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In situ HAFM study of the thermal dehydration on gypsum (010) surfaces

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ABSTRACT

Hydrothermal AFM has been used to study the thermal dehydration reaction on gypsum (010) surfaces in solutions at different saturation states, and in the absence of a bulk liquid phase. Experiments were carried out at temperatures ranging from 25 to 130 °C. Whereas supersaturated solutions (β = 1.8–5) caused gypsum growth in the entire temperature range, solutions close to equilibrium (β = 1.02) caused various responses of the gypsum surface. The most prominent was a sharp transition from fast growth to very fast dissolution at ~120 °C suggesting a sudden nucleation of a phase more stable than gypsum. No structural relation could be found between the parental gypsum (010) surface and the crystallizing phase.

In the absence of a bulk liquid phase, dehydration takes place via the nucleation and spreading of etch-pit like pattern. Laterally, the thermal etch pits spread in an unrestricted way. In the vertical direction, pit growth was limited to a few micrometers. Dehydration by monolayer pits and nucleation of the dehydration process at monolayer steps on the (010) surface were never observed. Thus, unlike growth or dissolution, surface energy related to kink sites or individual point defects seems to be insufficient to trigger dehydration. The temperature-dependent lateral pit growth yields an activation energy of 119 ± 11 kJ/mol. The product phase disintegrates at the parental surface into nano-size particles without any morphologically noticeable transition zone.

Keywords: AFM/SFM/STM, crystal growth, crystal synthesis, kinetics, phase transition, surface studies