Twinning in meteoritic and synthetic perovskite

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ABSTRACT

Transmission electron microscope observations of end-member perovskite from two carbonaceous chondrite meteorites show that fine-scale twinning is common. Three twin laws are observed: (1) a 90° rotation around [01], (2) a 180° rotation around [01], and (3) a 180° rotation around [21]. The meteoritic perovskite is predominantly twinned according to 3 above, in contrast to terrestrial perovskites, in which operations 1 and 2 are more common. Twinning on (121) [pseudocubic (111)] occurs during cooling through the cubic-orthorhombic phase transition.

Experiments on synthetic perovskite indicate that twinning on (121) is the predominant twin law observed in material that was cooled rapidly (>50 °C/min). In experiments using slower cooling rates, (101) twins are more prevalent than (121) twins. These results indicate that meteoritic perovskite displaying (121) twins was heated to temperatures above the cubic-orthorhombic phase transition (~1573 K) and rapidly cooled. This constraint strongly limits the mechanism responsible for the formation of perovskite in these meteorites.

INTRODUCTION

The perovskite structure is of great importance, both for understanding mantle geophysics (e.g., Williams et al., 1987) and in certain technological applications such as ferroelectrics and superconductors (e.g., Newnham, 1987). The microstructures of compounds with the perovskite structure have been widely studied by electron microscopy, but only a few investigations have considered the microstructures in end-member perovskite (e.g., Doukhan and Doukhan, 1986; Hu et al., 1992). End-member perovskite is rare in terrestrial rocks; perovskite usually shows substantial solid solution with incompatible elements, typically large rare earth elements (La and Ce), Na, and Nb, which accounts for varietal names such as loparite and dysanalite. The few occurrences of near end-member perovskite are restricted to metamorphic rocks that have undergone deformation. Thus, it is difficult to differentiate microstructures arising from deformation events from those resulting from phase transitions. In some carbonaceous chondrite meteorites, however, we have the opportunity to study essentially pure CaTiO₃ perovskite from undeformed rocks.

We report here on our transmission electron microscope (TEM) studies of microstructures in meteoritic perovskite. Perovskite (CaTiO₃) is a common accessory mineral in Ca- and Al-rich refractory inclusions (CAIs) in some carbonaceous chondrite meteorites. Much of this perovskite occurs in refractory rims, where it is intergrown with other high-temperature minerals, mainly spinel and hibonite. Isotope and trace-element studies indicate that these refractory rims are evaporative residues from a high-temperature flash-heating event early in the history of our solar system (Boynton and Wark, 1987; Wark et al., 1988). However, major uncertainties exist regarding the thermal history of these refractory rims; these uncertainties include the maximum temperature attained and the relative heating and cooling rates that the inclusions experienced. The occurrence and structural characteristics of end-member perovskite provide information regarding the origin of refractory rims on CAIs.

Ideal perovskite is cubic, space group Pm3m, with a = ~0.382 nm. The structure consists of corner-sharing TiO₆ octahedra that form a regular three-dimensional framework, with Ca occupying the large cuboctahedral sites formed by the octahedra (Fig. 1a). At room temperature, Ca is slightly too small for its site, causing the TiO₆ octahedra to tilt and rotate slightly (Fig. 1b), thereby reducing the symmetry from cubic to orthorhombic (Sasaki et al., 1987). The orthorhombic unit cell (denoted by the subscript o) is related to the pseudocubic subcell (subscript c) by the following relations: aₜ = √2aₒ, bₒ = 2aₒ, and cₒ = √2aₒ. We use the standard space group setting for orthorhombic perovskite, Pnma.

It is well known that a reversible transition occurs in CaTiO₃ between high-temperature cubic symmetry and low-temperature orthorhombic symmetry (e.g., Megaw, 1973; Müller and Roy, 1974; Liu and Liebermann, 1988; Liebermann et al., 1990). However, uncertainties exist regarding the nature of the transition from cubic to orthorhombic symmetry, as well as the nature of the transition mechanism. A consequence of the cubic to orthorhombic transition mechanism is the development of microtwinning on the major pseudocubic axes as the
structure loses symmetry on cooling through the transition temperature.

**EXPERIMENTAL**

We studied perovskite from type A and type B CAIs from the Allende meteorite, and a single type A inclusion from the Vigarano CV3 carbonaceous chondrite (the reader is referred to the review paper of Grossman, 1980, for a summary of CAI classification). The perovskite occurs as rounded, isolated grains that are typically <10 μm in size but average about 1–2 μm in diameter (Fig. 2). Quantitative energy-dispersive X-ray analyses of the perovskites show no detectable elements other than Ca and Ti. A total of six regions of interest were extracted from polished thin sections, attached to Cu grid supports, and ion thinned to electron transparency using 5-kV Ar ions. From these specimens, we were able to study over 50 perovskite grains.

Cooling-rate experiments were performed using synthetic perovskite prepared by sintering pellets of stoichi-
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Fig. 3. Schematic and SAED patterns of the [012] zone. The open circles are the allowed reflections, and the open squares designate forbidden reflections that are generated by multiple diffraction.

ometric mixtures of reagent grade CaCO₃ and TiO₂ in air at 1773 K for 48 h. The pellets were then ground in an agate mortar and pestle, repelletized, and heated at 1973 K for 24 h. X-ray powder diffraction patterns contain only the sharp peaks of perovskite; no peaks from impurity phases were observed. For the cooling-rate experiments, 50-mg to 100-mg samples of powdered CaTiO₃ were loaded into Pt capsules and suspended in a sealed vertical-tube furnace, equilibrated at 1873 K, and cooled to 1073 K at 10, 50, and 100 °C/min, and then drop quenched. Aliquots of the synthetic material were prepared for TEM observation by grinding the sample in acetone and dispersing it onto holey carbon thin films attached to Cu grids. High-resolution images and electron diffraction patterns were obtained using JEOL 2000FX (200 kV) and JEOL 4000EX (400 kV) transmission electron microscopes (TEM). Optical diffractograms of small regions in high-resolution TEM images were recorded on an optical bench.

TWINNING

Twinning is well developed and common in the perovskite grains we studied. We observed twinning according to three twin laws: (1) a 90° rotation around [01], (2) a 180° rotation around [110], and (3) a 180° rotation around [21]. Only the first two operations are common in natural terrestrial perovskites (White et al., 1985; Hu et al., 1992). Although [21] twinning has been identified in perovskite heated to high temperatures (Liebermann et al., 1990) and in several terrestrial perovskites, it is apparently poorly developed and rare in end-member perovskite (Kay and Bailey, 1957; White et al., 1985; Hu et al., 1992). The meteoritic perovskite that we studied typically shows fine-scale twinning by a 180° rotation around [121], which is in contrast to terrestrial perovskites, where (101) twins predominate.

The 180° rotation twin around [121]

The [012] zone of orthorhombic perovskite corresponds to the [111] zone of the cubic subcell and shows a strong pseudohexagonal symmetry. Figure 3 shows an experimental selected-area electron diffraction (SAED) pattern together with a schematic diffraction pattern for the [012] zone. Because of the thickness of the perovskite grains, multiple diffraction effects could not be avoided. Multiple diffraction gives rise to 0kl reflections with l = even and k = odd and h00 reflections with h = even that violate the extinction conditions for the 2, screw axis along a*. Other reflections forbidden by space group extinctions are produced by twinning on the normal to (121) (illustrated schematically in Fig. 4). The major effect of the twin operation is to produce systematic rows of diffraction spots in SAED patterns at \( \frac{1}{2} \) 0kl where k is even and l is odd (Fig. 4). Although the actual twin operation is a twofold rotation around [121], it has the appearance of a 120° rotation around [012] (the pseudocubic [111]). In finely twinned crystals, the SAED patterns show that up to three orientations of twin-related domains are generating the observed diffraction effects (Fig. 5).

Figure 6 is an HRTEM image of the interface between two twin-related domains. The (100) planes (0.54-nm periodicity in the image) meet at an angle of \( \sim 120° \). The lack of strain contrast at the boundary between twins suggests that there is minimal disruption of the structure. TEM images indicate that the boundaries between twins are irregular and complicated by overlap in thick regions of the sample (Fig. 7), although lamellar (121) twins also occur. The HRTEM images indicate that the composition plane between twins is inclined to the [012] zone axis.

The 180° rotation twin around [101]

Twins of this type are impossible to recognize in [101] SAED patterns because of the superposition of the diffraction spots (i.e., pseudomerohedral twinning). White et al. (1985) documented this type of twinning using high-
Fig. 5. SAED pattern of the [012] zone showing three orientations (subscripts 1, 2, and 3) of $a^*$ in a finely twinned region. Compare with Figs. 3 and 4.

resolution TEM images from the [101] zone axis. They observed lamellar defects parallel to the $b$ axis, which they interpreted as the composition plane between two twin domains. We found that twinning by a rotation of 180° around [01] can also be identified from zone axes other than [101]. For example, SAED patterns from [100] contain 0k0 reflections with $k$: odd and 0kl reflections with $k$: odd and $l$: even; these are forbidden by space group extinctions (specifically, they violate the extinctions for the 2, screw axis along $b^*$ and the $n$ glide). These reflections do not result from multiple diffraction; however, the reflections can be generated if a twin operation occurs such that [001] and [100] zones are intergrown and in a twin relationship. The composite SAED pattern that results from a crystal that has undergone this type of twinning is shown schematically in Figure 8. In the experimental SAED pattern it should be noted that [001] and [100] are not exactly coincident (as shown by the asymmetrical distribution of diffraction intensities around the central spot), but they are displaced from one another by $-0.5\degree$. The [100] zone of orthorhombic perovskite is equivalent to the [110] zone in the pseudocubic cell.

HRTEM images from [100] of perovskite show strong (011) lattice fringes (0.44 nm) and a 0.38-nm (020) spacing along $b$ (Fig. 9). HRTEM images from the [001] zone contain regions with a 0.76-nm periodicity along $b$ (Fig. 9). Optical diffraction patterns indicate an intergrowth of [100] and [001] twin domains. The twin boundaries are abrupt but irregular, indicating that the composition plane is a higher order plane or a composite of several interfaces. We have also observed rare lamellar twins with (010) as the composition plane.

**DISCUSSION**

Perovskite in the refractory inclusions in meteorites possessed cubic symmetry at the high temperatures ($\sim 1650$-$1500 \text{ K}$) estimated for its formation (Grossman and Larimer, 1974). On cooling, perovskite undergoes a displacive phase transition from high symmetry (cubic) to lower symmetry orthorhombic. The fact that twinning on the normal to (121) is so seldom observed in terrestrial end-member perovskite may be related to the temperature of formation, the rapidity of quenching, and the rarity of end-member perovskite in terrestrial rocks. The majority of terrestrial rocks that contain perovskite formed at temperatures below the cubic-orthorhombic transition temperature. For the few occurrences where the temperatures exceeded the transition temperature, the cooling rates were slow enough to destroy the (121) twins by annealing. In order to test this hypothesis, we performed experiments using synthetic perovskite heated to high temperature, followed by variable quench rates. Our cooling-rate experiments are semiquantitative but indicate that (121) twins are common only in the fast cooling-rate experiments ($\geq 50 \text{ °C/min}$), whereas in the slow cooling-rate experiments ($\leq 50 \text{ °C/min}$), (101) twins predominate. A similar result was obtained in experiments by Wang et al. (1992) on terrestrial perovskite, which showed that (121) twins were dominant only in crystals quenched from 1693 K. If these experiments can be directly compared with the meteoritic perovskite, the results indicate that the meteoritic perovskite displaying (121) twins was not only heated to high temperatures ($> 1573 \text{ K}$) but was also quenched rapidly.

Twinning in perovskite can also result from deformation processes, and many CAIs show petrographic evidence for deformation (mainly kink bands in gehlenite).
Fig. 7. HRTEM image of (121) twins viewed down [012]. Regions I and I' are individual twins separated by region II, where they overlap. Insets are optical diffraction patterns showing the orientation of a* in each region.

However, several studies have shown that the deformation of perovskite results in the formation of predominantly (101) twins (Doukhan and Doukhan, 1986; Wang et al., 1992). Thus, we conclude that the microtwinning results from the unusual thermal history of these perovskite samples. The microtwinning and, in particular, the (121) twins probably formed during crystal growth in the stability field of cubic perovskite, or during the transition from cubic to lower symmetry on cooling.

The constraints of flash heating, imposed by petrographic and trace-element data (Wark et al., 1988), coupled with rapid cooling deduced from the cooling-rate experiments, place limits on the processes involved in the

Fig. 8. Schematic and selected-area electron diffraction (SAED) patterns for the [100] zone (I) and [001] zone (I') of perovskite. Examples of the reflections from the [001] zone are indicated by arrows. Combining patterns I and I' generates pattern II, which corresponds directly to the experimental SAED pattern.
formation of refractory rims on CAIs. Murrell and Burnett (1987) summarized potential mechanisms for the formation of refractory rims including formation by (1) deceleration heating in parent body atmospheres, (2) deceleration heating in nonuniform gas densities in the solar nebula, (3) flash heating during transit through nebular hot spots, (4) differential sublimation of CAI melts, (5) direct condensation, and (6) recondensation of vaporized material. Option 4 can be eliminated because crystallization times are so long for molten CAIs (<10^6 s, Stolper and Paque, 1986) that significant annealing of the perovskite is to be expected. Options 5 and 6 invoke condensation processes and also have difficulties accounting for fast cooling because of the evidence for a continuous series of gas-solid reactions extending down to ~400 K in altered CAIs (Hashimoto and Grossman, 1987; Keller and Buseck, 1991). Options 1–3 satisfy the criteria for flash heating and cooling, but options 2 and 3 should produce rim sequences of varying thicknesses, depending on the size of the hot spots or gas density fluctuations, whereas the petrographic evidence indicates that rim sequences are generally of relatively constant thickness. Thus, of these six options, we believe from crystallographic and petrographic observations that option 1 best satisfies the criteria. An additional possibility not considered by Murrell and Burnett is that these refractory rims could result from primordial lightning in the solar nebula. It has been shown that lightning can provide the requisite flash heating and also has the characteristic of rapid cooling (Eisenhour and Buseck, 1993), but experiments in appropriate starting materials are required to evaluate this process fully.

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