LETTERS

Incommensurate c-domain superstructures in calcian dolomite from the Latemar buildup, Dolomites, Northern Italy

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ABSTRACT

Early exposure cap microdolomites (<50 °C) and low-temperature hydrothermal (<177 °C) calcian dolomite crystals from the Latemar buildup, Dolomites, northern Italy, are microstructurally heterogeneous. Selected-area electron-diffraction patterns contain incommensurate superstructure reflections from domains that are approximately 2.5 nm wide. These domains are quasiperiodic with wavelengths of 5 to 20 nm. The scale of these modulations varies with composition of the bulk crystal.

Previously described c-domain superstructures in dolomite are reported as commensurate with the host structure; c-diffraction spots are situated exactly halfway between the principal (a and b) reflections. Re-examination of published diffraction patterns reveals that some are actually incommensurate. Individual c-domains are monoclinic and have been interpreted to be more calcium-rich than the host dolomite. Newly recognized c-domains resemble previously described c-domains but are distinct because they are incommensurate with the dolomite host and produce diffraction spots with irrational indices.

In samples from the Latemar buildup, the c-axes of the host and modulations are parallel, but the [110] directions are not parallel. Further, the length of $c_{\text{dolomite}}^* \approx c_{\text{superstructure}}^*$, but the lattice spacing of $d_{110}^{\text{superstructure}}$ is more than twice $d_{110}^{\text{dolomite}}$. The superstructure phase is metrically monoclinic and is interpreted to incorporate more calcium than dolomite. Domains are, however, too small to analyze directly. Excess calcium may account for the more than doubling of the domains’ a–dimension relative to that of dolomite. Inclination of the domain lattice relative to the host lattice may vary as a function of calcium content.

INTRODUCTION

Transmission electron microscope observations of calcian dolomite have revealed a number of crystallographic variations (Reeder and Wenk 1979; Gunderson and Wenk 1981; Reeder 1981, 1983; Wenk and Zhang 1985; Van Tendeloo et al. 1985; Reeder and Prosky 1986; Reeder et al. 1990; Reksten 1990a; Wenk et al. 1991; Reeder 1992; Ward and Reeder 1992; Frisia and Wenk 1993; Frisia 1994; Schubel 1997). Figure 1 schematically depicts the [001]- and [010]-zone diffraction patterns of calcite, homogeneous dolomite, dolomite with c-domains, and dolomite with d-domains. Throughout this letter, calcite and dolomite are indexed with the rhombohedral lattice and hexagonal axes.

The rhombohedral carbonates produce four types of reflections in diffraction patterns, as discussed in detail by Wenk and Zenger (1983), Van Tendeloo et al. (1985), Wenk and Zhang (1985), Reksten (1990a), and Reeder (1992). In summary, reflections found in diffraction patterns of calcite ($R3c$) are termed “a” reflections (first column of Fig. 1). In the hexagonal unit-cell setting, the R lattice requires that all reflections meet the condition $-h + k + l = 3n$ (Hahn 1996). In addition, the c-glide results in the systematic absence of reflections with odd l index.

In dolomite, the ordered stacking of Ca and Mg in alternating octahedral layers along the c-axis destroys the c-glide plane and results in space group symmetry R3. Diffraction patterns of dolomite include, therefore, both the a-reflections of calcite and those with odd l indices. These additional reflections are termed “b” reflections. Note that b-reflections are present in Figure 1 for the [010]-zone diffraction pattern, but not in the [001]-zone, because none of the reflections have odd l index in the [001] zone.