

FORMATION MECHANISM OF α -QUARTZ FROM OPAL-A BY HYDROTHERMAL SYNTHESIS

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Introduction

The transitions of amorphous silica via various metastable phases (cristobalites, tridymites, silica-X and silica-K) to α -quartz are important from the geological perspective, especially with regards to sedimentation and diagenesis. The transition depends on the starting material, type and concentration of mineralizers, temperature, pressure and time of synthesis (BETTERMANN & LIEBAU, 1975). In the framework of our research we have shown that morphologically well-developed, micron-sized, low-temperature or α -quartz crystals can be obtained directly from opal-A at 250°C and 40 bar, without any intermediate phases being present.

Methods

The isothermal method was used, where in the whole volume of an autoclave a constant temperature is applied. Tetraethylorthosilicate (TEOS) was used as the silica precursor, distilled water as the solvent and NaOH as the mineralizer. The experiments were performed at pH = 12, 250°C, 40 bar and for different hydrothermal synthesis times. The obtained products were investigated with scanning and transmission electron microscopy, X-ray diffraction (XRD) and Raman spectroscopy.

Results and discussion

With the extension of the synthesis time, different silica products were formed. With a synthesis time of 8 h, polydisperse spheres of non-crystalline opal-A, which was determined by XRD and Raman spectroscopy, were obtained (Fig. 1a). After 12 h of synthesis, the spheres coalesced and formed amorphous aggregates (Fig. 1b). With a prolongation of the experiment to 24 h, XRD patterns showed that the obtained product is still amorphous; however, the Raman spectre revealed the

beginning of the formation of α -quartz. When a longer reaction time was applied, the XRD detected α -quartz and also a significant change in morphology was noticeable. After 72 h of synthesis the XRD revealed the prevalence of α -quartz, and some small amount of opal-A was additionally detected by Raman. The transition from rounded quartz particles to quartz with already developed certain crystal faces was recognised (Fig. 1c). After 144 h the XRD pattern showed that the obtained product is pure low-temperature quartz, with no other phases being present. The solid product consisted of double-terminated, short-prismatic 3–4 μ m crystals of quartz with well-developed, rhombohedral and prismatic crystal faces (Fig. 1d).

Conclusions

We studied the development of α -quartz crystals from nanoscale silicon dioxide spheres of opal-A in relatively low p-T conditions. The formation mechanism can be explained over several growth steps. After the TEOS hydrolysis and condensation reactions the nucleation of opal spheres begins (MASALOV *et al.*, 2011). This is followed by their aggregation. The next step includes the crystallization and formation of α -quartz nanocrystals from opal-A. As their size increases, they develop crystal faces. In the above-mentioned p-T conditions the following reaction sequence is taking place: opal-A \rightarrow coalescence of spheres \rightarrow formation of nanocrystalline quartz \rightarrow micron-sized quartz with well-developed crystal faces.

References

- BETTERMANN, P. & LIEBAU, F. (1975): Contributions to Mineralogy and Petrology, 53: 25–36.
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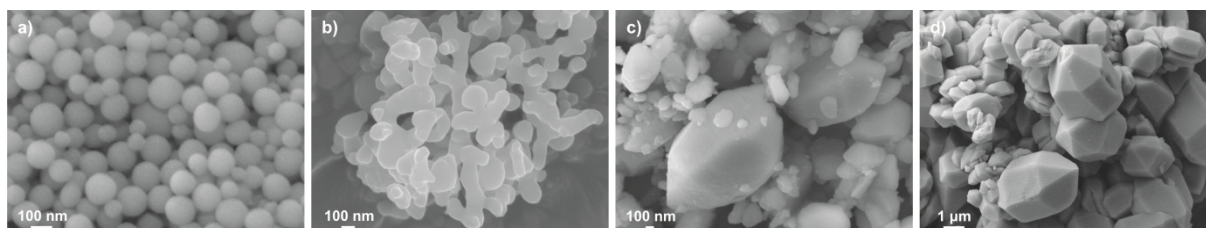


Fig. 1. a) spheres of opal-A; b) coalescence of spheres; c) quartz with the beginning of formation of crystal faces; d) quartz with well-developed crystal faces.