New look at phase diagram of cuprite under pressure

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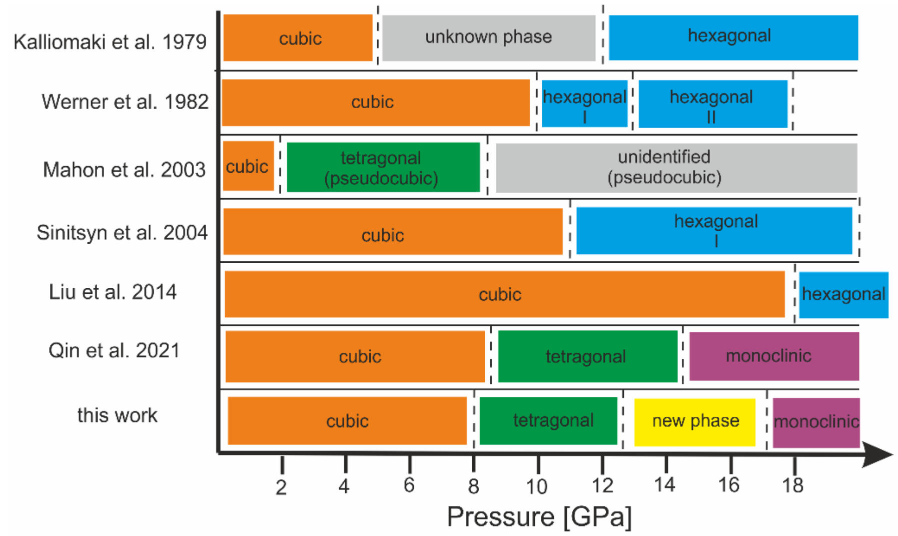
Abstract

Although the scientific literature presenting researches of cuprite under pressure already covers several papers, the real appearance of its phase diagram still remains unclear. On one hand cuprite is pretty simple compound which crystallizes at cubic crystal system, Pn-3m, at ambient pressure. On the other hand, when external pressure is applied, cuprite undergoes many phase transitions.

One of the first extensive studies were conducted by Kalliomaki et al..[1] In this paper researches claimed that cuprite under pressure undergoes two phase transitions, firstly at ca 5 GPa to some unknown structure and then at 12 GPa to some hexagonal structure. Werner and Hochheimer came to different conclusions.[2] They claim that first phase transition to unknown hexagonal structure occurs at 10 GPa and the second to another hexagonal at 18 GPa. These results were based on X-ray powder experiment. Mahon et al.[3] repeated the high-pressure, powder X-ray experiments. Authors revealed that firstly cubic structure undergoes transition to tetragonal phase, between 0.7 and 2.2 GPa, and later to some unidentified pseudo-cubic phase at 8.5 GPa. Results of applying high-pressure and heating the sample of cuprite were investigated by Sinitsyn et al..[4] First transition, at room temperature, to a hexagonal phase II occurred at ca. 11 GPa and another one to different hexagonal phase III at 21 GPa. There were performed also multiple DFT calculations. Liu et co-workers[5] showed that cubic Cu_2O under pressure should transforms to the metastable hexagonal phase between 18 and 20 GPa. The most recent experimental data based on single-crystal X-ray diffraction measurements conducted by Qin and co-workers,[6] confirmed existence of cubic to tetragonal phase transition at 10.4 GPa (from Pn-3m space group to $P4_2$/nnm space group) and revealed novel monoclinic phase which appears at 16.1 GPa (space group P1a or P12/a1).

On the basis of our experiments it seems that the situation is even more complicated. The hexagonal phase does not exists, but we understand why many scientists believed in its existence. Also, we suspect that a new phase may exist, but interpretation may change as a fact of developing techniques and access to them. It could be just a question of interpretation based on data of insufficient quality. For better understanding the situation we present these information as a simplified chart below.



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