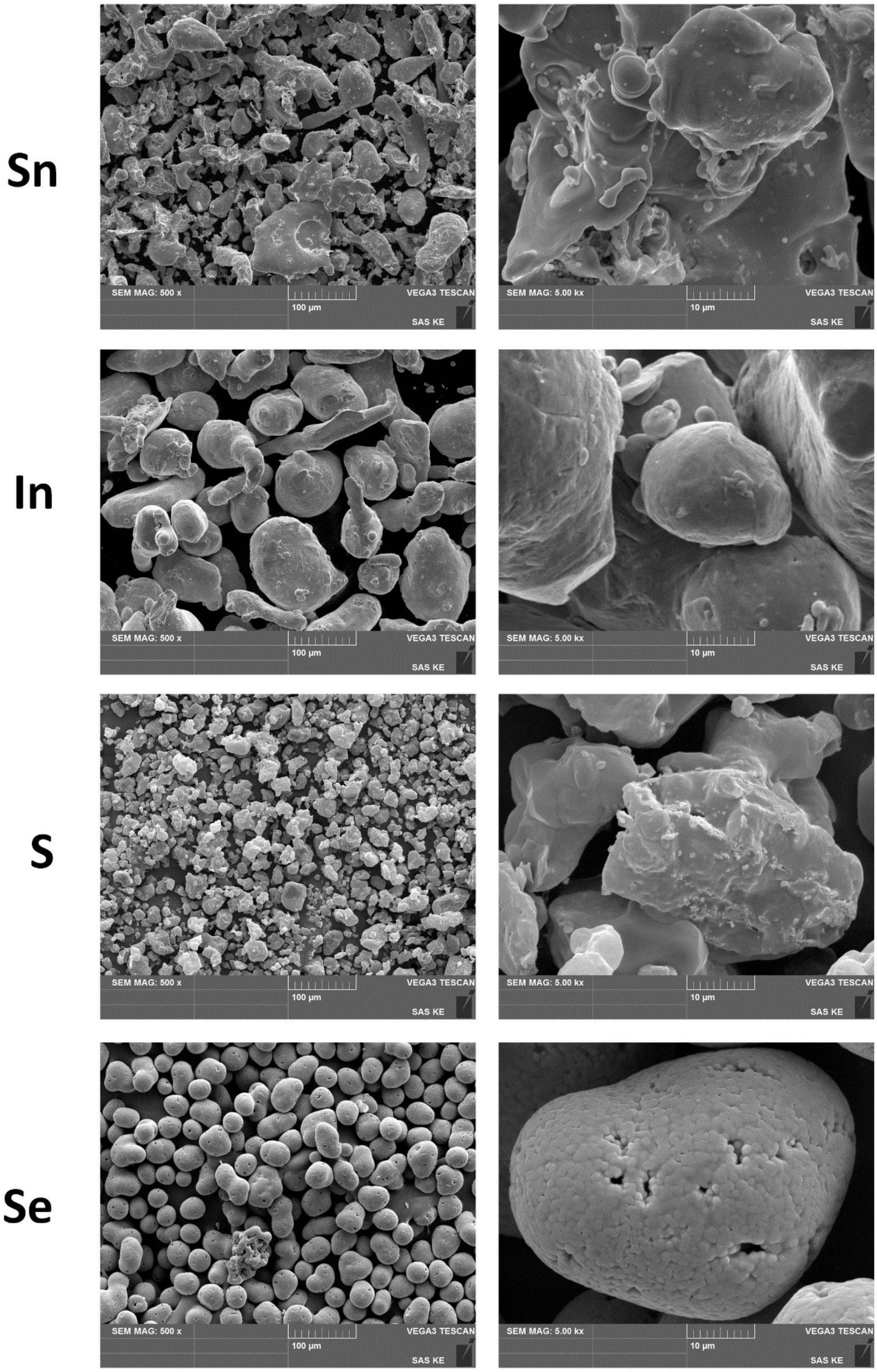

Fig. S2: SEM images of the used metallic Sn and In and chalcogens S and Se at different magnifications: (a) 500 x, (b) 5 kx

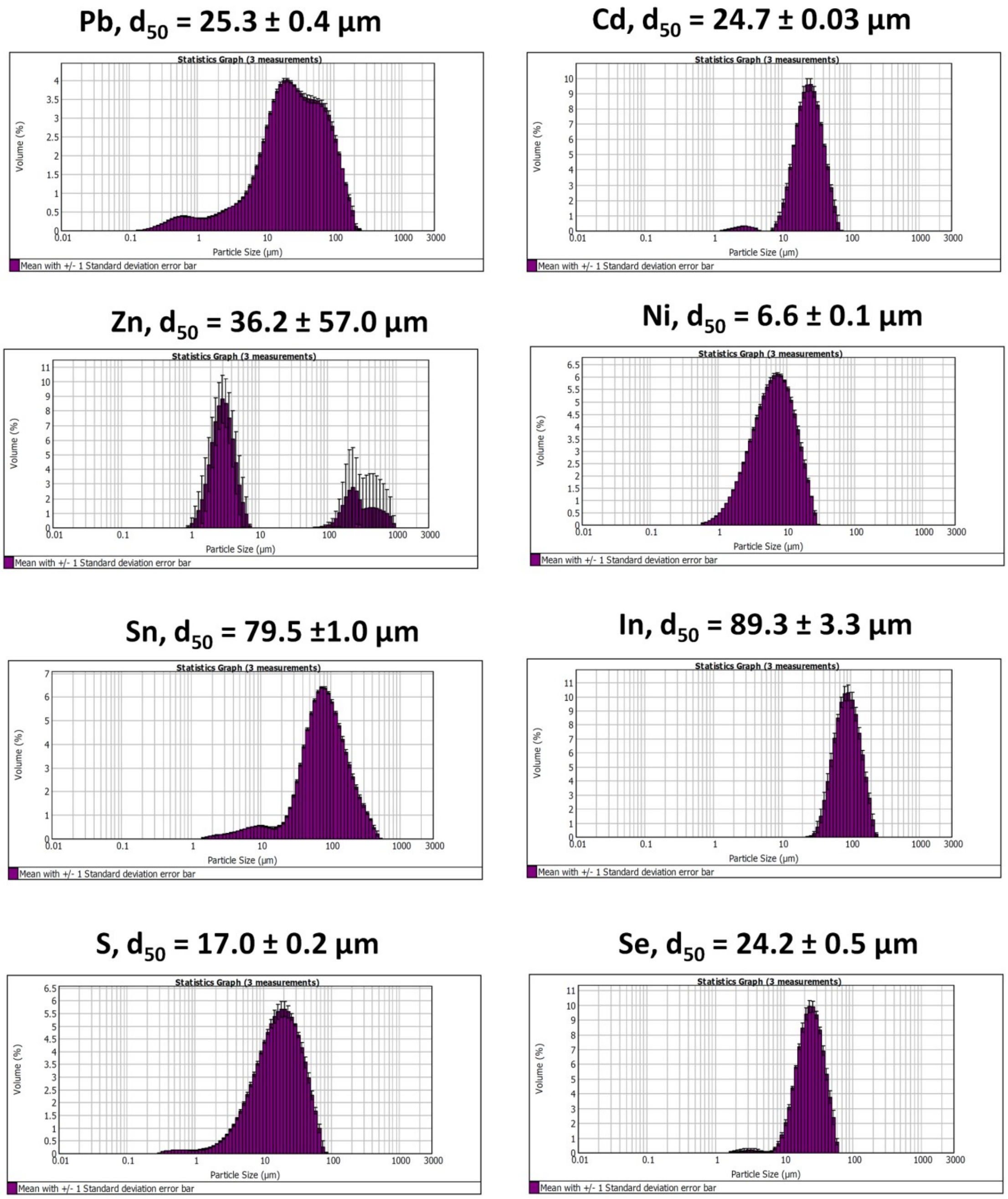

Fig. S3: Particle size distributions of the used starting materials with corresponding d_{50} values

Fig. S4: Photograph of the lid after opening the milling chamber after the MSR reaction showing most probably red selenium powder

Section S2: Mechanochemical synthesis of selenides performed at 750 rpm

The initial experiments were run at 750 rpm, which is the highest rotational speed that is generally used in our lab. Whereas for metal-sulfur reaction mixtures, this milling speed turned out to be well-selected (the results are discussed in the main text), metal-selenium mixtures were too reactive for the MSR event to be clearly observed via observing the sudden pressure increase at this milling speed. In Fig. S5, the gas pressure and temperature changes during milling of the Me + Se mixtures run at 750 rpm are presented. For the Zn-Se and Pb-Se systems, the MSR events were not observed, however, the presence of the corresponding selenides was confirmed in the mixtures treated for 10 and 20 s, respectively (see the XRD pattern in Fig. S6 and S7, respectively). The great reactivity and occurrence MSR for the Zn-Se system is in accordance with [1-2]. For Sn-Se and Ni-Se mixtures, the MSR event was evidenced via an abrupt pressure increase within the first 30 seconds. The XRD patterns in Fig. S8 and S9 clearly show the successful formation of the desired phases. When milling Cd + Se mixture, a sudden increase in pressure was not observed within the first minute, however, the formation of CdSe could already be seen in the XRD pattern (Fig. S10). The CdSe product can crystallize in hexagonal and cubic system and both phases can be detected after 1 minute, with cubic one being more pronounced. It is probable that this system is also susceptible to hexagonal-to-cubic phase transformation after MSR, similarly to ZnS [1], and most probably, the pure hexagonal phase was formed initially after MSR a little bit earlier. The intensity of non-reacted cadmium was quite high, as usually after MSR, the content of unreacted metals is smaller. But the content of unreacted metal might be also influenced by multiple phenomena, including milling conditions. After 5 minutes, all the reactants were consumed and the XRD pattern is dominated by very broad peaks of cubic phase and a very small amount of hexagonal phase residues. In the case of 2In + 3Se system, the diffractions of reactants are already absent after 1 minute of treatment and the XRD pattern is similar after 5 minutes (Fig. S11). An abrupt pressure increase was not observed. The main product seems to be In_3Se_4. To sum up, out of six studied Me + Se systems, in four cases MSR completion was confirmed via XRD, however, just in two of them, it was also evidenced via gas pressure measurements. To investigate whether the decrease in the milling speed will help MSR to be better observable via gas pressure changes, it was reduced to 400 rpm for Me + Se systems.

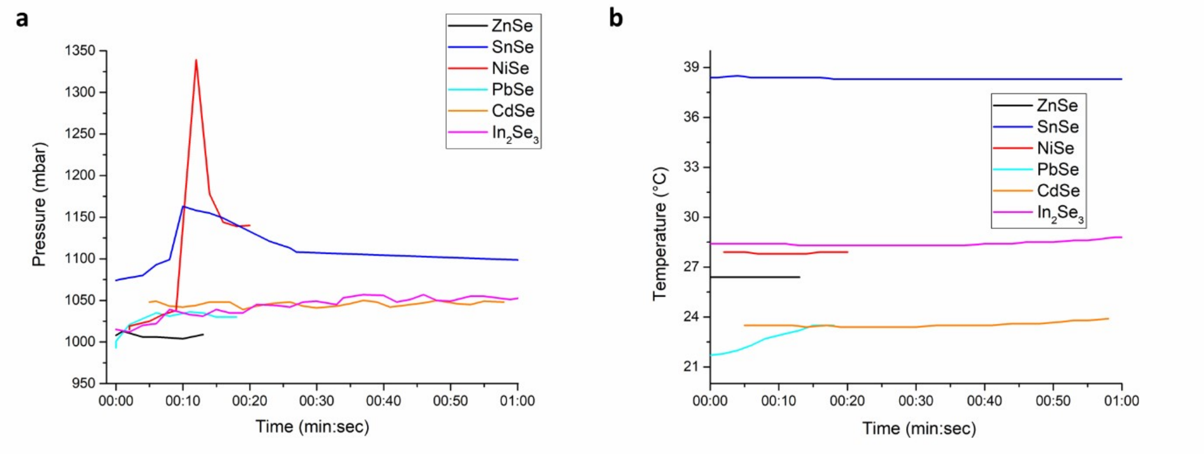

Fig. S5: Representative gas (a) pressure and (b) temperature curves for Me-Se mixtures treated at 750 rpm. In_2Se_3 was treated until 5 minutes and the pressure and temperature has gradually reached to 1135 mbar and 42.8 °C, respectively.

XRD patterns for selendies synthesized at 750 rpm

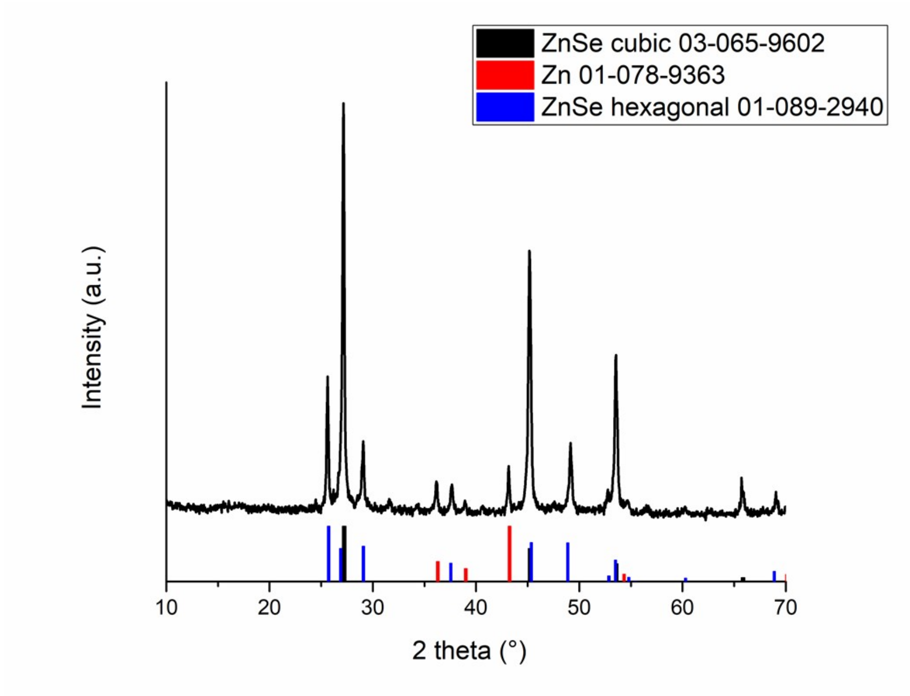

Fig. S6: Zn + Se, milled at 750 rpm for 10 seconds

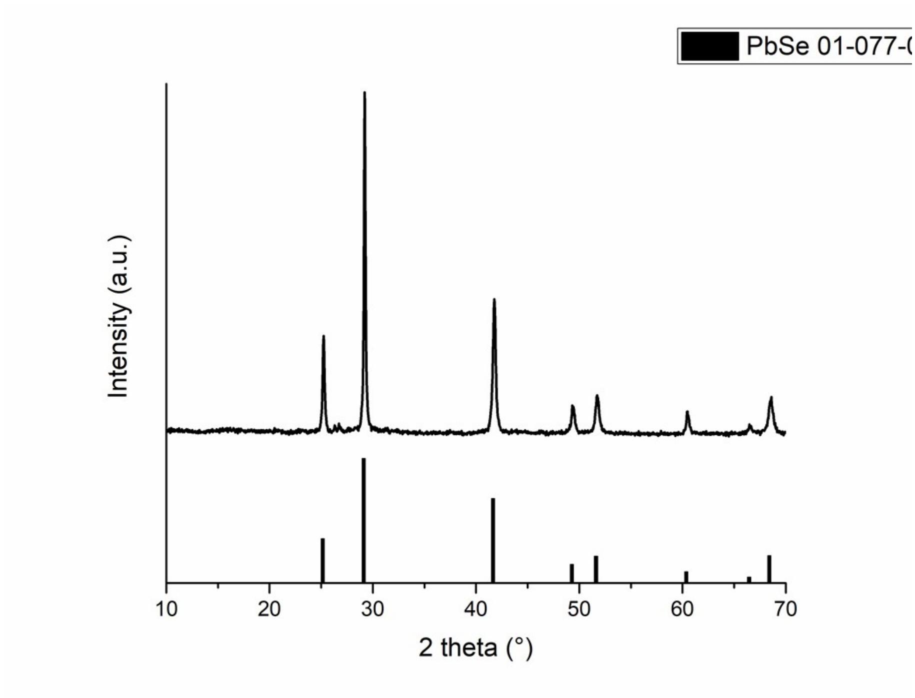

Fig. S7: Pb + Se, milled at 750 rpm for 20 s

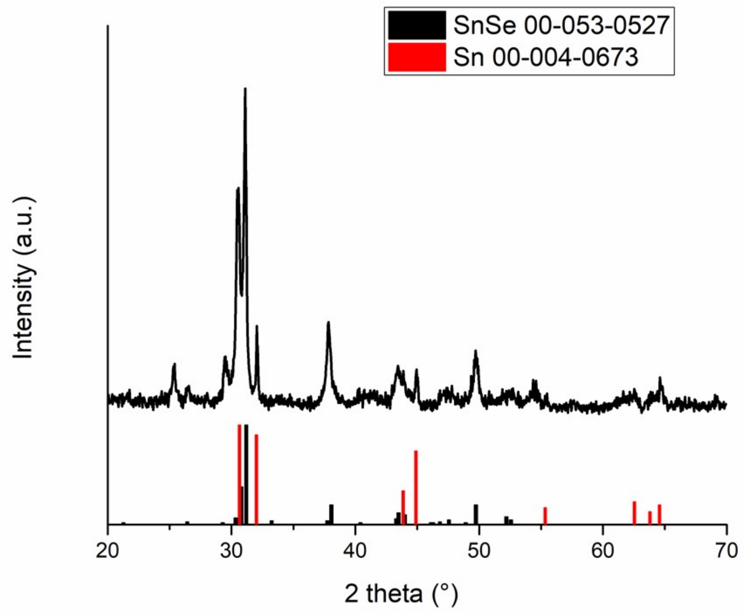

Fig. S8: Sn + Se, milled at 750 rpm for 30 s

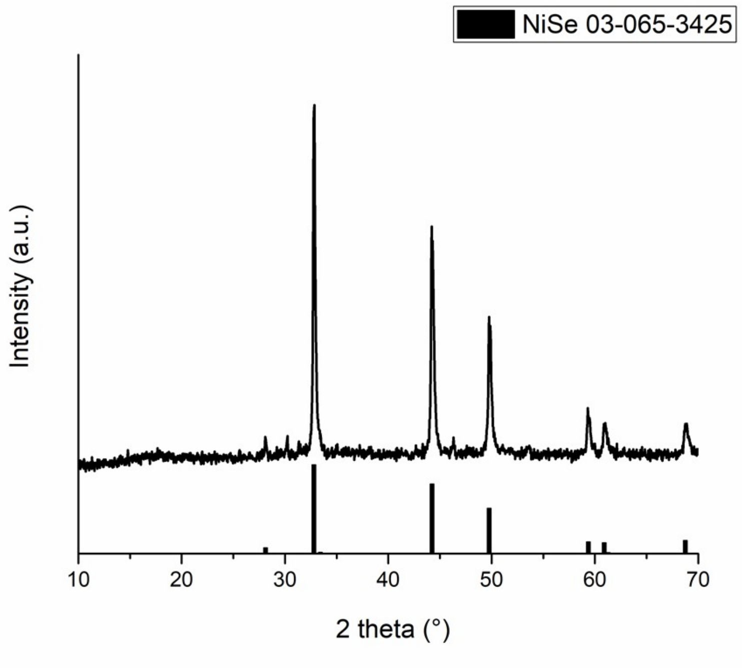

Fig. S9: Ni + Se, milled at 750 rpm for 35 s

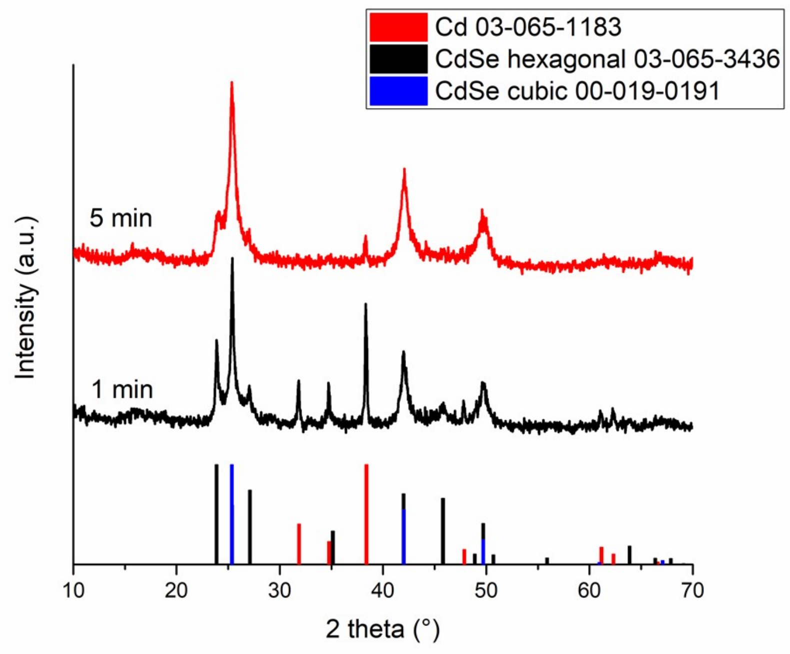

Fig. S10: Cd + Se, milled at 750 rpm for 1 min and 5 min

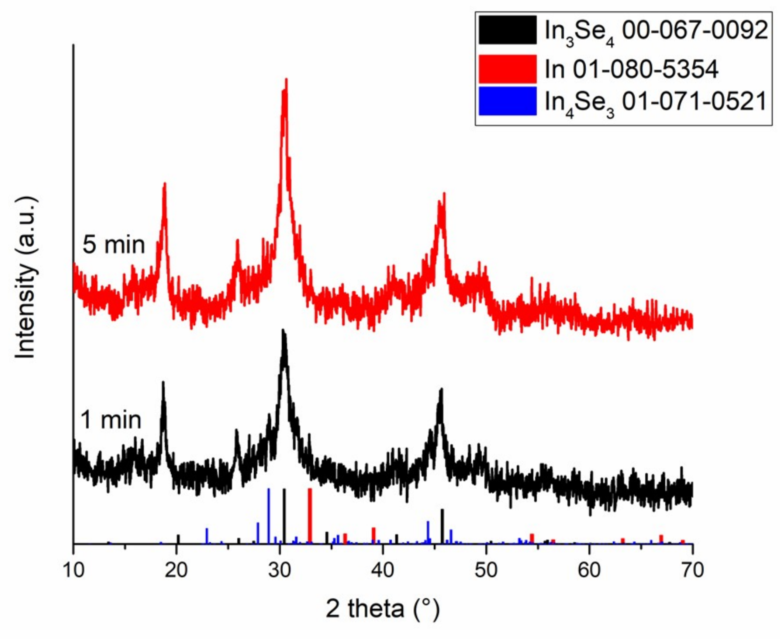

Fig. S11: 2In + 3Se, milled at 750 rpm for 1 min and 5 min

Section S3: Supplementary data regarding properties that impact on the course of MSRs for the mechanochemical synthesis of sulfides at 750 rpm and selenides at 400 rpm

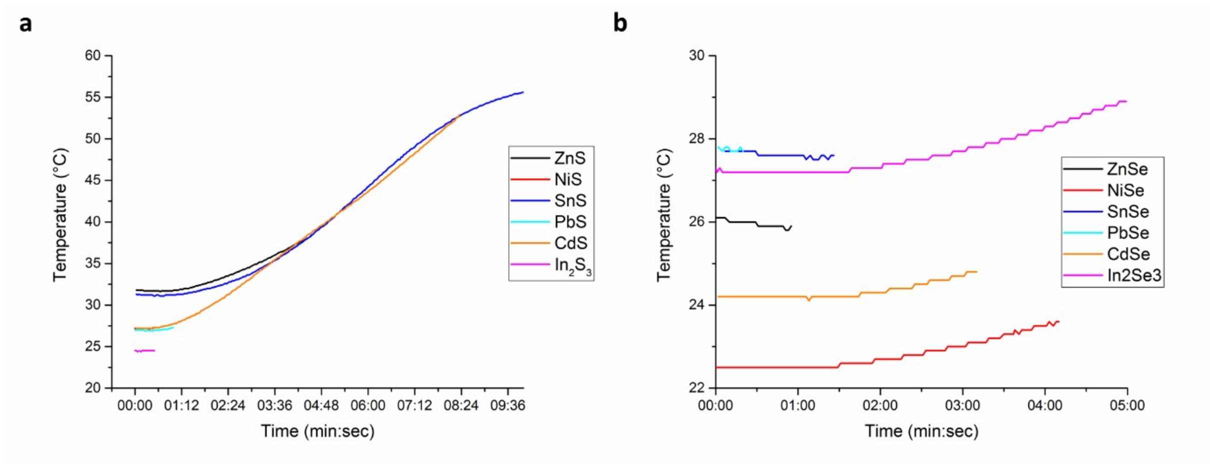

Fig. S12: Representative gas temperature curves: (a) Me-S mixtures treated at 750 rpm, (b) Me-Se mixtures treated at 400 rpm

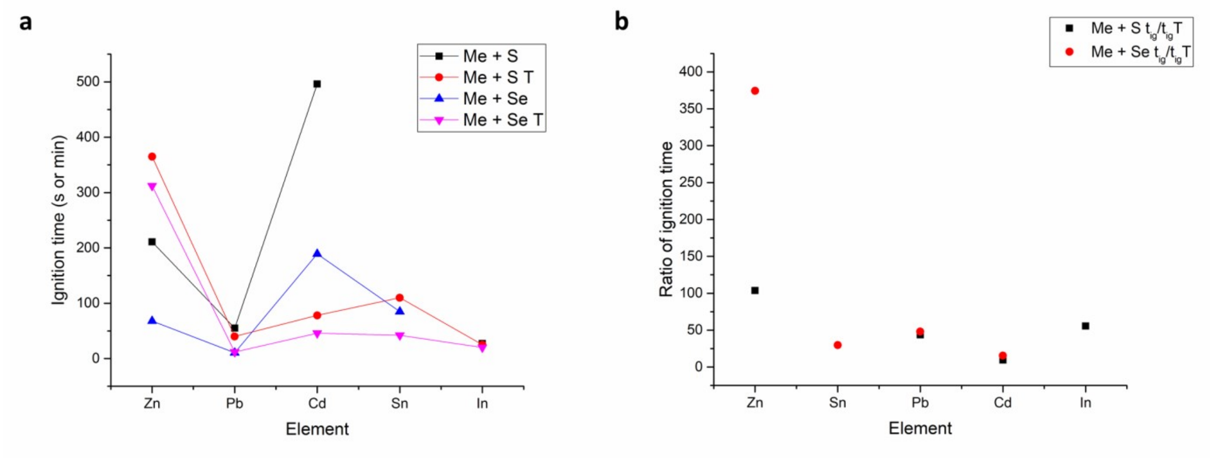

Fig. S13: (a) Ignition times evidenced for Me + S and Me + Se reaction mixtures in our study (in seconds) and in [3] (in minutes), (b) ratios of ignition times in our study and that reported in [3]. By T, the results from the study [3] are labeled. For the present study, ignition times are reported in seconds and the ones from [3] are reported in minutes.

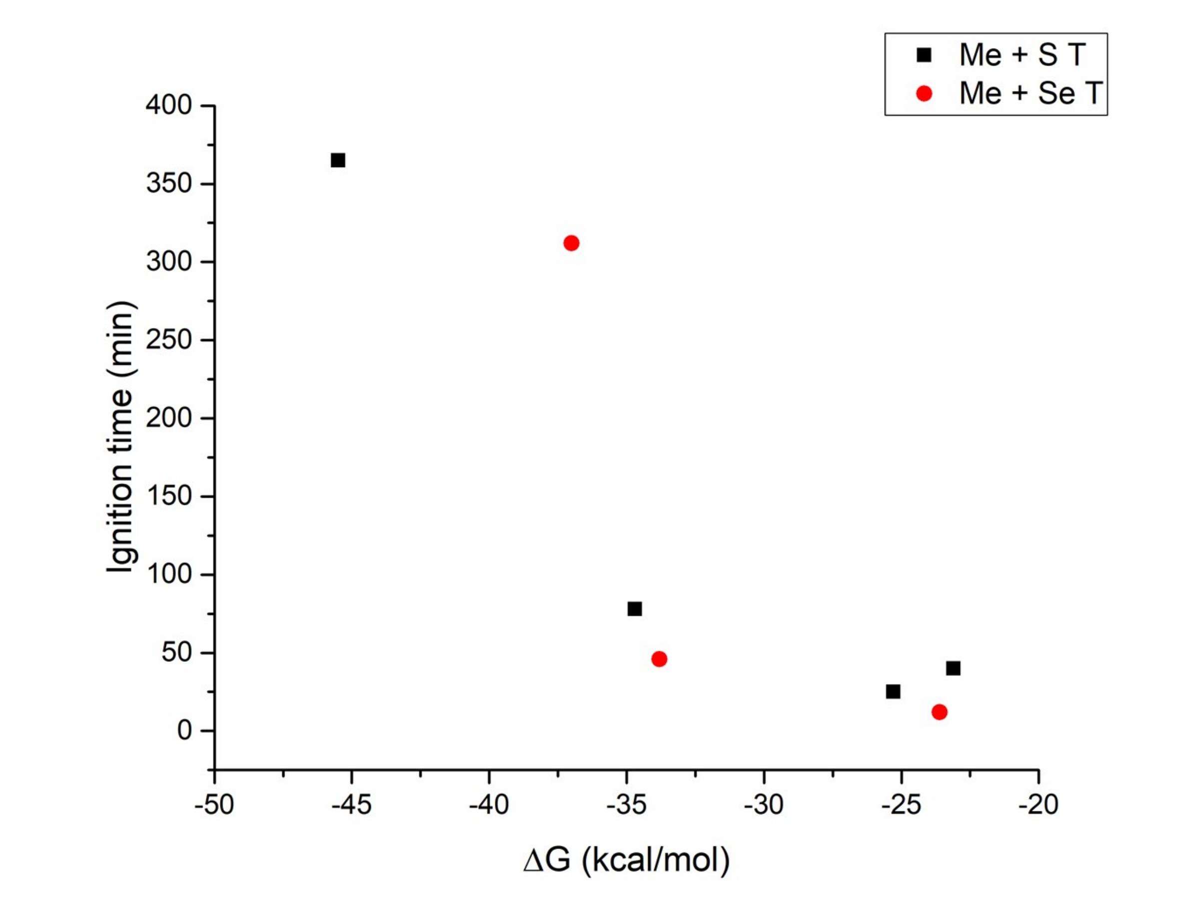

Fig. S14: The dependence of t_{ig} on the Gibbs energy of the products as reported in [3]. Source data for Δ*G* are taken from [4].

Section S4: XRD patterns for sulfides synthesized at 750 rpm

In the cases when Rietveld refinement results are presented, the $Y_{exp} - Y_{cal}$ plots that are shown are after the refinement to estimate the phase composition. The imperfect fits are a results of the fact that one function describing the shape of all the peaks has to be used.

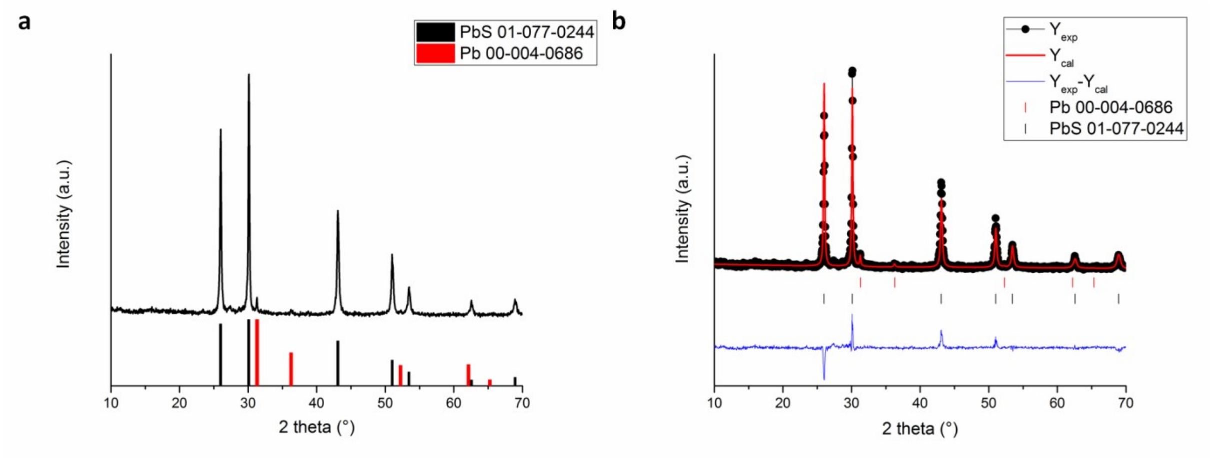

Fig. S15: (a) Pb + S, milled at 750 rpm for 1 min, (b) corresponding Rietveld refinement result

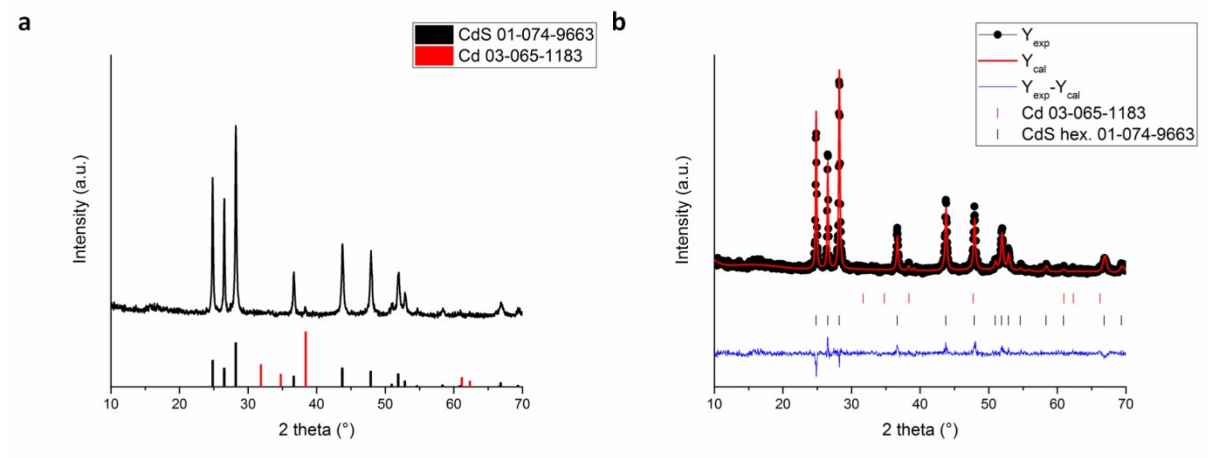

Fig. S16: (a) Cd + S, milled at 750 rpm for 8 min, (b) corresponding Rietveld refinement result

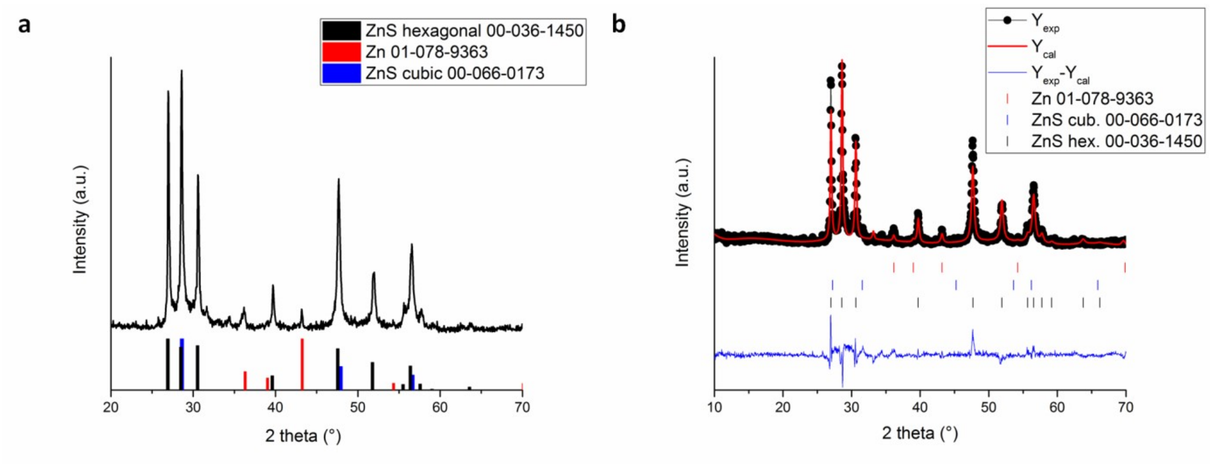

Fig. S17: Zn + S, milled at 750 rpm for 3 min, (b) corresponding Rietveld refinement result

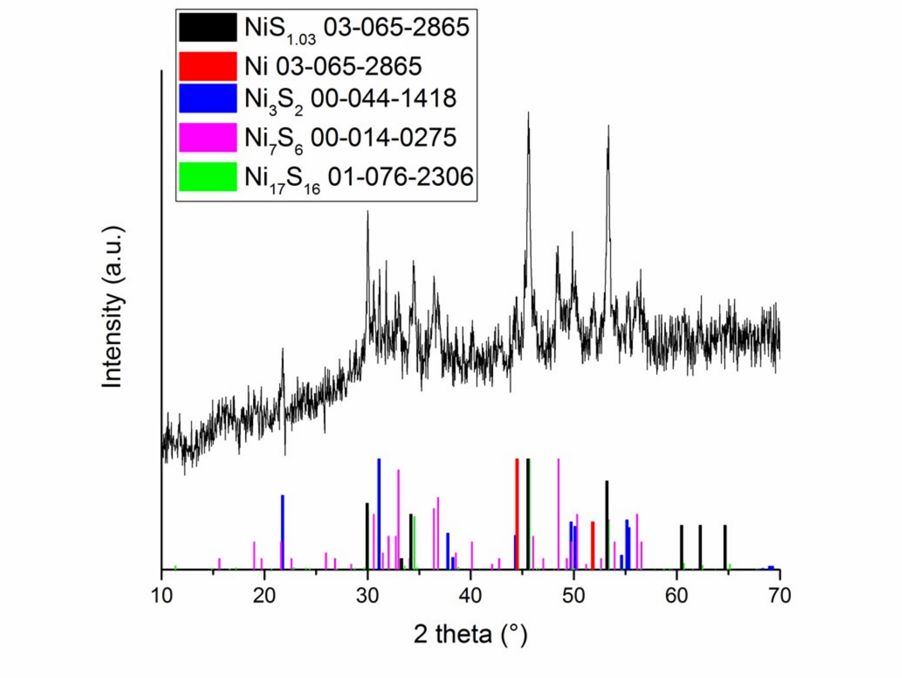

Fig. S18: Ni + S, milled at 750 rpm for 25 s.

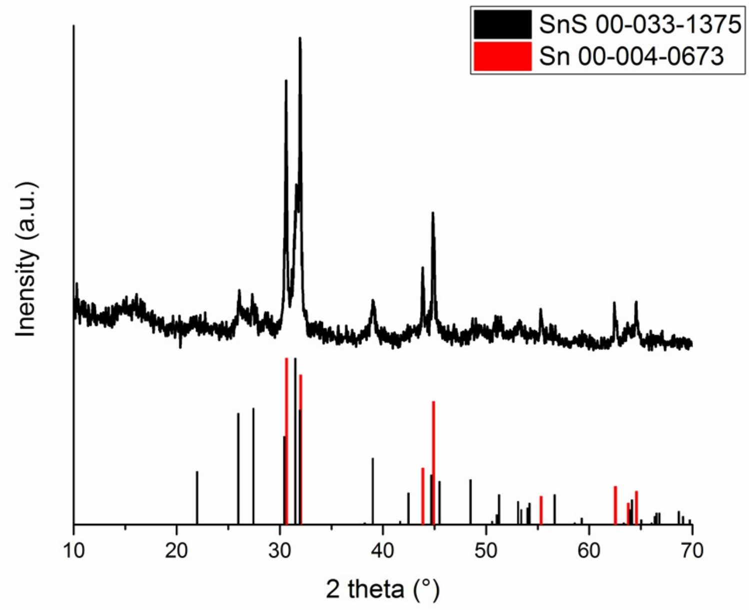

Fig. S19: Sn + S, milled at 750 rpm for 4.5 min

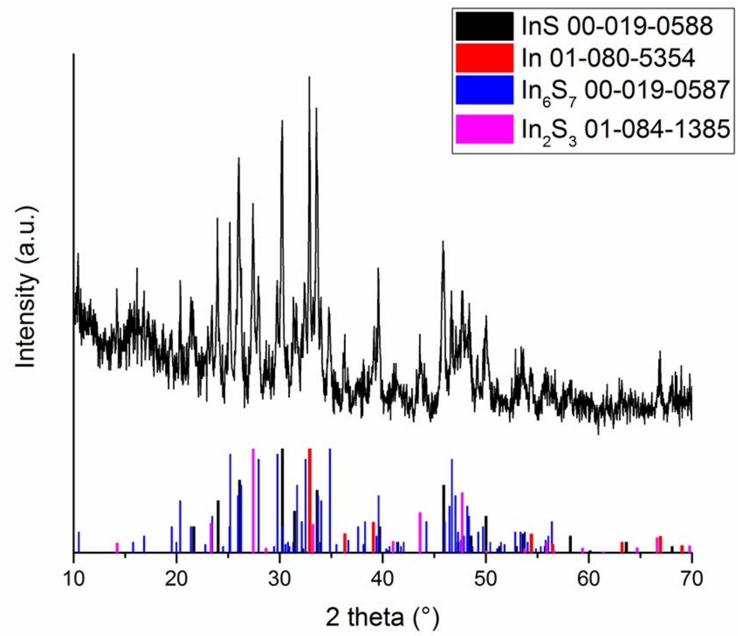

Fig. S20: 2In + 3S, milled at 750 rpm for 35 s

Section S5: XRD patterns for selenides synthesized at 400 rpm

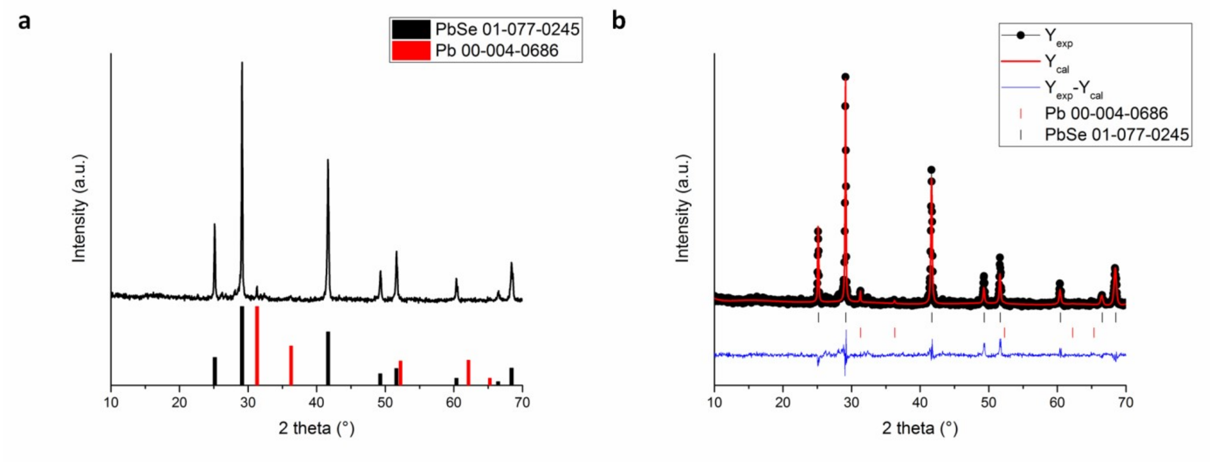

Fig. S21: Pb + Se, milled at 400 rpm for 15 s, (b) corresponding Rietveld refinement result

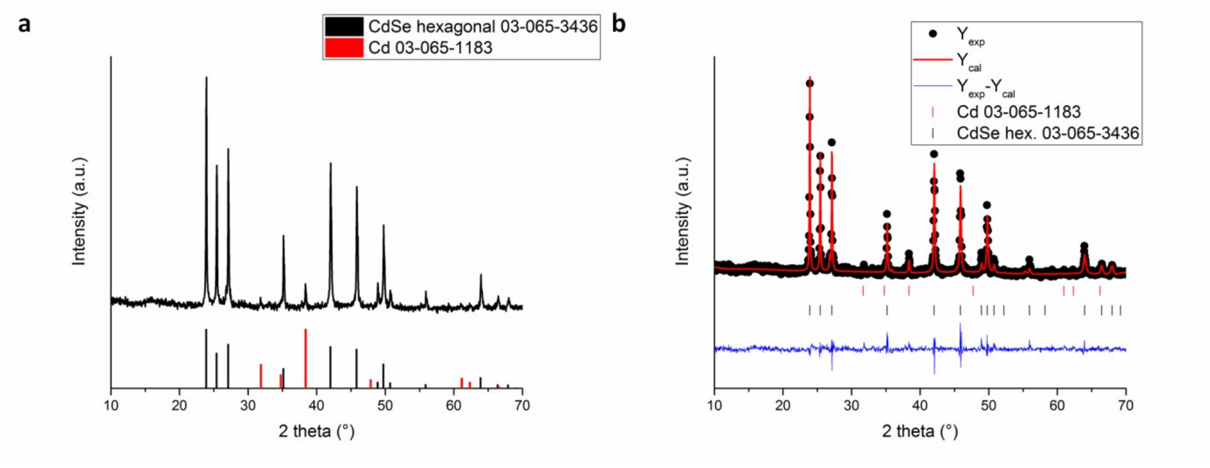

Fig. S22: Cd + Se, milled at 400 rpm for 3.5 min, (b) corresponding Rietveld refinement result

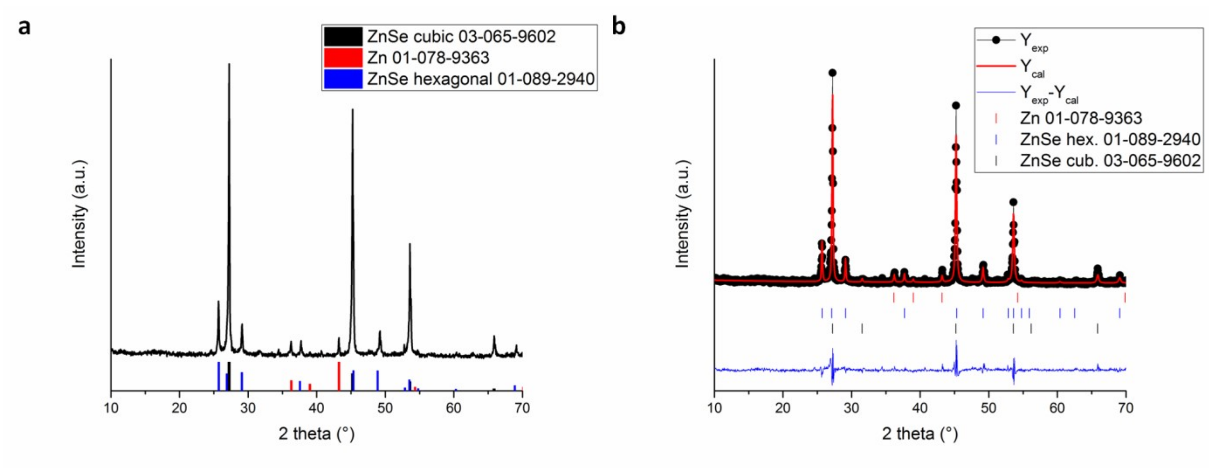

Fig. S23: Zn + Se, milled at 400 rpm for 1 min, (b) corresponding Rietveld refinement result

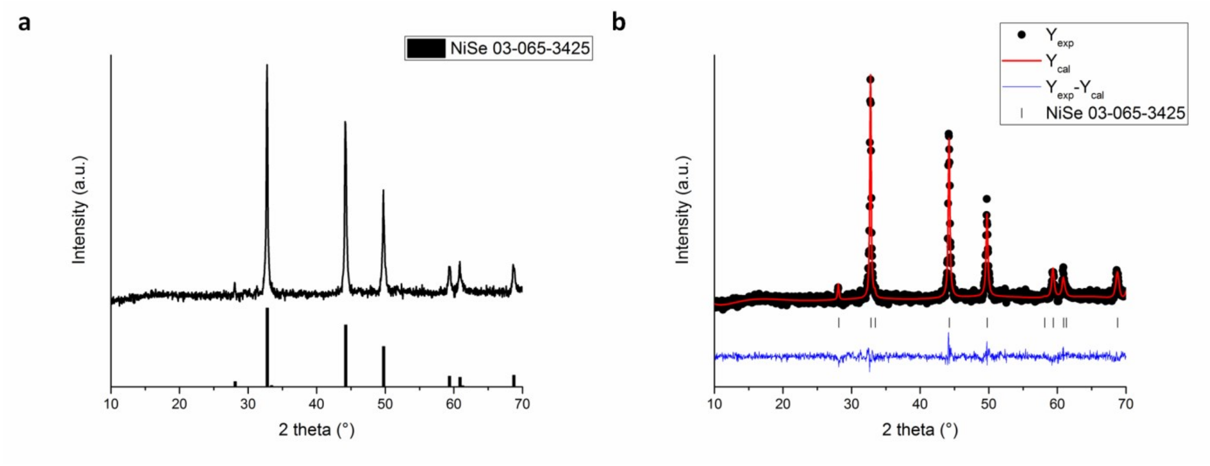

Fig. S24: Ni + Se, milled at 400 rpm for 2 min, (b) corresponding Rietveld refinement result

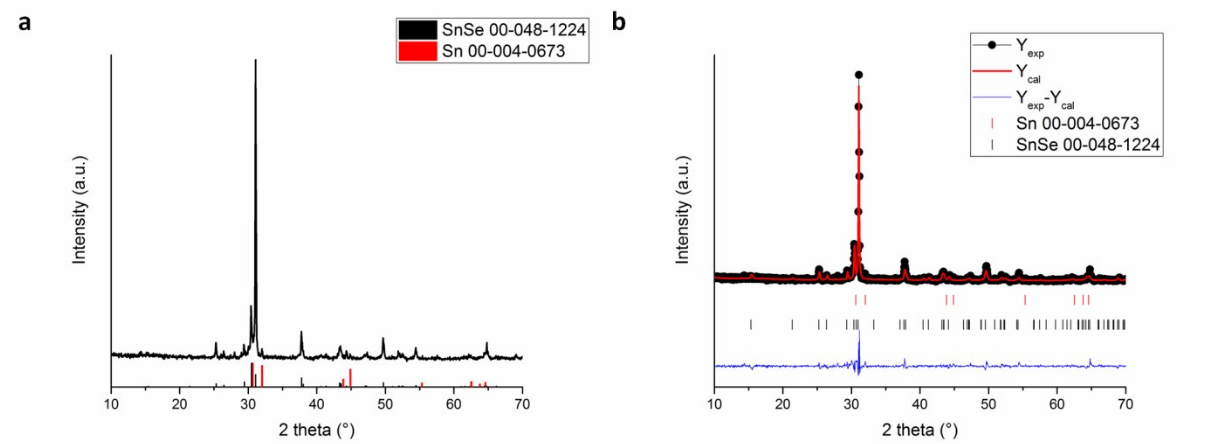

Fig. S25: Sn + Se, milled at 400 rpm for 1.5 min, (b) corresponding Rietveld refinement result

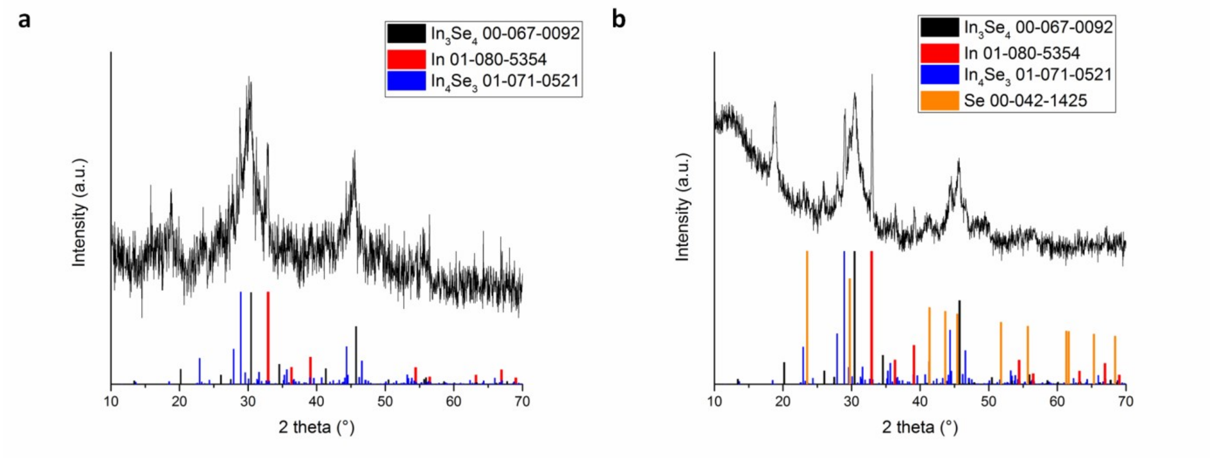

Fig. S26: 2In + 3Se, milled at 400 rpm for 5 min measured on: (a) Bruker D8 Advance, (b) Philips X'Pert Pro

Section S6: XRD patterns for the selected experiments, where accidently MSR was not observed, albeit in majority cases yes

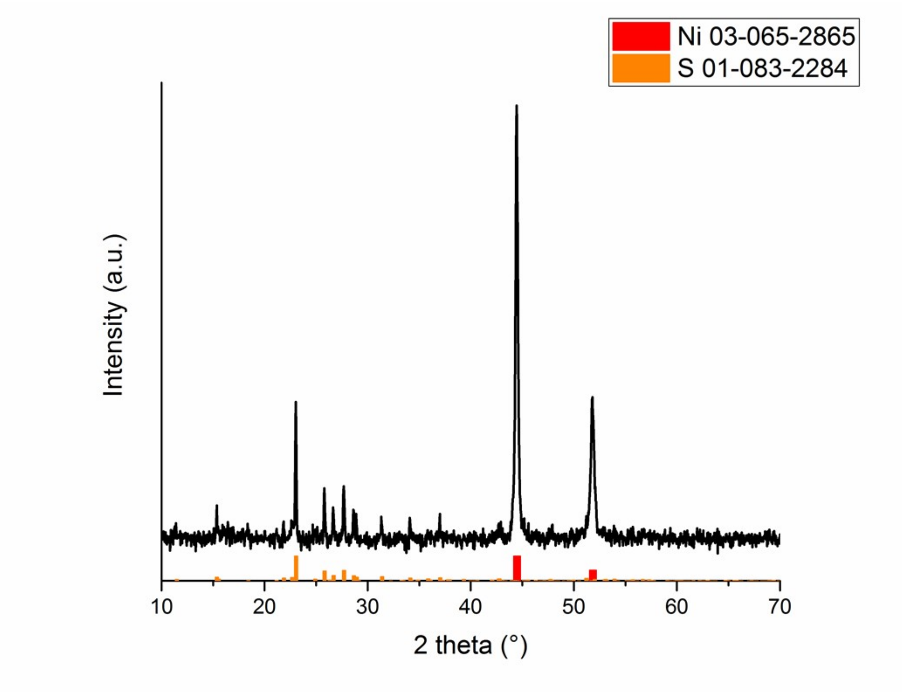

Fig. S27: XRD pattern of the Ni-S mixture milled at 750 rpm for 2 min without the occurrence of MSR event

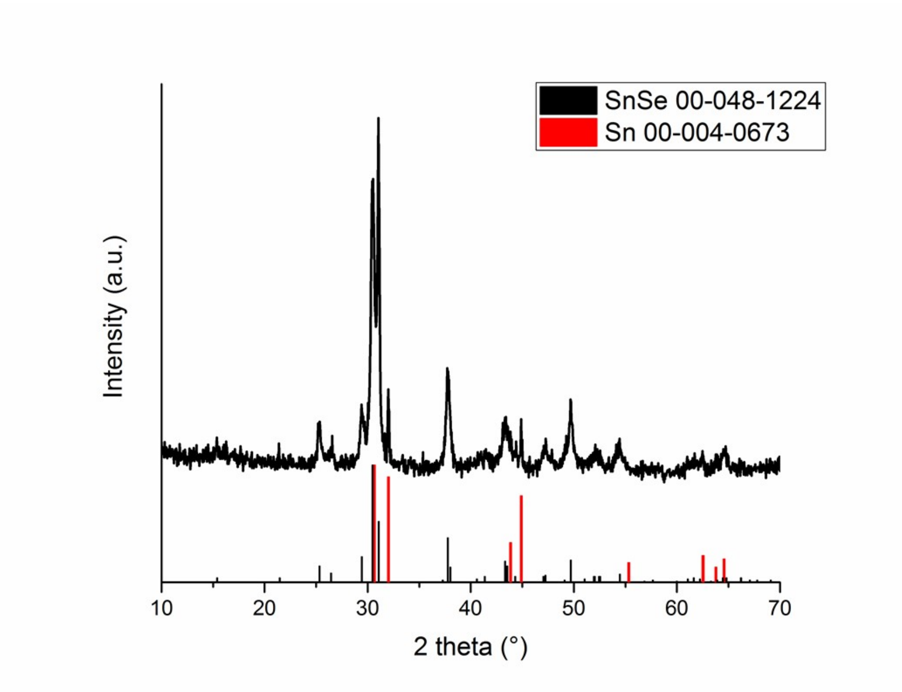

Fig. S28: XRD pattern of the Sn-Se mixture milled at 400 rpm for 5 min without the occurrence of MSR event

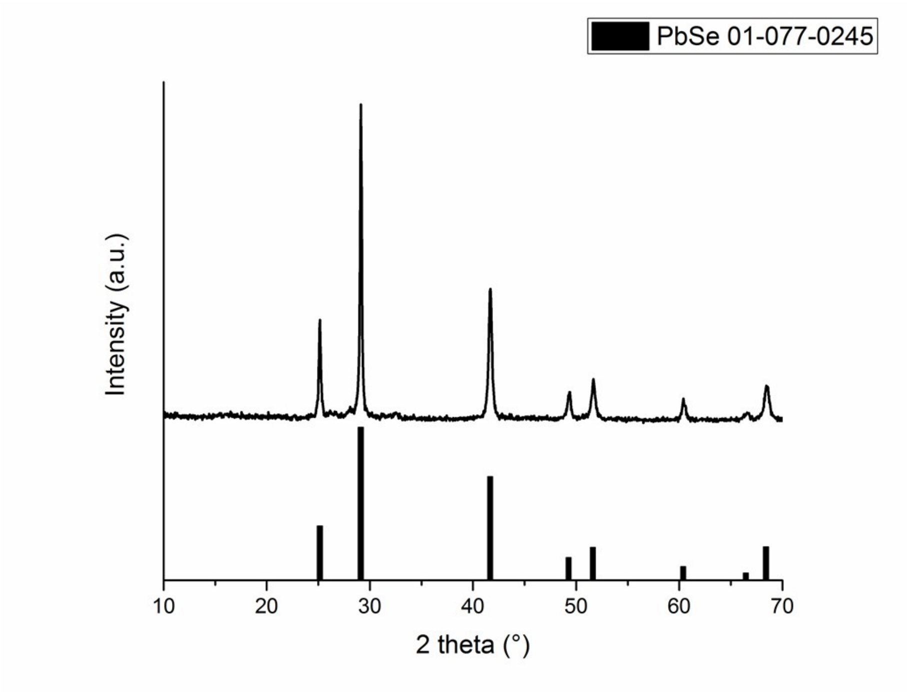

Fig. S29: XRD pattern of the Pb-Se mixture milled at 400 rpm for 3 min without the occurrence of MSR event

References in the supplementary file

1. Ohtani, T., et al., *Chemistry Letters* **2015,** *44*, 1234-1236.
2. Aviles, M. A., et al., *Inorganic Chemistry* **2019,** *58*, 2565-2575.
3. Tschakarov, C. G., et al., *Journal of Solid State Chemistry* **1982,** *41*, 244-252.
4. Vaughan, D. J.; Craig, J. R., *Mineral Chemistry of Metal Sulfides*. Cambridge University Press: Cambridge, 1978; p 493.