TEM investigation of Ca-rich plagioclase: Structural fluctuations related to the $\text{I}T$-$\text{PT}$ phase transition

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ABSTRACT

We used transmission electron microscopy (TEM) to understand microstructural changes accompanying the reversible $\text{I}T$-$\text{PT}$ phase transition in Ca-rich plagioclase as a function of Na content. The transition produces $c$- and $d$-type domains that have $\text{PT}$ symmetries, and the symmetries of domain walls are $\text{I}T$. Based on diffractograms and contrast differences of high-resolution TEM (HRTEM) images, we infer that structural differences occur on a scale of tens of nanometers, giving rise to structural fluctuations. These variations can be followed on a nanometer scale using HRTEM images. We propose a model with a body-centered Al-Si framework and single Ca sites for the $\text{I}T$ domains. The $\text{PT}$ domains of anorthite with high Al-Si ordering are homogeneous. In contrast, structural fluctuations occur in both anorthite with lower Al-Si ordering and in Na-bearing plagioclase. The magnitudes of the fluctuations decrease with increases in Na content.

Keywords: $\text{I}T$-$\text{PT}$ phase transition, Ca-rich plagioclase, HRTEM, structural fluctuations

INTRODUCTION

Plagioclase feldspars are major constituents of Earth’s crust. Chemically, they are solid solutions of albite (NaAlSi$_3$O$_8$) and anorthite (CaAl$_2$Si$_2$O$_8$). Structurally, they consist of a framework of AlO$_4$ and SiO$_4$ tetrahedra that are linked by shared O atoms. Upon cooling, different Al-Si ordering schemes develop to avoid the energetically unfavorable Al-O-Al linking (Loewenstein 1954; Putnis 1992). The first plagioclase that crystallizes from a melt should evolve during cooling to a two-phase assemblage (e.g., Carpenter 1994). This process is, however, kinetically inhibited, and metastable microstructures form (Smith 1974; Kroll and Ribbe 1980). Such microstructures are of interest because they have the potential of recording cooling histories (e.g., Brown and Parsons 1994; Carpenter 1994).

Albite-rich plagioclase has $\text{CT}$ symmetry, and calcic plagioclase has $\text{I}T$ and $\text{PT}$ symmetries (e.g., Carpenter 1994). Complexities arise through the presence of incommensurate phases for slowly cooled, ordered plagioclase with intermediate Ca contents.

A reversible phase transition from $\text{I}T$ to $\text{PT}$ in anorthite, first discovered by Brown et al. (1963), occurs at 514 K (e.g., Ghose et al. 1993). The temperature of the transition decreases with increases in the albite content (Redfern et al. 1988). The symmetry change is related to displacive crumpling of the Al-Si framework and the loss of the body-centering among the Ca atoms. Different $\text{PT}$ atomic configurations occur depending on the extent of the framework crumpling, and they are revealed by differences in cell parameters (Salje 1987). In this paper, we focus on the $\text{I}T$-$\text{PT}$ transition and associated microstructures in Ca-rich plagioclase.

Generally the $\text{I}T$-$\text{PT}$ phase transition has been studied by bulk methods such as X-ray diffraction (e.g., Angel et al. 1990; Carpenter et al. 1990) and infrared (IR) spectroscopy (Redfern and Salje 1987; Atkinson et al. 1999). Transmission electron microscopy (TEM) has also been used and revealed the occurrence of $\text{PT}$ domains and domain boundaries (e.g., McLaren 1973; Czank et al. 1973; Van Tendeloo et al. 1989; Tribaudino et al. 2000). Such domains were considered to be displaced with respect to each other (i.e., antiphase domains), and boundaries were supposed to have $\text{I}T$ symmetries (e.g., Van Tendeloo et al. 1989; Tribaudino et al. 2000). However, McLaren (1973) pointed out that not all $\text{PT}$ domains are displaced with respect to each other and that high-resolution TEM (HRTEM) is required to study the walls between $\text{PT}$ domains. Therefore, here we refer to these features as $\text{PT}$ domains and domain boundaries. Van Tendeloo et al. (1989) showed the presence of micrometer-sized $\text{PT}$ domains with sharp interfaces in anorthite. In contrast, McLaren (1973) showed smaller (tens of nanometers) $\text{PT}$ domains separated by boundaries in plagioclase with An$_{95}$Ab$_5$ (An: anorthite; Ab: albite) composition. Tribaudino et al. (2000) studied a synthetic anorthite, and they also found small, elongated $\text{PT}$ domains separated by boundaries.

The $\text{I}T$-$\text{PT}$ phase transition is of interest as it couples with Al-Si ordering (Redfern et al. 1988), which is associated with the $\text{CT}$-$\text{I}T$ phase transition and related to variations of strain and elastic proper-

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