MS089.O04

Phase transitions and crystal structures of η''-$Cu_{(3+x)}Si$ and η'''-$Cu_{(3+x)}Si$

Cinthia Antunes Correa[1,2], Morgane Poupon[1], Olivier Pérez[2], Robert Král[1], Petra Zemenová[1], Jérôme Lecourt[2], Jaromír Kopeček[1], Petr Brázda[1], Mariana Klementová[1], Lukáš Palatinus[1]

[1]*Department Of Structure Analysis - Institute Of Physics Of The Czech Academy Of, Prague, Czech Republic,* [2]*Department of Physics of Materials, Charles University in Prague, Ke Karlovu 5, Prague 2, Czechia*

E-mail: cinthiacac@gmail.com

The binary phase diagram of Cu-Si [1] was extensively studied and is considered well established. Three phases are reported in the Cu(3+x)Si phase-field: η'' below 470°C, η' between 470°C and 560°C, and η up to 859°C, where it melts congruently. The crystal structure of η' was obtained by Palatinus et al. [2], but so far no conclusive structure model for any of the other phases was published. We investigated samples of Cu(3+x)Si with nominal composition 74%, 76% and 78% copper by temperature dependent powder x-ray diffraction, differential scanning calorimetry, and in-situ high-temperature single crystal x-ray diffraction, within the temperature range of 30°C to 750°C. The temperature dependent powder x-ray diffraction revealed a complex phase diagram, where six distinct phases could be identified within the Cu(3+x)Si phase-field: in order of increasing temperature, η''', η'', η', η3, η2 and η1. Single crystal x-ray diffraction data enabled us to elucidate the crystal structures of η''' and η''. Both diffraction patterns could be indexed in a trigonal unit cell with a=4.0700(3) Å, c=14.685(2) Å and with modulation vectors q1=(α,β,1/3) and q2=(-α-β,α,1/3). The solution could be performed in (3+2)D superspace, but the extreme modulation impeded the refinement in the superspace. Hence, a supercell approximation was used for both structure refinements. The structures are incommensurately modulated. η''' has α=0.2783(10), β=0.2068(10), which allowed to use a 14x14x3 supercell, space group P-3, and η'', having α= β =0.2509(10), could be described in a 4x4x3 supercell, space group P-31c. Powder diffraction patterns were used to characterize the phase transitions and most of the subsequent phases. The transition from η''' to η'' is characterized by a change of the components of the modulation vectors from (α,β,1/3) to (α,α,1/3). During the next transition, from η'' to η', the c axis halves, maintaining the components of the modulation vector (α,α,1/3). η3 is most likely a (3+2)D structure similar to the previous ones, but so far the diffraction pattern could not be completely indexed. η2 appears when the modulation vector changes to (0,0,γ), and η1 becomes a regular crystal structure without modulation vectors. One unusual behavior present in the transitions is the shrinking of the unit cell parameters upon the transition to the higher temperature phases.

[1] Olesinski, R. W., Abbaschian, G. J., (1986). Bulletin of Alloy Phase Diagrams 7(2).

[2] Palatinus, L. et al. (2011). Inorg. Chem. 50, 3743–3751.

Keywords: copper silicide, incommensurately modulated structure, phase transition