Thermal transformation of Si-rich ferrihydrite to hematite via three (γ, ε, and β) Fe_2O_3 polymorphs

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Hematite is the final product of ferrihydrite thermal transformation via both hydrothermal and dry-heating pathways. When annealed in air, ferrihydrite is fully converted to α-Fe_2O_3 at the temperature below 500 ºC. Silicate, one of the most important impurity of natural ferrihydrites, was shown to hinder the transformation, and a gradual shift of the conversion temperature with increasing Si content in the initial oxyhydroxide was observed many times. However, the process was studied in detail only for relatively low-Si ferrihydrites. The aim of the study was to determine how a high silicate content affects the thermal ferrihydrite–hematite tranformation pathway. For this purpose, four ferrihydrites of increasing Si/Fe molar ratios (0.50, 0.75, 1.00 and 1.50) were synthesized by reaction of ferric sulfate with NaOH in the presence of appropriate Na_2SiO_3 concentrations. All the samples were then annealed at different temperatures up to 1000 ºC and the products were characterized using XRD, FTIR, SEM methods. TEM analyses and magnetic susceptibility measurements were also carried out for selected samples.

It turned out that the transformation of high-Si ferrihydrites is significantly more complex than in the case of low-Si ferrihydrites. Low temperature dehydration is followed by gradual amorphisation up to 600 ºC. At that temperature amorphous silica emerges and, after further temperature increase to 700–800 ºC, a distinct increase of magnetic suscepitibility is observed, related to the formation of nanocrystalline maghemite. This intermediate phase is then converted to orthorombic ε-Fe_2O_3 which, in turn, is transformed into a final α-Fe_2O_3. At the same time cristobalite-like phase is formed from the previously released silica. However, when the highest-Si ferrihydrite was annelaed, the presence of additional cubic β-Fe_2O_3 was found between 907 ºC and 930 ºC. Thus the conversion of ferrihydrite with Si/Fe = 1.50 to hematite proceeds via γ–ε–β pathway and slightly above 900 ºC three Fe_2O_3 polymorphs (ε, β, and α) coexist.

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