A simple variant selection in stress-driven martensitic transformation

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The study of orientation variant selection helps to reveal the mechanism and dynamic process of martensitic transformations driven by temperature or pressure/stress. This is challenging due to the multiple variants which may coexist. While effects of temperature and microstructure in many martensitic transformations have been studied in detail, effects of stress and pressure are much less understood. Here, an in situ variant selection study of Mn\(_2\)O\(_3\) across the cubic-to-orthorhombic martensitic transformation explores orientation variants at pressures up to 51.5 GPa and stresses up to 5.5 GPa, using diamond anvil cells in radial geometry with synchrotron X-ray diffraction. The diamonds not only exert pressure but also impose stress and cause plastic deformation and texture development. The crystal orientation changes were followed in situ and a \(\{110\}_c\), \(\langle 100\rangle\), \(\{010\}_c\) relationship was observed. Only the \(\{110\}_c\) plane perpendicular to the stress direction was selected to become \(\{100\}_c\), resulting in a very strong texture of the orthorhombic phase. Contrary to most other martensitic transformations, this study reveals a clear and simple variant selection that is attributed to structural distortions under pressure and stress.

Significance

Variant selection plays an important role during martensitic transformations in both metals and oxides. Due to its great effects on the crystallographic texture, it has received a great deal of attention in fields of physics, material science, and even Earth science. Previously, most studies focused on transitions in metals induced by temperature. Here, we investigate more complex oxides structures during the pressure/stress-driven martensitic transformation and find a very simple variant selection in cubic/orthorhombic Mn\(_2\)O\(_3\). The high-pressure orthorhombic phase inherits texture from the low-pressure cubic phase. Only one of the six cubic \(\{110\}\) planes becomes the orthorhombic \(\{100\}\) plane: the one perpendicular to the compression direction. This will become a reference to demonstrate the variant selection behavior under high pressure.

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(20, 30–33), and investigated the texture and lattice strain evolution in situ as well. The phase transitions in sesquioxide compounds (M₂O₃, M = Fe, Mn, Al, Cr, Ti, In, etc.) are of great interest for materials science because of unique physical properties (34) as well as for geophysics due to the relevance of their high-pressure structures to deep Earth minerals (35). Crystallized in a C-type rare-earth structure (α-Mn₂O₃, space group Ia-3, mineral bixbyite) at ambient conditions, a direct transition to the postperovskite (pPV) structure (δ-Mn₂O₃, space group Cmcm) has been observed above 27 GPa (36, 37). Cubic bixbyite consists of alternating layers of less distorted and more distorted octahedra, while the crystal structure of the pPV phase consists of alternating layers of octahedral and bicapped trigonal prisms (Fig. 1). This could explain why Mn₂O₃ transformed into a pPV type directly under high pressure instead of following the phase transitions found in other sesquioxide minerals (36) and also suggests a martensitic nature of this phase transition. Cubic α-Mn₂O₃ is a highly symmetric structure, while the high-pressure pPV phase is in a lower-symmetry orthorhombic structure, which makes it a good example to investigate variant selection under stress.

Results and Discussion

We deformed the sample of Mn₂O₃ powder in a DAC in compression from ambient pressure to 51.5 GPa at room temperature and observed the texture evolution through the phase transition in situ using r-DAC XRD (SI Appendix, Fig. S1). Platinum was used as a pressure calibrant. Diffraction data were analyzed with the Rietveld refinement method (38) as implemented in the software package MAUD (39). Fig. 2 shows unrolled diffraction images of Mn₂O₃ at various pressures. The curved shape of the diffraction peak position as a function of azimuth represents the crystal lattice strain and is caused by the compressive stress generated in the nonhydrostatic environment. The systematic peak intensity variation with azimuth reflects the lattice preferred orientation (texture) of the phases in the sample. At low pressure there is a pure cubic phase with large lattice strain and strong texture appearing at 10.3 GPa (Fig. 2 A and B). At 24.1 GPa, several extra diffraction peaks (represented by red arrows in C) indicate the presence of the high-pressure phase. Green arrows on the right side indicate the compression direction. Unit cell parameters (G) and molar volume (H) of cubic and orthorhombic-type Mn₂O₃ under pressure. The dashed lines fit of the Birch–Murnaghan equation of state with K₁' fixed to be 4. (I) t/G as a function of pressure. The low initial t/G value of orthorhombic phase is a consequence of the large volume collapse during the phase transition.
arrows, Fig. 2C) appear, indicating the start of the phase transition. The high-pressure peaks initially show no lattice strain (straight lines) and then the strain increases with pressure, as shown in Fig. 2D at 28.5 GPa. Peaks of the low-pressure phase remain to 31.6 GPa, after which the phase transition is complete. This is consistent with the results reported by Yamanaka et al. (40) and Santillán et al. (36). The pressure was then continuously increased to 51.5 GPa, but no significant changes of diffraction patterns were observed (Fig. 2E). After decompression, the quenched sample returned to the low-pressure cubic phase with the same original lattice preferred orientation, indicating that this phase transformation is reversible (Fig. 2F).

Lattice parameters and lattice strain of both cubic and orthorhombic structures were extracted from the refinement results (Fig. 2 G–I). The lattice parameters and volume of the low-pressure phase in our measurement are comparable with Yamanaka et al. (40) and a bit higher than that of Santillán et al. (36). This difference might be caused by different pressure media. In the latter work, Ar was used as a pressure medium, whereas the former used a methanol-ethanol mixture and we used no pressure medium. The same effect has also been observed in HoVO$_3$ (41) and SmVO$_4$ (42), where lattice parameters are larger and also showed more obvious scatter when the experimental conditions induced large deviatoric stresses.

The molar volume decreases by 10% across the phase transition between 24.1 and 31.6 GPa (Fig. 2H). A large pressure-induced volume collapse from 10 to 22% has previously been reported in transition-metal compounds like Fe$_3$O$_4$ (43), Fe$_2$O$_3$ (44), and MnS$_2$ (45). Both experiments and calculations have proved that the volume collapse is driven by a spin-state transition. At high pressure a high spin state is unstable compared with the low spin state. $\alpha$-Mn$_3$O$_4$ displays a high spin state as estimated by calculations (46) and neutron diffraction (47, 48). Therefore, it is reasonable to suggest that the large volume collapse in Mn$_2$O$_3$ during the phase transition is caused by the spin-state change under high pressure.

Fig. 2f displays the stress-bulk modulus ratio $t/G$ as a function of pressure for both the cubic and pPv phases of Mn$_3$O$_4$. This value representing the average lattice strain was obtained using the Triaxial Stress Isotropic E strain model implemented in MAUD and used for a first evaluation of the stress level in physically deforming aggregates (52). In addition, the stress was also estimated from the platinum foil according to previous reports (49, 50). In the cubic phase, the $t/G$ value first increases strongly with pressure and then remains almost stable in a range of pressure between 15.8 and 21.8 GPa, before it begins to decrease with the appearance of the high-pressure phase. This decrease might imply that grains with higher strain transformed to orthorhombic phase first. Also, in r-DAC experiments there are stress gradients between the center and the periphery of the sample. In the high-pressure phase, the initial lattice strain is almost zero but then it increases slowly with pressure. The much smaller lattice strain of the high-pressure phase compared with the C-type phase have also been observed in the unrolled diffraction patterns. In the two-phase mixture state (Fig. 2 C and D), it is quite clear that for the pPv phase diffraction peak positions show minimal dependence on the azimuthal angle compared with those of the low-pressure phase. There is almost no lattice strain in the high-pressure phase at the beginning of the phase transition. The large volume collapse during the phase transition could be responsible for this lattice strain release and also causes the lattice strain of the low-pressure cubic phase to decrease.

The preferred orientation distributions were calculated by imposing axial symmetry about the compression direction. Inverse pole figures (IPFs), which describe the orientation of the compression axis relative to crystal coordinates, were obtained for both phases of Mn$_3$O$_4$ (Fig. 3A). Pole densities are represented in multiples of a random distribution (m.r.d.), where 1 m.r.d. corresponds to no preferred orientation. The starting material (0.6 GPa) was initially randomly oriented. Above 10.3 GPa ($t/G = 0.0298, t \sim 2$ GPa) the low-pressure cubic phase displayed a 110 texture, the strength increasing with pressure (and stress) and reaching its largest value of $3.2$ m.r.d. at about 20.2 GPa ($t/G = 0.0325, t \sim 3.5$ GPa). This 110 texture is a typical compression texture for fcc metals that deform by [111] (110) slip (51). Above the phase transition (24.1 GPa, $t \sim 4$ GPa), the strength of the 110 texture began to decrease while the high-pressure phase developed a very strong texture at 100 with an intensity of 11.3 m.r.d. At this pressure, the average lattice strain of the cubic phase decreased to 0.026, while the orthorhombic phase displayed a much smaller lattice strain of about 0.0003 due to the phase transition and consequent volume collapse. The 100 texture became slightly stronger with further compression, increasing to 14.6 m.r.d. at 51.5 GPa ($t/G = 0.0135, t \sim 5.5$ GPa). The texture change during the phase transition suggests a relationship of {110} // {100}, where {110} are the lattice planes perpendicular to the stress direction. From unrolled diffraction images (Fig. 2A), it can be seen that during the phase transition, diffraction peak (400) of the cubic phase transferred to (040) of the orthorhombic phase, suggesting a relationship of (100) // [010]. These two parallel relationships define the full orientation relation across the phase transition, although there might be some ambiguity due to the axial symmetry of the compression.
experiment. The texture we obtained here for the Pv phase is quite different from that reported for Mn$_2$O$_3$ experiments using Ar as a pressure medium (36). In that work, the Pv phase showed a weak lattice preferred orientation of the (010) plane perpendicular to the loading axis of the DAC, which changed to (100) and (110) after annealing. It should be noted that an axial DAC geometry was used in that study, which is not ideal for the investigation of textures.

The preferred orientation in both cubic and orthorhombic phases can be compared with pole figures (PFs) (Fig. 3 A and C) projected along the compression direction. They have axial symmetry to conform to the geometry of the deformation experiment. For cubic (110), two maxima are observed: one parallel to the compression direction at η = 0° and a weaker concentration at η ~ 60°. It is clear that only one (110) plane is in the center (compression direction) while four planes are at around 60° and one at 90°. For the orthorhombic phase (Fig. 3C), there is only one maximum at the center of the 100 PF, indicating all (100) lattice planes are preferentially oriented perpendicular to the compression direction. Due to the multiplicity of cubic symmetry, pole densities are never as strong as single symmetry equivalent variants of the compression direction for orthorhombic Mn$_2$O$_3$. The type-III IPF in Fig. 4D (corresponding to cubic (110) planes shown in red in Fig. 3B) has a maximum indicating that planes with Miller indices close to (153) are oriented approximately normal to the compression direction.

Our study provides an example of almost-perfect variant selection during a phase transition under stress. For Mn$_2$O$_3$, the cubic (110) and orthorhombic (100) lattice planes have many similarities in atomic arrangements as clearly shown in Fig. 1 C and D. Viewed along [110], the cubic phase consists of alternating layers of less distorted and more distorted octahedra. In the orthorhombic phase, the volume collapse associated with the transition produces a more compact arrangement with alternating layers of octahedral and bicapped trigonal prisms along (100). This explains the texture transfer of (110), to (100), during the phase transition. In addition, the axial stress applied in our experiments will lead to stronger strain of lattice planes perpendicular to the compression direction than others. Thus, these planes will more easily transfer to the high-pressure phase and consequently result in the variant selection during the phase transition.

**Materials and Methods**

Mn$_2$O$_3$ powder was purchased from Sigma-Aldrich. The high-pressure r-XRD was conducted at BL10XU of Spring 8, Japan. A panoramic-type DAC with large openings was used to allow r-XRD (SI Appendix, Fig. S1). The sample was ground into fine powder and loaded in an X-ray-transparent boron-epoxy gasket with a hole drilled at the center and inserted into a kapton tilt, were calibrated using a CeO$_2$ standard before the experiment. The experiment was carried out at room temperature. More details about data analysis and modeling can be found in SI Appendix.

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