

HETEROEPITAXIAL GROWTH OF MnCO_3 ON CALCITE (10-14)

Pérez-Garrido, Carlos¹ Astilleros García-Monge, José Manuel² Fernández-Díaz, Lurdes³ Prieto Rubio, Manuel⁴

¹Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. C/ José Antonio Novais 2. 28040, Madrid (Spain) ²Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. C/ José Antonio Novais 2. 28040, Madrid (Spain) ³Departamento de Cristalografía y Mineralogía. Universidad Complutense de Madrid. C/ José Antonio Novais 2. 28040, Madrid (Spain) ⁴Departamento de Geología. Universidad de Oviedo. C/ Jesús Arias de Velasco. 33005 Oviedo (Spain)

The formation of solid solutions grown from multicomponent aqueous solutions is an especially extensive phenomenon observed both in nature and laboratory, since many minerals and synthetic compounds form solid solutions with complicated zoning patterns. Compositional and oscillatory zoning can be considered as heteroepitaxy, because it suggests a growth on the substrate with very similar crystal structure but different chemical composition and lattice constants. In this work we continue the study of heteroepitaxial growth in solid solution – aqueous solution (SS–AS) systems, focusing on the processes that take place during the growth of one end-member directly on the other one. As a model system we have chosen the growth of rhodochrosite (MnCO_3) on calcite (CaCO_3) (104) substrate. These compounds form a solid solution crystallizing in the trigonal space group *Rc*. They have the different lattice constants: $a_{\text{hex}} = 4.990 \text{ \AA}$, $c_{\text{hex}} = 17.061 \text{ \AA}$ for calcite and $a_{\text{hex}} = 4.780 \text{ \AA}$, $c_{\text{hex}} = 15.66 \text{ \AA}$ for rhodochrosite. Because of their identical structure, this system is suitable to study epitaxial growth taking place in such systems.

Experiments were carried out at 25° C in situ in a fluid cell of a Digital Instruments Multimode AFM. Freshly cleaved, optically clear (104) calcite surfaces were used as substrates. The supersaturation with respect rhodochrosite ranged between 6.76 and 60.0. After an induction period, during which no dissolution was observed, nuclei of the new phase formed on the calcite substrate. This nuclei readily reach a significant height ($2.2 \pm 0.5 \text{ nm}$), which remained approximately constant during their lateral spread. A clear epitaxial relationship between the islands of the new phase and the calcite (104) surface was observed, with the islands preferentially growing parallel to [42] (~ 15 times faster than [010] in the calcite substrate). This behaviour determines that they rapidly develop an elongated needle-like shape. Moreover, growth along [42] is highly anisotropic and the ends of these “needles” are differently truncated. The lateral growth of the islands leads to their coalescence and the formation of a quite homogeneous nanometric layer. This layer finally armours the calcite substrate from further interaction with the solution. The characteristics of the epitaxial growth are in agreement with a Volmer – Weber growth mechanism controlling the process. The results obtained in these experiments will be compared with other similar SS – AS systems.

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submitted by: **Astilleros, José
Manuel**

email: **jmastill@geo.ucm.es**

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