Phase transitions and crystal structures of $\eta''(\text{Cu}(3+x)\text{Si})$ and $\eta'''(\text{Cu}(3+x)\text{Si})$

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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: $\eta''$ below 470°C, $\eta'$ between 470°C and 560°C, and $\eta$ up to 859°C, where it melts congruently. The crystal structure of $\eta'$ 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, $\eta'''$, $\eta''$, $\eta'$, $\eta_3$, $\eta_2$ and $\eta_1$. Single crystal x-ray diffraction data enabled us to elucidate the crystal structures of $\eta'''$ and $\eta''$. 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 $q_1=(\alpha,\beta,1/3)$ and $q_2=(-\alpha-\beta,\alpha,1/3)$. 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. $\eta'''$ has $\alpha=0.2783(10)$, $\beta=0.2068(10)$, which allowed to use a 14x14x3 supercell, space group P-3, and $\eta''$, having $\alpha=\beta=0.2509(10)$, 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 $\eta'''$ to $\eta''$ is characterized by a change of the components of the modulation vectors from $(\alpha,\beta,1/3)$ to $(\alpha,\alpha,1/3)$. During the next transition, from $\eta''$ to $\eta'$, the c axis halves, maintaining the components of the modulation vector $(\alpha,\alpha,1/3)$. $\eta_3$ is most likely a (3+2)D structure similar to the previous ones, but so far the diffraction pattern could not be completely indexed. $\eta_2$ appears when the modulation vector changes to $(0,0,\gamma)$, and $\eta_1$ 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.


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