DIFFRACTION STUDIES OF ORDER-DISORDER AT HIGH PRESSURES AND TEMPERATURES

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ABSTRACT

Recent developments at synchrotron X-ray beamlines now allow collection of data suitable for structure determination and Rietveld structure refinement at high pressures and temperatures on challenging materials. These include materials, such as dolomite (CaMg(CO\textsubscript{3})\textsubscript{2}) that tends to calcine at high temperatures, and Fe-containing materials, such as the spinel MgFe\textsubscript{2}O\textsubscript{4}, which tend to undergo changes in oxidation state. Careful consideration of encapsulation along with the use of radial collimation produced powder diffraction patterns virtually free of parasitic scattering from the cell in the case of large volume high-pressure experiments. These features have been used to study a number of phase transitions, especially those where superior signal-to-noise discrimination is required to distinguish weak ordering reflections. The structures adopted by dolomite, and CaSO\textsubscript{4}, anhydrite, were determined from 298 to 1466 K at high pressures. Using laser-heated diamond-anvil cells to achieve simultaneous high pressure and temperature conditions, we have observed CaSO\textsubscript{4} undergo phase transitions to the monazite-type and at highest pressure and temperature to crystallize in the barite-type structure. On cooling, the barite structure distorts, from an orthorhombic to a monoclinic lattice to produce the AgMnO\textsubscript{4}-type structure.

INTRODUCTION

Many materials of technological interest as well as those constituting the planet have the potential for cation disorder over different crystallographic sites. The entropy of disorder can drastically alter the stability of these materials to an extent that is strongly dependent on pressure and temperature [1-3] and can affect elasticity as well [4]. Constraints on models of the Earth’s interior, for example, depend critically on measurements of crystal structure, elasticity and stability at the pressure and temperature (PT) conditions relevant to the planet. The \textit{in situ} studies required to determine the effects of pressure and temperature on the crystal structure are scanty however, and trends in the thermodynamic parameters important for characterizing these systems tend to be based on comparisons of unit-cell volumes of quenched samples [1, 5]. The degree of order measured \textit{ex situ} may not be the most relevant measurement, since the degree of order may change as the sample is quenched, and may indeed be dependent on the rate of quenching, making it difficult to compare results between experimental runs and between research groups. The values obtained from quench experiments often only define boundaries to
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the stability field. We have sought to explore the possibility of more constrained and reproducible measurements, focusing on changes in crystal structure, and lately elasticity, and to make these measurements \textit{in situ} while simultaneously maintaining high PT.

The technical developments required to carry out these measurement have been pursued by a number of groups over the decade. For measurements requiring the highest possible temperature stability, over a period of days, and only moderate pressures (< 12 GPa) the large volume devices, such as the so-called Paris-Edinburgh cell [6] and DIA apparatus [7] are suitable. Increasingly both laser and internally heated diamond anvil cells are providing data suitable for the determination and refinement of crystal structure. Case studies of the dependence of order-disorder on PT for some technically challenging materials are given here.

**EXPERIMENTAL**

For crystallographic studies of site order-disorder a number of other important technical issues, apart from stability of PT while data are collected, require attention. If the order-disorder transition involves a change in space group, the appearance and disappearance of weak reflections is often the signature of the transition. In those case where there is no change in space group subtle differences in Bragg scattering need to be monitored. In order to monitor changes in short range order total scattering studies [8] are now routinely performed at ambient pressure. Some total scattering measurements are being performed on crystalline materials at high pressure though these are not yet quantitative. Many of these studies, if they are to be quantitative, require the collection of powder diffraction data, which is as “clean” as possible. This is a difficult task when collecting monochromatic data suitable for Rietveld refinement.

![Diagram](image_url)

**Fig. 1** (above) A typical cell assembly for the collection of data suitable for Rietveld refinement at beamline X17 of the NSLS. The sample (1 mm in diameter) is contained in a cell assembly consisting of boron-epoxy (BE) pressure transmitting medium, a graphite-disc heater is connected to power through Pt foil in contact with the WC anvils. NaCl is layered with sample (S) in the assembly to act as a pressure marker. Data (right) are collected at both paths A and B (the blue and red paths respectively) and the patterns subtracted, after appropriate scaling, to produce a pattern containing only diffraction from the sample (right).
while stable PT are maintained simultaneously. The use of point counters with well-collimated incident and diffracted beams will exclude much of the parasitic scattering from high-pressure cells [9]. Even at high brightness sources this requires long data collection times, practically excluding time-resolved measurements. For this and other reasons practically all data used in structure refinement studies is now collected using area detectors, imaging plates (IP) or charge coupled devices (CCD).

The use of area detectors usually precludes the use of diffracted beam collimation and one must then resort to post-experimental data massaging techniques to remove scattering from the high-pressure cell assembly [10, 11]. For example, an IP system is interfaced to the SAM-85 installation at the National Synchrotron Light Source (NSLS) for the collection of in situ X-ray powder diffraction data suitable for Rietveld analysis. In order to minimize the effects of parasitic scattering a disk-type heater, rather than the usual and more reliable graphite sleeve, is used to remove this element from the beam path (Fig. 1). Diffraction effects resulting from the boron-epoxy (BE) pressure-transmitting medium are removed by subtraction of a “blank” spectrum of BE from the powder-diffraction pattern taken through both sample and cell material (Fig. 1).

Although pattern-subtraction techniques [7, 10] have proven successful, they may not always be suitable. When measurement of the diffuse elastic contribution to the pattern is important, subtraction techniques may eliminate this component. In many cases of order-disorder studies more and not fewer components need to be added to the cell assembly (Fig. 1) as the reducing environment of BE and the lack of containment fail to prevent decomposition in the case of iron-containing samples and those prone to calcination at high temperatures. In this case, containing the sample in a noble metal, such as gold, is desirable. This then requires diffraction to be performed at a high-energy beamline and makes pattern-subtraction techniques difficult as the cell assembly becomes more complex. In these cases the use of a radial collimator is recommended [12] (Fig. 2)

Fig. 2. Radial collimators aligned with sample position at Ω. The front set of slits is 100μm and the back-slits are 300μm in width, with 100 and 300 μm gaps, respectively, in the Ta metal in which they are machined. The slits are oscillated about the vertical axis to collect a complete powder diffraction pattern.
Fig. 3. Experimental set-up at ID-30 ESRF for the collection of data at high PT from the Large volume press. A set of radial slits (Fig. 2) are aligned between the sample and IP detector to minimize parasitic scattering from the cell assembly. The two-dimensional detector images were integrated to produce the conventional one-dimensional 2θ-intensity patterns using Fit2D [13].

CASE STUDY 1: DOLOMITE

Phase relations in the geologically important (Ca,Mg,Fe)CO₃ system are dominated by interactions among the metal-site disordered calcite-structure (space group \( \text{R}3 \)) and the ordered dolomite structure (space group \( \text{R}3 \_c \)) where Ca and (Mg, Fe) order into sites in alternating layers [14]. These phases make up the majority of shallow limestones and dolostones and are the principal components of deep-seated carbonatites. Recent results suggest dolomite may be stabilized to high pressures [15] through phase transitions, and at high PT due to cation disorder [1, 3, 16]. Together, the results obtained thus far for dolomite suggest it may be the stable carbonate phase in the mantle [1, 2, 14-24].

CRYSTAL STRUCTURE OF DOLOMITE AT 3 GPa

Several studies have attempted to define the state of cation order in dolomite as a function of P and T, mostly from quench experiments. Our recent experiments at high PT (Fig. 3) avoid the problems inherent in quench experiments by determining the structure of dolomite and order parameter \( s \) at 3 GPa and from 298 to 1466 K using the \textit{in situ} capabilities at the ID30 beamline at the ESRF [3, 25]. We developed a large volume cell assembly to suppress calcination and collected synchrotron X-ray diffraction data to investigate the state of disorder at high PT. This
The cell consisted of a gold capsule containing the dolomite sample and a BN insulating sleeve. Since only moderate pressures were required this allowed us to use a 2 mm diameter sample, which allowed collection of diffraction data free of parasitic scattering from the cell assembly.

The order parameter, $s = 2x_{Ca} - 1$, varies from $s = 1$ (where $x_{Ca} = 1$) for a completely ordered dolomite to $s = 0$ (where $x_{Ca} = 0.5$) for a completely disordered dolomite. On heating, there is no measured change in $s$ until $1234\,\text{K}$ ($s = 0.83(1)$). At this temperature $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ cations exchange and disorder increases smoothly to $T = 1466\,\text{K}$ ($s = 0.12(5)$). We were unable to observe the complete disappearance of the (015) ordering reflection (Fig. 4) at even the highest temperatures attained in these experiments.

A comparison of our results with those of other studies is given in Fig. 5. Here the results of full Rietveld refinement are compared to the determination of $s$ using the ratio of the ordering reflection and the nearby (006) which is reported to be relatively insensitive to ordering. Several lessons emerge from this comparison. The value of $s$ obtained from quench experiments determining the order parameter using the ratio of the (015)/(006) reflections (Fig. 4; blue diamonds in Fig. 5) underestimate both the rate at which disordering occurs and the temperature at which complete disorder is achieved. This is surprising since consistency between the results in Fig. 5 would imply more disorder is quenched into one of the samples. Quench experiments that determine $s$ from full structure refinement (red squares) are consistent with the in situ determination. Secondly, estimations of the state of order based on the ratio method for data determined in situ (triangles in Fig. 5) are not completely consistent with the results of full Rietveld refinement (green squares) at high values of $s$ but do give a reasonable estimate of the state of order as complete disorder is approached. This later point is particularly gratifying since estimating the state of order while measuring physical properties such as sound velocities is not always easy.

Fig. 4. Decrease in intensity of the ordering reflection (015), which is still present at the highest temperatures studied, as $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ disorder over available sites in dolomite.

Fig. 5. Comparison of change in order parameter ($s$) as a function of temperature at 3 GPa, determined from the ratio method (Fig. 4) from quench (Luth) and in situ (this study) experiments as well as from full Rietveld refinement.
While *simultaneous* collection of data suitable for full structure refinement is desirable, a reliable estimate determined from an intensity ratio may serve to link separate experiments to determine structure and physical properties.

The molar free energy describing the $R \bar{3} \rightleftharpoons R \bar{3}c$ transition in dolomite follows a modified Bragg-Williams thermodynamic model and this has recently been published [3]. The model provides an excellent agreement with our experimental data (Fig. 5) and the maximum enthalpy of disorder $\sim 14$ kJ mol$^{-1}$, agrees with published calorimetric data [22]. The thermodynamic description derived from these data qualitatively reproduces the aragonite + magnesite $\rightleftharpoons$ dolomite reaction boundary [1, 2]. It also suggests a pressure dependence of the state of order and further studies of this pressure dependence are planned. Further, a number of other compositions crystallize in the dolomite structure, with pressure reported in some case to favor ordering and in others to favor disordering [21, 26].

**CASE STUDY 2: MgFe$_2$O$_4$ SPINEL**

Because of their chemical and structural simplicity, their geological and technological importance, and the dependence of their properties on the state of order, the spinels are the subject of numerous experimental and theoretical investigations concentrating on structure. We have recently completed an *in situ* high PT experimental study of the inverse magnesioferrite spinel, MgFe$_2$O$_4$, complementing the recently reported study of a normal spinel, MgAl$_2$O$_4$, carried out using neutron diffraction [27].

Spinels have the general formula AB$_2$O$_4$. The structure consists of tetrahedrally coordinated cations at 8a ($1/8$, $1/8$, $1/8$), octahedrally coordinated cations at 16d ($1/2$, $1/2$, $1/2$), and O atoms on the body diagonals of a cube at 32e ($u$, $u$, $u$), where $u$ is approximately $1/4$ in space group $Fd \bar{3}m$ (Fig. 6). In “normal” spinels, the A cation occupies the tetrahedral (iv) site and the B cation occupies the octahedral (vi) site, $^{iv}[A]^{vi}[B]_2O_4$. In fully “inverse” spinels, the tetrahedral site contains only B cations and the octahedral site contains an equal number of A and B cations, so the octahedral site is disordered, $^{iv}[B]^{vi}[AB]O_4$. Any intermediate spinel may be expressed as a mix of the normal and inverse end-members, with a general formula: $^{iv}[A_{1-x}B_x]^{vi}[A_{x/2}B_{1-x/2}]_2O_4$, where $x$ is denoted the “inversion parameter”. This $x$ is the fraction of B cations (in the case of MgFe$_2$O$_4$, Fe$^{3+}$) on the tetrahedral site. In normal spinels, $x = 0$, and in inverse spinels, $x = 1$. A value of $x = 2/3$ corresponds to a completely random distribution of A and B cations. The order-disorder process in spinels is termed “non-convergent” because there is no symmetry change upon cation disordering.
The effects of pressure on order-disorder processes in spinels are described in a number of publications [4, 5, 28, 29], based on the relative unit-cell volumes and states of cation order in a number of samples quenched from high PT conditions. Inverse spinels with 2-3 cation charges tend to become more ordered with increasing pressure at constant temperature. Hazen and Yang [4] point out the importance of in situ experiments in determining the true state of order in spinels. To test some of the predictions derived from compressibility of quenched samples at room temperature [4, 5] we have concentrated on MgFe\textsubscript{2}O\textsubscript{4} and on

![Graph](image)

**Fig. 7.** Pressure dependence of the order parameter (see text for definition) at various temperatures for MgFe\textsubscript{2}O\textsubscript{4} spinel. The errors in both pressure and order parameter are smaller than the symbols.

![Graph](image)

**Fig. 8** Acoustic data plotted as a ratio of P- to S-wave travel times (t) collected at 8 GPa as a function of temperature. Two distinct trends are observed on heating and cooling. The anomaly at 700-800 °C on heating corresponds to the temperature where the cation relaxation process is expected to occur as the Mg\textsuperscript{2+} and Fe\textsuperscript{3+} cations re-order towards their equilibrium position. A different cation distribution is probably frozen in the structure on cooling. The pressure difference on heating is estimated to be about 0.5 GPa, and 1-2 GPa on cooling. Beyond 1000 °C the S wave (not P) disappears, reappearing on cooling.
determining its crystal structure and elastic properties using data collected simultaneously at high PT. Analysis of the X-ray powder diffraction data obtained using standard Rietveld structural refinement techniques [3, 30] suggest that indeed the order-disorder reaction is pressure dependent, with pressure promoting ordering (Fig. 7). Interestingly, preliminary ultrasonic data collected at high PT suggest these changes in order are associated with large changes in the P- and S-wave velocities (Fig. 8).

The structural behavior of MgFe$_2$O$_4$-spinel was firstly determined from in situ synchrotron X-ray powder-diffraction data at room pressure and temperatures on heating and cooling [30] followed by determination of the pressure dependence of the order parameter, determined from Rietveld structure refinement (Fig. 7). The later data were collected in a manner similar to that used for the collection of data for dolomite (Figs. 2, 3). Cation order in MgFe$_2$O$_4$, analyzed in terms of the inversion parameter, \(x\), \([{\text{IV}}^\text{IV}[\text{Mg}_1-x \text{Fe}_x]^\text{VI}[\text{Mg}_{x/2} \text{Fe}_{1-x/2}]_2\text{O}_4\) shows a clear dependence on pressure Fig. 7).

We also carried out experiments to test the hypothesis that changes in order-disorder would change elastic properties of minerals [5]. Preliminary analysis of data collected on MgFe$_2$O$_4$ suggests that indeed there are large changes in the compressional (P) rather than in the shear (S-wave) velocities as the spinel is heated and cooled (Fig. 8). Anomalies in the sound velocities are observed at temperatures corresponding to the sample moving toward an equilibrium cation distribution at \(\approx 750^\circ\text{C}\) at 8 GPa. At the highest temperatures where cations are expected to disorder along an equilibrium pathway, the S-wave, but not the P-wave, signal disappears. Upon cooling the S-wave is reacquired, a different state of order is probably frozen in, and the P- and S-wave travel times are different from those obtained upon heating. Clearly the state of order is a powerful modifier of the elastic properties. These results have implications for the stability and elastic properties of materials in the Earth’s interior and need to be checked in other spinels and in other minerals showing order-disorder reactions.

### CASE STUDY 3: ANHYDRITE

The versatility and capabilities of beamline optics and laser heated diamond anvil cells is demonstrated in a recent exploratory study of the high-pressure structures adopted by CaSO$_4$. The high pressure phases of the \(A^{2+}B^{6+}\text{O}_4\) sulphates, selenates, molybdates and tungstates are considered to be related by systematic trends, based on relative cation size and similarities with other cationic systems [31]. These trends are now mostly well-established for binary oxides of \(A^{(2+, 3+, 4+)}B^{6+, 5+, 4+}\text{O}_4\) stoichiometry. The CaBO$_4$ (\(B = \text{S, Se, Te}\)) structures are intriguing, with CaSO$_4$ crystallizing as common minerals in hydrous (gypsum) and anhydrous (anhydrite) forms and the structure adopted by anhydrite is not shared by any other of the \(A^{2+}B^{6+}\text{O}_4\) chemistries. The sequence of high pressure phase transitions in anhydrite is therefore of importance in establishing a bridge between ‘lower-pressure’ (smaller cation) sulfates and chromates, anticipated ‘moderate-pressure’ (larger cation) forms of sulfates and chromates that crystallize in monazite-and barite-type structures and the ‘high-pressure’ structures of the selenates, molybdates and tungstates that form in primarily barite- and scheelite-type structures (Fig. 9).
We have observed and positively identified three structure types of CaSO$_4$ at high pressure and temperature; the monazite-type, the barite-type and its distorted-AgMnO$_4$ variant. In addition, we also have evidence for the existence of the orthorhombic structure first encountered by Chen et al. (2001).

The starting material for the high-pressure experiments was a small piece of natural CaSO$_4$ from Bancroft, Ontario (Stony Brook collection #140019), ground to a fine powder in acetone and oven-dried. It was mixed with trace powdered pyrolytic graphite to obtain an even light-grey mixture that would heat under laser-irradiation. The sample was loaded with a ruby sphere for pressure calibration (Mao et al., 1986) using the fluorescence method (Forman et al., 1972) in a stainless-steel gasket with a 125 $\mu$m diameter hole. In the loaded sample, the graphite was not detectable by diffraction. Two-dimensional diffraction data were collected on a MarResearch Mar345 image plate detector (Fig. 3), previously calibrated and corrected for geometrical distortions using NBS SRM 660a, LaB$_6$ powder, with wavelength calibrated against the I-K edge, $\lambda = 0.3738(1)$ Å. At high pressure, the sample was heated by an online YAG laser heating system. In the single-sided configuration used, the confocal laser and x-ray beams illuminated the sample during exposure and, simultaneously, thermal emission from the sample was collected by SpectraPro spectrometer via a Lagrangian telescope for estimation of the

Fig. 9. Coordination environments around the A (central cation) and B (tetrahedral) sites of common ABO$_4$ oxide structure types.
temperature. During exposure the sample was moved in small increments so as to have an even coverage of the sample for increased averaging of powder statistics.

Treatment of data after collection follows details described earlier for the data collected in the large volume press (Fig. 3). The experiment was initially intended only as a reconnaissance to investigate the findings of Chen et al. (2001), thus data were only taken at a few points; at ambient conditions, 11.5, and 21.4 GPa, during heat treatment at nominally ~21 GPa and 1450 K. Once we observed crystallization of the new phase not described by Chen et al. (2001), we then took steps to recover the sample, taking data on temperature quench and over several decompression steps.

The results obtained are shown in Fig. 10 where the phases encountered in this series of exploratory experiments at high PT are summarized. On increasing the pressure to 11.8 GPa we obtain the known monazite-type CaSO$_4$ phase [32, 33]. Rietveld-refinement provided cell parameters of $a = 6.3769(9)$ Å, $b = 6.6439(9)$ Å, $c = 6.1667(8)$ Å with $\beta = 102.220(10)$ $^\circ$ in space group $P2_1/n$ and $V = 255.35(6)$ Å$^3$; equivalent to a density of $\rho_{\text{calc}} = 3.541$ g cm$^{-3}$, or 19.7% more dense than anhydrite at ambient conditions ($\rho = 2.959$ g cm$^{-3}$).

Several diffraction patterns were taken while pressure was increased to 21.4 GPa and also as power on the laser was gradually increased until thermal emission was visible. A change in the diffraction pattern was obtained, and data collected at 21 GPa nominal and 1450 K was indexed as a primitive orthorhombic unit cell with $a = 6.3402$, $b = 7.5456$ and $c = 4.9542$ Å [34]. A powder diffraction pattern calculated on the basis of a barite structure suggested it as the probable structure type to which the monazite form of CaSO$_4$ transforms at high PT (Fig. 9, 10). Using a 5-parameter background, refinement of peak-shape function (GU, GW, LX, asym),

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**Fig. 10 summary of phases observed for CaSO$_4$ at high PT in the laser heated DAC.**
atomic positions and anisotropic displacement factors for each atom (45 parameters total), we obtained a fit with Rp and wRp of 12.96 % and 16.91 %, respectively and a $\chi^2 = 2.748$ confirming the structure is indeed related to that of barite.

Immediately on cooling the splitting of the (121) and (211) reflections and appearance of numerous other less intense reflections, not present in the barite pattern, suggested the formation of another phase (Figs. 10 and 11). A monoclinic distortion to a subgroup of the barite structure (in setting Pbnm) to $P2_1/n$ is sufficient to reproduce to general diffraction features shown in Fig. 10. The cell parameters obtained at 11.8 GPa ($a = 6.448$ Å, $b = 7.595$ Å, $c = 5.085$ Å with $\beta = 91.664$ ° is very close to that predicted [31] for a possible intermediate phase between the anhydrite and barite structures, the AgMnO₄-type structure ($P2_1/n$, $a = 5.64$ Å, $b = 8.33$ Å, $c = 7.12$ Å, $\beta = 92.25$ °; JCPDS 20-0487). From profile-fitting of the data obtained at 19.9 GPa (immediately on cooling from the barite phase at 1450 K, as shown in Fig. 10), we obtain cell parameters of $a = 4.9577(4)$ Å, $b = 7.5243 (4)$ Å, $c = 6.3397(7)$ Å, $\beta = 90.829(5)$ ° and $V = 236.47(3)$ Å³ equivalent to a density of $\rho = 3.824$ gcm⁻³, very close to that of the barite-related phase of CaSO₄ (Figs. 8,9).

Further reduction in pressure resulted in the complete back-transformation to the anhydrite phase (Fig. 10). Upon reclosing the cell however we noticed the color of the anhydrite + graphite sample changed from grey to honey colored, and upon re-exposure of the decompressed sample,
with the cell closed finger tight, peaks not associated with the anhydrite structure type were observed. These new peaks that can be compared with those described by Chen et al. [35], who propose an orthorhombic cell of \(a = 6.602 \text{ Å}, b = 7.759 \text{ Å} \) and \(c = 5.970 \text{ Å}\) from an assemblage of 70% anhydrite and 30% new orthorhombic phase. Comparison of peak positions and particularly of peak intensities suggests that we do not have the same ratio of anhydrite + the proposed orthorhombic phase as was recovered by Chen et al [35] and that the cell parameters are slightly different. Nonetheless, it does suggest that the phase is a low-pressure phase, obtained on recovery [35] and not that encountered by them at high PT. They [35] also report that the conditions for best preservation of the orthorhombic phase are on slow pressure release from the high pressure state, contrary to what would normally be expected for recovery of a high-pressure phase in a metastable region.

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