Iron sulphides play important role in natural processes and are widely used as geochemical indicators. Despite extensive research in last decades many questions about this highly-complex system remain unanswered. Although it is generally accepted that Fe-sulphides nucleate from the amorphous precipitates [1], the exact understanding of the subsequent phase transformations becomes complicated by metastable transient phases, extensive solid solutions and unquenchable polymorphs. To explore some of these issues we synthesized mackinawite-like near-amorphous precipitate from Fe-chloride, sulphur and diethanolamine using ultrasonic irradiation. This “first precipitate” was further solvothermally treated at temperatures up to 200 °C; to preserve the intermediate metastable phases, small amount of Fe in starting reagents was substituted with Cu. For characterisation of the products we employed XRD (PW1710, Philips Analytical B.V., Germany) and various TEM techniques (JEM-2100, Jeol Inc., Tokyo, Japan).

The cell parameters of fresh undoped FeS correspond to the reference values for layered FeS (mackinawite) [2], while doping with Cu results in the expansion of the unit cell along the c-axis, proportional to the amount of Cu in the starting composition [3]. Incorporation of Cu between the (001) layers of mackinawite strengthens the structure and enhances its crystallinity. The incorporation of transition metals in the structure is a temporary process and these interactions strongly influence the pathways for the subsequent phase transitions (Fig. 2). While during solvothermal treatment undoped FeS transforms directly to pyrite (FeS$_2$), the Cu-rich mackinawite transforms into different Cu-Fe-S phases, depending on the amount of Cu absorbed in the initial precipitate: large amounts of Cu results in the formation of bornite and chalcopyrite, while at low Cu concentrations a mixture of Cu-rich mackinawite and cubic FeS [4] is obtained, which are not observed in pure Fe-S system (Fig. 1). The investigation of such product showed that structural defects can be preserved during structural transformation.

References:

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Fig. 1: The near-amorphous first precipitate, obtained with sonochemical synthesis, transforms during solvothermal treatment into different (Cu, Fe)-S phases, depending on the initial amount of Cu in the starting reagents, while low amounts of Cu propagates a mixture of Cu-rich mackinawite and cubic FeS.

Fig. 2: Incorporation of Cu between S-S layers of mackinawite structure during sonochemical synthesis results in expansion of unit cell in c-axis and has a significant influence on phase transformation of Fe-sulphides during further solvothermal treatment.