Short range Ca-Ba order-disorder in double carbonates

Alejandro Ruiz Fernández (1), José Manuel Astilleros (1,2*), Lurdes Fernández-Díaz (1,2), Francisco Javier García García (3)

(1) Departamento de Mineralogía y Petrología. Universidad Complutense de Madrid, 28040, Madrid (España)
(2) Instituto de Geociencias (CSIC-UCM), 28040, Madrid España)
(3) ICTS-CNME, F. CC. Químicas, Universidad Complutense de Madrid, 28040, Madrid (España)
* corresponding author: jmastill@ucm.es

Palabras Clave: Orden a corto alcance, Intensidad difractada difusa, Carbonatos mixtos de Ca-Ba, Crecimiento de cristales en geles. **Key Words:** Short range order, Diffuse scattering intensity, Double Ca-Ba carbonates, Crystal growth in gels.

INTRODUCTION

The precipitation of carbonates from supersaturated solutions has been extensively studied over the past decades. Many of these investigations have focused on the influence of specific cations on different aspects of $CaCO_3$ crystallisation, including crystal morphology, precipitation kinetics and polymorph selection. The determination of cation/calcium distribution coefficients, for instance, provides valuable constraints on the composition and temperature of paleowaters, as well as on the diagenetic reactions affecting these materials (Lowenstein and Hölner, 2012). In this study, we investigate the phases precipitated in the $(Ba,Ca)CO_3$–H_2O system. To this end, counter-diffusion crystallisation experiments were conducted using reactive aqueous solutions within a gel matrix. This system is mineralogically complex: in addition to the formation of $CaCO_3$ polymorphs (calcite, aragonite, and vaterite) and witherite ($BaCO_3$), several double carbonates of composition $BaCa(CO_3)_2$, including barytocalcite, paralstonite, and alstonite, may also precipitate. Furthermore, a fourth $BaCa(CO_3)_2$ polymorph, the so-called *C*2-phase (Spahr et al., 2019), has been reported only recently and has so far been synthesised under high-temperature solid-state conditions. Notably, the *C2*-phase is the predominant product in our crystallisation experiments conducted at ambient temperature. Beyond its mineralogical significance, the formation of these solid solutions is of considerable environmental interest, as they may be used to immobilise nuclear waste streams containing aqueous rare earth elements (REEs) (Spahr et al., 2022). Although REE contents in natural calcites are typically below 0.1 mol%, the structural flexibility of $BaCa(CO_3)_2$ phases suggests that significant amounts of these elements could, in principle, be incorporated into their structures. In a later stage, we aim to use the results of this study to better understand the immobilisation of REEs. At present, however, our interest in these phases is fundamental, as they provide an excellent model system for investigating order–disorder processes in compositionally complex solid solutions. Here, we present a transmission electron microscopy (TEM) characterisation of the *C*2-phase, with particular emphasis on its short-range order. To date, no electron microscopy studies have been reported for this polymorph.

METHODS

Crystallisation experiments were performed using a double-diffusion setup (Fernández-Díaz et al., 2006). The system consists of a U-shaped tube in which the horizontal arm is filled with a silica hydrogel column (150 mm in length and 9 mm in diameter), while the two vertical arms (A and B) act as reservoirs for the reactant solutions. These reservoirs were filled with 8 cm^3 of $CaCl_2$ + $BaCl_2$ and Na_2CO_3 solutions, respectively. The gel was prepared by acidifying a sodium silicate (Na_2SiO_3) solution (Merck; specific gravity 1.059 g cm^{-3}, pH 11.2) with 1 N HCl to an initial pH of 5.5, and subsequently introduced into the U-tube. The resulting gel contains a network of micron-sized pores in which the solution is immobilised, effectively suppressing convection (Henisch, 1988). Under these conditions, mass transport is governed by molecular diffusion, leading to the establishment of concentration and pH gradients along the gel column. All experiments were conducted at 25 ± 0.1 °C. Crystal growth was monitored by optical microscopy, and the experiments were terminated several weeks after the onset of nucleation. The resulting crystals were then extracted and characterised using scanning electron microscopy (SEM, TESCAN Vega 4) and transmission electron microscopy (TEM, JEOL JEM 2100).

RESULTS

In Fig. 1, a collection of zone axis electron diffraction, ZAED, patterns down different directions from different $(Ba_xCa_{1-x})_2(CO_3)_2$ crystals are presented. Indexation is done according to the monoclinic unit cell as reported ($a \approx$ 6.7 Å, $b \approx$ 5.1 Å, $c \approx$ 4.2 Å, $\alpha \approx 90°$, $\beta \approx 109.2°$, $\gamma \approx 90°$ and with space group *C*2, nº 5). Therein, it is notorious the presence of highly structure diffuse intensity which is accompanying, and decorating, the reciprocal lattice for the *C*2-phase. The tilting experiments in the electron microscope tell us that in reality we face with the presence of a 3-dimensional surface or contour of diffuse scattering. This is very typical of substitutional disorder and, hence, there exist short range order between Ca and Ba. Discussions on the shape of the surface and the subsequent consequences in real space will be presented.

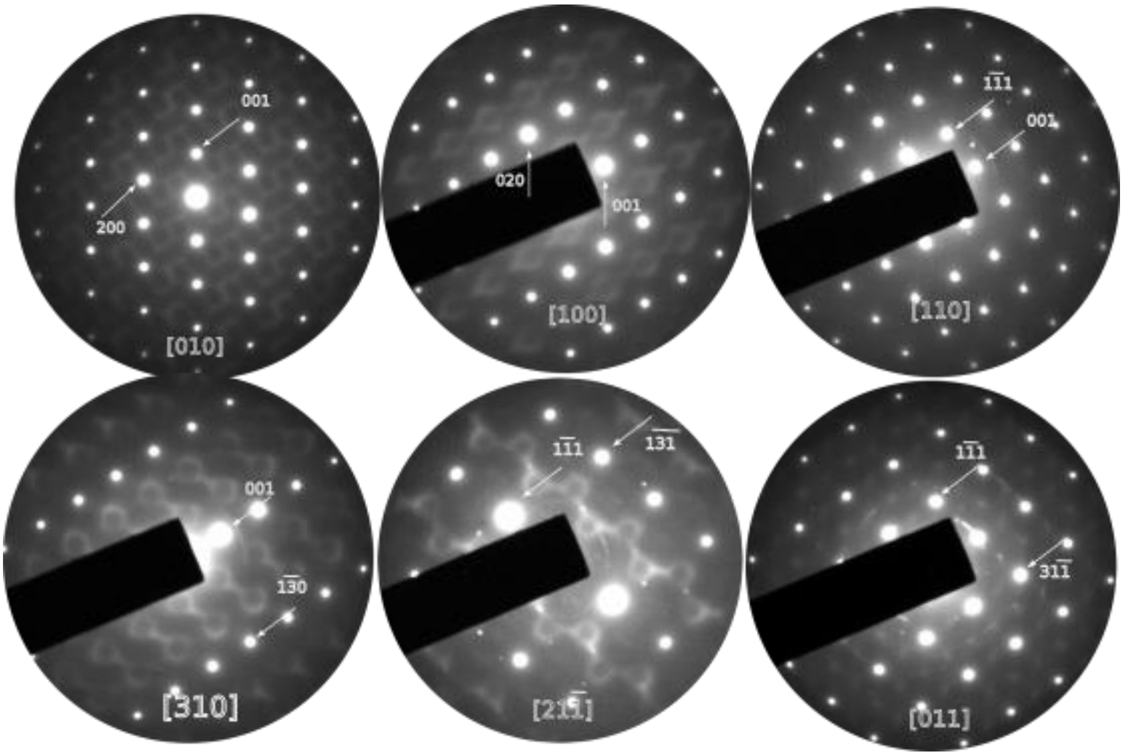

***Fig 1**. Serie of selected area electron diffraction patterns recorded in different $Ba_xCa_{1-x}CO_3$ crystals. Note the presence of a very characteristic locus of diffuse scattering. Indexation of the reciprocal lattice is done according to the C2-phase.*

REFERENCES

Fernández-Díaz, L., Astilleros, J.M., Pina, C.M. (2006): The morphology of calcite crystals grown in a porous medium doped with divalent cations. Chem. Geol., **225**, 314-321. DOI: 10.1016/j.chemgeo.2005.08.024.

Henisch, H.K. (1988): Crystals in gels and Liesegang rings. Cambridge University Press. Cambridge, 197 p.

Lowenstein, T.K., Hönisch, B. (2012): The Use of Mg/Ca as a Seawater Temperature Proxy. Paleontol. Soc. Pap., **18**, 85-100. DOI:10.1017/S1089332600002564.

Spahr, D., Bayarjargal, L., Vinograd, V., Luchitskaia, R., Milmanc, V., Winkler, B. (2019): A new $BaCa(CO_3)_2$ polymorph. Acta Cryst., **B75**, 291-300. DOI: 10.1107/S2052520619003238.

—, —, —, Etter, M., Raddatz, J., Winkler, B. (2022): Incorporation of Europium into $(Ba,Ca)_2(CO_3)_2$, J. Solid State Chem., **307**, 122759. DOI: 10.1016/j.jssc.2021.122759.