

Structural and mechanical properties of magnesium aluminate nanoceramics under high pressure

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ABSTRACT

Nanoceramics may have different structural and physical properties compared to their coarse-grained counterparts. Here, we report the high-pressure study of micro- and nano-crystalline MgAl₂O₄ in order to examine the effect of particle size on the structural stability. A reversible pressure-induced phase transition (cubic to tetragonal) is observed in MgAl₂O₄ nanocrystals under non-hydrostatic pressure at room temperature, in contrast to the previously reported structural transition of MgAl₂O₄ at high pressure and high temperature. It is also found that the compressed MgAl₂O₄ microcrystals do not fracture further below 60 nm, suggesting a plastic deformation mechanism transition. MgAl₂O₄ with a grain size above ~60 nm exhibits normal cracking behaviors, but shows metal-like plastic deformation behaviors below this critical size. It is implied that combined ductility and strength can be achieved in nanoceramic MgAl₂O₄.

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MgAl₂O₄ has a cubic crystal structure with the space group of Fd-3m at the ambient condition.¹ It is considered as an important material from material physics to geoscience due to its high melting point, good mechanical properties, high chemical stability, and excellent optical properties.² MgAl₂O₄ is also a common component of low-pressure peridotite xenoliths, which is a significant mineral for aluminum cations in the shallow upper mantle. Therefore, it is necessary to study its structural and mechanical properties under different conditions. Phase transitions in MgAl₂O₄ have been extensively investigated in the geoscience community using diamond-anvil cell (DAC) and multi-anvil apparatus.^{3–8} Iriune *et al.* reported a denser phase form of MgAl₂O₄ at a pressure of higher than 40 GPa.³ MgAl₂O₄ dissociates into the mixture of MgO and

Al₂O₃ at a temperature of 1200–1600 °C under a pressure of 15–16 GPa and again reacts to the CaFe₂O₄-type structure MgAl₂O₄ at 25–27 GPa and finally forms to the CaTi₂O₄-type structure phase above 40 GPa and 2000–3000 °C.^{7,8} In another investigation, ε-MgAl₂O₄ was mentioned to form at about 1000 °C and above 25 GPa into a high-density phase.⁹ Theoretical calculations upon phase transitions of MgAl₂O₄ have also been reported.^{10,11} We note that these phase transitions in MgAl₂O₄ took place under simultaneous high-pressure and high temperature conditions. However, materials may exhibit different properties under a non-hydrostatic pressure compared with those under a quasi-hydrostatic pressure, and the behavior of MgAl₂O₄ under a highly non-hydrostatic pressure at room temperature remains unknown to date.

The mechanical performance of MgAl_2O_4 ceramic is crucial, as well as its structural properties. Metals usually plastically deform before fracture, which is mainly due to the nucleation and motion of the dislocations.¹² Unlike metals, ceramics usually form cracks and then expand under stress, so most ceramics are hard and strong, but very brittle, which limits many potential applications. Making strong and ductile ceramics is a long-term pursuit of scientists and engineers, and a better understanding of the deformation behavior of ceramics under service environment is clearly beneficial. Some researchers proposed that brittle ceramics may exhibit ductility like metals in nanoscale due to the increased diffusivities, as the dislocation activities were strongly suppressed by cracking.¹³ However, there may exist various reasons to affect the ductility of ceramics. The deformation mechanisms of nanocrystalline ceramics are still unclear. As an important geological material, the mechanical properties and deformation mechanisms of MgAl_2O_4 need to be better understood, which is helpful in both geoscience and physics. In this Letter, the phase transition and cracking effect of MgAl_2O_4 powders, and its possible plastic deformation mechanism, were discussed under non-hydrostatic compression.

We conducted DAC X-ray diffraction (XRD) measurements of micro- and nano- MgAl_2O_4 . In these experiments, MgAl_2O_4 powders, with average particle sizes of $0.5 \mu\text{m}$ and 100 nm , were compressed to $\sim 50 \text{ GPa}$ at room temperature in the diamond anvil cells. The samples were loaded into a laser-drilled $\sim 100 \mu\text{m}$ diameter hole of stainless-steel gasket. The culets of diamonds were $300 \mu\text{m}$. The powder sample was sandwiched within the two opposite anvils and the gasket. Since no pressure-transmitting medium was used, a non-hydrostatic pressure environment was established in the sample for detecting the plastic deformation behaviors. A micro-sized ruby ball was used as a pressure calibrant.¹⁴

The *in situ* angle-dispersive high-pressure XRD measurements on both micro- and nano-sized MgAl_2O_4 were conducted at beamline 12.2.2 of the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory). The synchrotron monochromatic X-ray beam was focused to $\sim 30 \times 30 \mu\text{m}^2$ with a wavelength of 0.4959 \AA (X-ray energy $E = 25 \text{ keV}$). The X-ray diffraction patterns were collected at pressure intervals of several GPa by the image plate Mar345 with the resolution of $100 \mu\text{m}/\text{pixel}$. Cerium dioxide (CeO_2) powder was employed to calibrate the distance between the sample and the detector. Seven diffraction peaks for MgAl_2O_4 [(111), (220), (311), (400), (422), (511), and (440)] were taken into account in our analysis.

We also performed the scanning electron microscope (SEM) and transmission electron microscope (TEM) measurements to characterize the raw samples and the high-pressure-recovered samples. The electron voltage for the SEM characterization is 5 kV . Focused ion beam (FIB) machine (FEI Versa 3D) with an ion beam voltage of 30 kV and a current of 7 nA (gradually decreasing to 3 nA , 0.5 nA , and 100 pA , etc.) was utilized for the TEM sample preparation. For polishing the thin foils, we changed the beam energy to 2 kV and 48 pA . High resolution TEM (HRTEM) observations were performed on an aberration-corrected transmission electron microscopy FEI Titan G2 60–300 equipped with high angle annular dark field (HAADF) and bright field (BF) detectors. The operation voltage was 300 kV .

XRD patterns of MgAl_2O_4 nanocrystals under non-hydrostatic pressures are shown in Fig. 1. The XRD peak profiles of bulk MgAl_2O_4 are similar to those of nano- MgAl_2O_4 . As the pressure is increased, the diffraction peaks shift to higher 2θ angles as the unit cell of samples

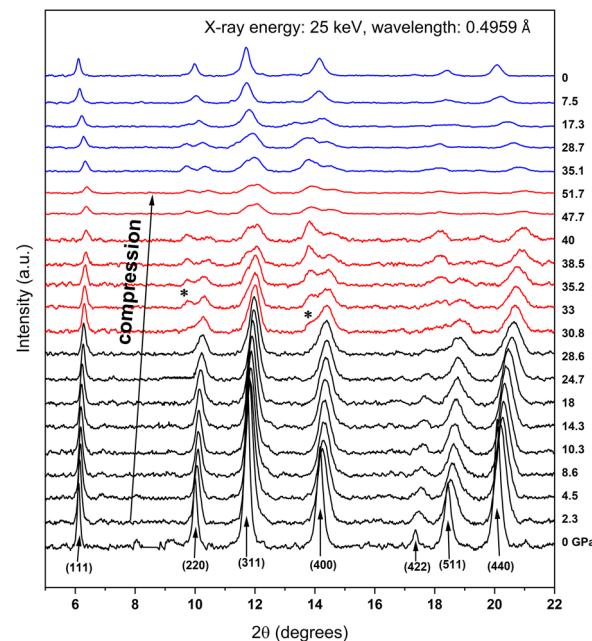


FIG. 1. The XRD patterns of nano- MgAl_2O_4 taken at various pressures. Black and red patterns represent the patterns taken during the compression (increasing pressure) process, whereas blue curves indicate the patterns taken during the decompression (decreasing pressure). Asterisks mark the new diffraction peaks from the high-pressure phase of MgAl_2O_4 .

contract under compression. In the compression of nano- MgAl_2O_4 , the peak (200) and the peak (400) split into two obvious peaks at 33.0 and 30.6 GPa , respectively. The emerging peaks labeled with asterisks in Fig. 1, obviously not from a steel gasket or ruby, possibly come from the pressure-induced new phase of MgAl_2O_4 . There are three known polymorph phases of MgAl_2O_4 , CaFe_2O_4 -type ($Pnam$ space group), CaTi_2O_4 -type ($Bbmm$ space group), and another HP phase ($Bbmm$ space group), which were reported to form at high temperature and high-pressure conditions.^{3,8,15} Interestingly, no phase transitions in bulk MgAl_2O_4 were previously reported at room temperature up to 65 GPa under a quasi-hydrostatic pressure (4:1 mixture of methanol-ethanol as the pressure transmitting medium).¹

Our attempts to fit the XRD patterns above 30 GPa using the known high-pressure polymorphs of MgAl_2O_4 mentioned above did not lead to a satisfactory fit. Therefore, we tried to index the diffraction patterns. It follows that the new phase of nano- MgAl_2O_4 induced by pressure has a primitive tetragonal lattice. After searching through the database on ternary oxides, we found that the diffraction patterns above 33 GPa can be fitted with the TiZn_2O_4 -type structure ($P4_22$ space group), as shown in Fig. 2(c). This indicates that the cubic nano- MgAl_2O_4 possibly transforms into a tetragonal TiZn_2O_4 -type structure above $\sim 33 \text{ GPa}$ under a non-hydrostatic condition. The crystal structures before and after the phase transition are illustrated in Figs. 2(a) and 2(b). The fitted lattice constants of the high-pressure tetragonal structure at 50 GPa are $8.7548(5) \text{ \AA}$, $8.7548(5) \text{ \AA}$, and $4.3150(9) \text{ \AA}$, respectively. The phase transition of nano- and bulk MgAl_2O_4 is quite different from Ref. 1, possibly due to the use of a no pressure medium in this work. The initial diffraction peaks return to the initial features

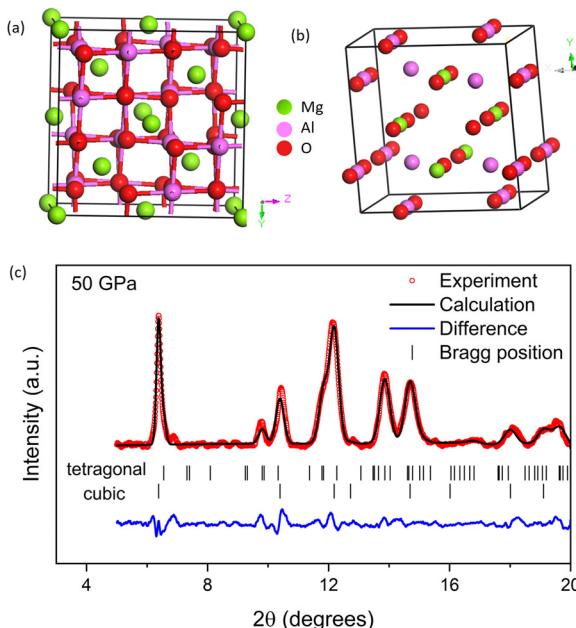


FIG. 2. The phase identification of MgAl_2O_4 microcrystals at 50 GPa. (a) The initial cubic structure of MgAl_2O_4 . (b) The possible high-pressure phase of MgAl_2O_4 under a non-hydrostatic condition. (c) Representative refinement pattern at 50 GPa.

upon decompression to ambient pressure, which indicates a reversible phase transition. The diffraction peaks of the quenched nano-sample are broadened due to the smaller grain size.

The compressibility of materials usually has grain size dependence,^{16–21} which are related to nucleation, large volume collapse, and instability of a new high-pressure phase.^{16,17} In our experiments, the bulk moduli (K_0) of micro and nano- MgAl_2O_4 at a non-hydrostatic pressure are fitted to be 312.5 ± 5.6 GPa and 318.6 ± 3.5 GPa, respectively. These values are different from those measured in a quasi-hydrostatic pressure [e.g., 196 GPa in bulk MgAl_2O_4 (Ref. 1) and 285 GPa in nano- MgAl_2O_4 (Ref. 22)]. The hardness of materials is known to increase with the bulk modulus.²³ Diamond is the hardest natural material on the Earth with a bulk modulus of about 444 GPa.²⁴ Based on our experiments, the bulk modulus of nano- MgAl_2O_4 is as high as 300 gigapascals, which hints its high hardness. Interestingly, we found that the bulk moduli of micro- and nano- MgAl_2O_4 are similar. One possibility to account for this behavior is that both micro- and nano- MgAl_2O_4 might undergo similar grain refinement under a non-hydrostatic pressure. MgAl_2O_4 is a brittle ceramic in which the coarse grains will crack into smaller grains under shear stress. In this case, the deviatoric stress that presents in the sample chamber at high pressure due to a highly non-hydrostatic condition would reduce the grain sizes of both micro- and nano-sized MgAl_2O_4 into similar grain sizes, which in turn lead to the comparable bulk moduli.

To examine the final grain size of both micro- and nano-sized samples at high pressure, we analyzed the full width at half maximum (FWHM) of the XRD peaks. Pressure dependence of the peak broadening of both sized MgAl_2O_4 under a non-hydrostatic environment is shown in Fig. 3. The FWHM of four selected diffraction peaks was analyzed, including peaks (111), (220), (311), and (440). The FWHM

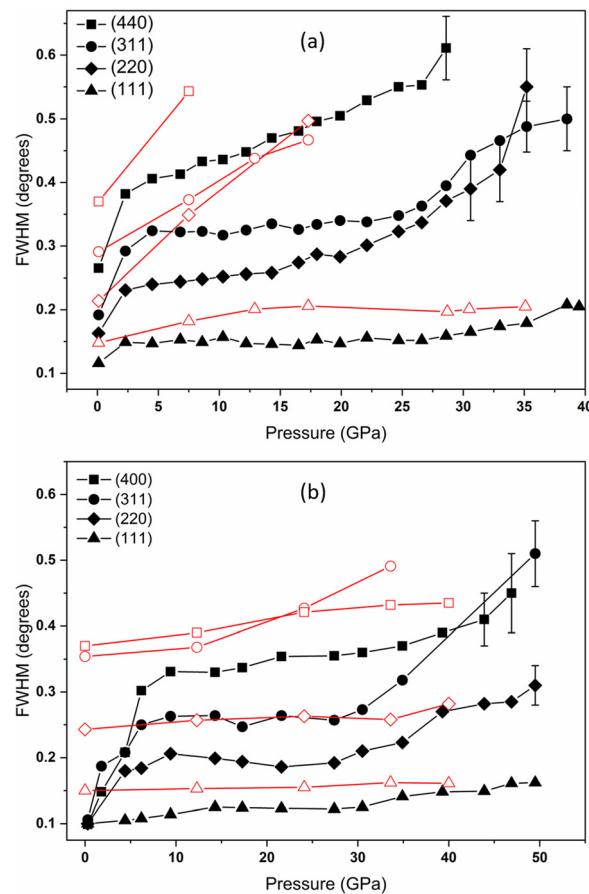


FIG. 3. The pressure dependence of the FWHM values of the four selected diffraction planes of (a) nano- and (b) micro- MgAl_2O_4 , under a non-hydrostatic stress environment. Solid black and open red symbols represent the non-hydrostatic compression and decompression processes, respectively. Vertical lines represent the error bars to the data.

value of peak (440) is the largest, while peak (111) has the smallest width. The broadening of diffraction peaks mainly results from the instrumental broadening, size refinement, and residual stresses in the sample. The broadening effect from the instrument can be neglected since the same instrument was utilized in our experiments. For bulk MgAl_2O_4 [Fig. 3(b)], the values of FWHM rapidly increase with pressures up to 10 GPa, where the large grains break into smaller grains. Above 25 GPa, the FWHM further increases a lot, which is mainly due to the stress effects. During the decompression process, the FWHM values decrease with the decreasing pressure. After the sample is fully decompressed to an ambient pressure, the FWHM values are found to be larger than the initial values, which arises from the grain diminution associated with the pressure-induced cracking. The final grain size of the quenched samples can be estimated using the Scherrer equation $\tau = \frac{K\lambda}{\beta \cos \theta}$, where τ is the mean size of the grains and K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9 but varies with the actual shape of the crystallite; λ is the X-ray wavelength, β is the value of FWHM, and θ is the Bragg diffraction angle. The similarity of the FWHM values

after decompression suggests that both quenched samples could have similar grain sizes.

To accurately determine the final grain sizes of these two samples quenched from high pressure, we conducted the SEM and TEM measurements. The obtained statistical distributions are presented in Fig. 4. The average grain sizes of the quenched micro- and nano- MgAl_2O_4 powders are similar, e.g., 63 nm and 60 nm, respectively. The compressed MgAl_2O_4 microcrystals (or nanocrystals with a grain size above ~ 60 nm) cease fracturing further less than 60 nm, indicating that cracking is not the major deformation process below this limited size. A different plastic deformation mechanism may occur.

Some materials have been investigated to possess both high strength (hardness) and high ductility, such as metal–ceramic nanolayered composites.^{25,26} This type of composites (TiN–Al,²⁷ TiC–Cu,²⁸ etc.) has significantly enhanced hardness, toughness, thermal resistance, etc. It has been shown that the metallic layer may induce the ductility through elastic–plastic deformation, whereas the ceramic layer contributes to the hardness until it is broken by cracks.²⁷ However, there are no reports on pure ceramics with both high strength and high ductility under highly stressed circumstance. It is acceptable that there are no dislocation activities in ceramics (suppressed by cracking), and enhanced diffusivities are devoted to the ductility of nanoceramics at high temperature.^{13,29,30} By high resolution TEM (HRTEM) measurements, we observed the existence of dislocations, stacking faults, and twinning in the nano- MgAl_2O_4 quenched from 25 GPa, as shown in Fig. 5. The dislocation lines in ceramics are much shorter than those in metals [Fig. 5(b)], because the stress required to propagate a dislocation in ceramic is very large (much higher than that in metals), and thus lots of dislocations nucleate from the interface, but do not propagate far. Crystalline defects (dislocations, stacking faults and twins, etc.) are activated in nanocrystalline MgAl_2O_4 under high pressure, which results in plastic deformation and improves the ductility of the MgAl_2O_4 nanoceramic. Previous studies also suggested that the high-pressure-induced deformation texturing in nano- MgAl_2O_4 indicates the enhancement of ductility in nanoceramics.²² Therefore, it is implied that combined ductility

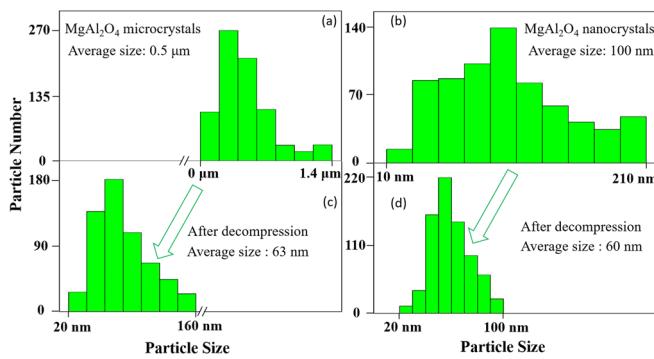


FIG. 4. Particle size distribution. (a) and (b) represent the original microcrystal MgAl_2O_4 and nanocrystal MgAl_2O_4 , while (c) and (d) are the corresponding size distribution of (a) and (b) quenched from ~ 35 GPa, respectively. The grain sizes of both micro- and nano- MgAl_2O_4 reduce after decompression process into the similar final grain sizes of around 60 nm.

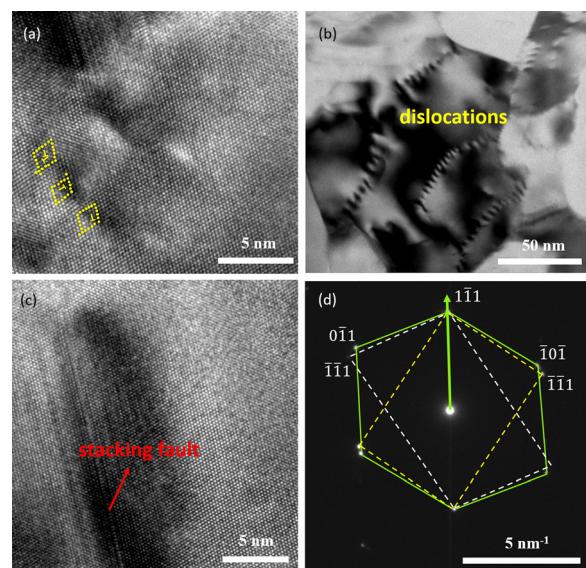


FIG. 5. TEM examinations of nano- MgAl_2O_4 quenched from ~ 25 GPa, revealing the transition of plastic deformation mechanisms from cracking to crystalline defects. Lattice dislocations (marked by yellow "T") in (a) can be observed together with short dislocation lines in (b), and a stacking fault in (c). (d) The electron diffraction pattern, in which two sets of diffraction spots indicate the present of deformation twins.

and strength can be simultaneously obtained in nanoceramic MgAl_2O_4 at an ambient temperature.

In this study, we report the structural stability of micro- and nano- MgAl_2O_4 powders under high pressure. A tetragonal pressure-induced phase transition is observed in nano- MgAl_2O_4 under a non-hydrostatic pressure. The minimum grain size of MgAl_2O_4 under high pressure due to cracking effect is about 60 nm. This critical grain size has no significant relationship with the initial grain sizes of MgAl_2O_4 , revealing a plastic deformation mechanism transition. Our TEM observations have revealed that crystal defects dominate plastic deformation (like metal behavior). Both ductility and strength can be simultaneously achieved in nanoceramic MgAl_2O_4 . These findings would pave the road for the scientific designing and industrial manufacturing of advanced ceramics.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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