High-Pressure Phase Transitions in AlPO₄ from First-Principles

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Based on first-principles density functional theory calculations, we predicted a ferroelastic transition in AlPO₄ between stishovite-like and m-CaCl₂ phases by confirming the energetic stability of stishovite-like phase and witnessing a pressure-induced phenomena of symmetry-breaking spontaneous strain, and furthermore, we established a new pressure-induced phase transition sequence for AlPO₄ up to 100 GPa at 0 K as follow: berlinite to moganite, to AlVO₄, to P2₁/c, to CrVO₄, to stishovite-like, and to m-CaCl₂ phase, with the corresponding transition pressure 4.1, 5.0, 7.0, 7.3, 31.9 and 46.4 GPa, respectively. For all these phases, equation of state parameters are reported. This transition sequence largely revises the previous one based on in-situ cold-compression experiments, by incorporating four new phases, moganite, AlVO₄, the P2₁/c, and stishovite-like, the former three of which were synthesized by our recent quench experiments and are theoretically investigated here for the first time. This newly-established phase transition sequence would serve as a model case because it is the most detailed one among all the berlinite-type ABO₄ compounds to date. This study would also provide deep insight into the polymorphism behavior of SiO₂ because of some instructive dissimilarities discerned between these two isoelectronic compounds, such as that all the mixed-coordinated phases in AlPO₄ exceptionally lack counterparts in SiO₂, and that moganite is stable after quartz phase in AlPO₄ but metastable in SiO₂.

Keywords: AlPO₄, SiO₂, phase transitions, high-pressure, first-principles, equation of state
**Prediction of NMR parameters by first-principles calculation: K-cymrite and polymorphs of AlPO_4**

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NMR spectroscopy is a powerful technique to study the local structure of solid materials. The interpretation of NMR spectra is greatly facilitated by the development of (1) advanced NMR techniques that provide direct through-bond and through space atomic connectivity information, and (2) first principles calculations of NMR parameters. For the latter, thanks to the development of periodic first-principles methods (Pickard & Mauri, 2001), the calculation of NMR parameters (chemical shift, and quadrupolar coupling constant and electric field gradient (EFG) asymmetry parameter for quadrupolar nuclei, such as $^{27}$Al) from crystal structures has become feasible. In this study, we have applied this technique to calculate the NMR parameters for K-cymrite (KAlSi$_3$O$_8$·H$_2$O) that has a disordered Si/Al distribution and several AlPO$_4$ polymorphs, and have compared them with the experimental data.

NMR parameters were calculated using GIPAW method (Pickard & Mauri, 2001) implemented in Quantum-ESPRESSO (Giannozzi et al., 2009). For AlPO$_4$-stishovite solid solution, a supercell of 2x2x2 was used, and 2 Si were replaced with Al and P. For K-cymirte, a supercell of 2x2x1 was used. Four different Al/Si disordered models were built.

For AlPO$_4$, 5 polymorphs including three recently discovered high-pressure phases were calculated. Their crystal structures, $^{27}$Al 3Q MAS and $^{31}$P MAS NMR as well as other more advanced two-dimensional (2D) correlation NMR results have already been reported (Kanzaki et al., 2011; Kanzaki & Xue, 2012). The calculated chemical shifts of Al and P sites in these phases are within a few ppm from the observed ones. This further strengthened our previous site assignment of NMR peaks based on 2D correlation NMR experiments. We also calculated the chemical shift for $^{31}$P in the SiO$_2$-AlPO$_4$ stishovite solid solution. The calculated chemical shift for $P^{VI}$ is about 105 ppm more negative than that of $P^{IV}$ site in cristobalite. A recent experimental NMR study of 1 wt% AlPO$_4$ dissolved stishovite observed a peak about 130 ppm more negative than that of cristobalite, which was attributed to $P^{VI}$ in stishovite (Stebbins et al., 2009). The general trend is consistent with our calculation, but there is a discrepancy of 25 ppm between the observed and calculated values. More detailed studies are necessary to resolve this discrepancy.

K-cymrite has a double-layered structure with Al/Si distributed in a single T site (Q$^4$). Our $^{29}$Si MAS NMR revealed six peaks, although it has generally been assumed that a maximum of five peaks arising from different Si/Al distributions in the four next nearest T neighbors (nSi, (4-n)Al, with n=0 to 4) should occur for a single Q$^4$ site (Xue and Kanzaki, 2012). We have shown from direct 2D J-coupling mediated $^{29}$Si NMR experiments that the Si(3Si1Al) and Si(2Si2Al) sites are each split into two peaks due to the existence of two populations of T-O-T angles (139° and 180°) (Xue and Kanzaki, 2012). In order to double-check this interpretation, the chemical shifts of Si(4Si), Si(3Si1Al) and Si(2Si2Al) sites were calculated for K-cymrite. The calculated chemical shifts of Si(3Si1Al) and Si(2Si2Al) sites show two distributions for each site separated by about 2 ppm, consistent with our experimental observation. The relative shifts between Si(4Si), Si(3Si1Al) and Si(2Si2Al) sites are also reproduced.

This study has thus demonstrated that first-principles calculation (GIPAW) of NMR parameters is a reliable mean to assist interpretation of NMR spectra for both ordered and disordered crystal structures.

**References:**


**Keywords:** NMR, first-principles calculation, chemical shift, crystal structure, AlPO$_4$, K-cymrite
Determination of Transition Boundary between Garnet and Perovskite in CaGeO3

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It is known that some ABO3 compounds are excellent analogues of MgSiO3 or CaSiO3, which are major constituents of the Earth’s mantle. Calcium germinate (CaGeO3) exhibits a sequence of phase transitions from a pyroxenoid to a tetragonal garnet phase, and subsequently to an orthorhombic perovskite phase. The phase boundaries in CaGeO3 have been also used as a pressure calibration point at high temperatures in high-pressure experiments, such as for SiO2 and Mg2SiO4. Therefore, the precise phase boundary of CaGeO3 needs to be determined. The transition pressure of CaGeO3 has been investigated in static high-pressure experiments using quench [1] and in situ methods [2]. According to previous high-pressure experiments, the transition pressure is ~6 GPa and this boundary had a negative slope. In contrast, Ross et al. [1] also estimated the value of dP/dT slope of this transition using calorimetry data, and calculated the slope to be 2-3 times more negative than the value determined from high-pressure experiments. Therefore, we reinvestigated the dP/dT slope of garnet-perovskite transition in CaGeO3 using the high-pressure experiments.

In this study, the use of a multi-anvil high-pressure system combined with a synchrotron radiation source made it possible to acquire precise data from samples under high-pressure and high-temperature conditions [3]. The starting material was CaGeO3 wollastonite, synthesized at 1473 K for 5 hours from a starting mixture composed of finely powdered CaCO3 and GeO2. In our experiments, pressure was applied to the sample by generating an anvil load from the desired oil pressure in the press. The sample was then slowly heated to avoid the temperature overshoot until it reached the desired temperature for a given oil pressure. After reaching the required pressure and temperature, we performed in situ measurements using the synchrotron X-rays. The duration of heating was 0.5-2.0 hours. At the end of the experimental runs, the sample was quenched by cutting off the electrical power. This heating procedure was the same as that used in typical quench experiments.

We performed approximately 30 experimental runs, and the boundary determined in this study is in general agreement with that reported in previous high-pressure experiments [1,2]. However, the value of our dP/dT slope was 2-3 times more negative than that in previous experiments [3]. The calculated value of the dP/dT slope using calorimetry data [1] is consistent with our value of dP/dT [3]. It is likely that the discrepancy between previous and our high-pressure experiments due to the kinetics of the structural phase transition. In previous in situ experiments [2], the P-T condition was changed several times during each run while observing the transition from the garnet to the perovskite structure. It is known that a metastable overshoot (pressure and/or temperature) is required to provide a sufficiently large energy driving force to overcome a nucleation and/or growth barrier for the transition in previous experiments [2]. To avoid any influence of the kinetic effect, we used the same heating cycle as that used in conventional quench experiments.

References

Keywords: Garnet, Perovskite, Phase transformation, High pressure and high temperature
T-P-V equation of state of NaCl based on simultaneous measurements of elastic wave velocities and density of NaCl

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The elastic compressional (P) and shear (S) wave velocities and densities of NaCl were simultaneously measured up to 12 GPa at 300 K, and up to 8 GPa at both 473 and 673 K, using a combination of ultrasonic interferometry, in situ synchrotron X-ray diffraction and radiographic techniques in a large-volume Kawai-type multi-anvil apparatus. We adopted experimental data after heating the sample to 873 K under fixed press loads, to minimize nonhydrostatic components due to local deviatoric stresses. At 300 K, both P and S wave velocities are found to change linearly with density up to 12 GPa, satisfying Birch’s law. High-temperature and high-pressure equation of state (EOS) of NaCl was developed using the measured P and S wave velocities and densities based on the 300 K fourth-order Birch-Murnaghan finite strain equation combined with the Mie-Gruneisen relation and the Debye thermal model. Here we present a new temperature-pressure-volume EOS of NaCl, as a primary pressure standard, without relying on any pressure scale, at high temperatures and high pressures.

Keywords: high temperature and high pressure, elastic wave velocity, density, NaCl, equation of state
Sound velocity and structure measurement of silicate glasses under pressure

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The degree of polymerization in silicate melt/glass is one of the most important parameters to understand the magma behavior. For silicate melts at ambient pressure, the degree of polymerization is highly related to composition, which is quantitatively described by a ratio of non-bridging oxygen (NBO) to tetrahedrally cation (T). In particular, the NBO/T is widely used to obtain viscosity information of various silicate melts and discuss the magma mobility in the Earth’s interior. Several viscometry studies reported that polymerized melts showed much higher values of viscosity than those of depolymerized ones. Interestingly, it should be noted that the pressure dependence of the high viscosity of polymerized melts was shown to be negative. This gives important questions of the compression effect on the degree of polymerization and its effects on properties of silicate melts. In this study, we have measured the sound velocity of polymerized glass (jadeite and albite glass: NBO/T=0) and depolymerized glass (diopside glass: NBO/T=2) at pressures up to 10 GPa by using ultrasonic technique and synchrotron radiation with a Paris-Edinburgh press. We have also obtained the X-ray structure factor, S(Q), of these glasses by using energy-dispersive X-ray diffraction method in order to understand structural changes in the intermediate-range order with pressure.

All experiments were conducted using a Paris-Edinburgh press, which is installed at the HPCAT 16-BM-B beamline, Advanced Photon Source (APS). High pressure sound velocity measurements were carried out using the ultrasonic pulse-overlap method. The outer pressure media consisted of machinable zirconia pallets and sintered boron-epoxy. Graphite cylinder was used as a sample container, with a gold foil placed on top and bottom of the capsule as markers for sample length measurement. Radiography images taken by CCD camera allowed us to calculate the sample length under high pressure. Pressure was determined by the equation of state of gold, which was located below the sample. The scattered X-rays were detected using a Ge solid state detector (Ge-SSD) with a 4096 multi-channel analyzer. Alumina above the sample was used as a buffer rod. The glass sample and the alumina buffer rod were polished with 0.001 mm diamond paste. Ultrasonic signals were generated and received by a LiNbO3 transducer. The signals were collected with a sampling rate of 5 x 109 point/second. Structure measurements were performed using the energy dispersive X-ray diffraction technique. The 16-BM-B is a bending magnet beamline which provides white X-rays (5-120 keV) with high brightness. The incident X-ray was collimated by two sets of vertical (0.1 mm) and horizontal (0.1 mm) slits. The diffracted signal was collimated with a 0.1 mm gap scattering slit 80 mm downstream from the sample and a 0.1 mm x 5.0 mm receiving slit 400 mm further downstream from the scattering slit. The Ge-SSD was mounted on a two-theta arm on a large Huber rotation stage, which allows accurate control on two-theta angle. The diffraction patterns were collected for 9 fixed diffraction angles (2theta = 3, 4, 5, 7, 9, 11, 15, 20, 25 degrees). Collecting time varied with the diffraction angles, as intensities decreased with increasing angle. All patterns were collected until the maximum intensity reached at least 2000 counts. Structure factor, S(Q), was obtained by combining X-ray diffraction profiles collected for 9 diffraction angles.

Pressure dependence of sound velocity of jadeite, albite and diopside glasses will be presented, along with structure factor S(Q) of the glasses at high pressure. We would like to discuss a direct correlation between the intermediate-range order structure and sound velocity in these glasses, and the influence of the degree of polymerization.

Keywords: sound velocity, structure, glass, silicate, high pressure
Mapping of residual pressure around an inclusion in sapphire by fluorescence spectroscopy

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Residual pressure distributes around a mineral inclusion taken in a mantle-derived mineral represented by diamonds (e.g. Nasdala et al., 2003). It can provide useful information about the depth in the origin of the diamond by determining the residual pressure around a mineral inclusion in a diamond with spectrophotometric technique (e.g. Kagi et al., 2009). Differential stress between an inclusion and host mineral such as a diamond arises from differences in thermal expansion and compressibility between a mineral inclusion and host mineral. Corundum is the second hardest mineral and substantial residual pressure around an inclusion can be expected as well as diamond.

In general, corundum (Al\textsubscript{2}O\textsubscript{3}) includes a small amount of Cr\textsuperscript{3+} in the structure and fluorescence spectra attribute to Cr\textsuperscript{3+} ions can be obtained. Fluorescence spectra of corundum consist of R1 line at 694.3 nm and R2 line at 692.9 nm. The peak shift of the R1 line is affected by the differential stress, but the R2 line is not (Chai and Brown, 1996). So, we can estimate residual pressure from the peak position of the R2 line.

In this study, we used sapphire samples a kind of corundum. Around a mineral inclusion in sapphire, we measured fluorescence spectra using a three-dimensional fluorescence mapping system every 5 micrometers or 10 micrometers and determined residual pressure of each measurement point from the peak shift of the R2 line using a pressure calibration curve (Mao et al. 1986). We studied two kinds of sapphire samples; one is from Kings plains creek, Australia, and the other is from Kanchanaburi, Thailand. Albite, zircon and rutile were contained as mineral inclusion around 100 micrometer in size, and some of the inclusions have a radial crack. The maximum residual pressures around the zircon in the sample from Australia and albite in that from Thailand were determined to be 0.60GPa and 0.25 GPa, respectively. In the presentation, we will discuss the uptake process of the inclusion and the growth history of the sapphire from the pressure distribution around the inclusion.

Keywords: inclusion, sapphire, residual pressure, fluorescence spectroscopy
Experimental study on the phase transition of graphite to hexagonal diamond

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Hexagonal diamond (lonsdaleite) is a metastable polymorph of carbon and consists of ABAB... stacked sp3-bonded (tetrahedral) carbons. It occurs as microscopic crystals associated with graphite and cubic diamond in carbonaceous meteorites such as the Canyon Diablo meteorite and impact craters and can also be synthesized from well-crystalline graphite by high pressure experiments (e.g. Bundy and Kasper, 1967; Yagi et al., 1992). The phase transition of graphite to hexagonal diamond is considered to be a martensitic process, where [100] of hexagonal diamond is located parallel to [001] of the host graphite. However, we recently found a variety of such coaxial relations between graphite and hexagonal diamond based on TEM observations of samples synthesized by laser-heated diamond anvil cell (DAC). This suggests that the martensitic phase transition process is not always simple, but can be complex. Here, we conducted further research on the transition mechanism by using highly-oriented graphite samples with different crystallinities under different hydrostatic conditions.

We performed a series of high-pressure and high-temperature experiments at a pressure of 25 GPa and temperatures of 1800-2200K. Three types of highly-oriented graphite were used as starting materials: 1) highly-oriented graphite (HOG, Murakami et al, 1992), 2) highly-oriented pyrolitic graphite (HOPG) and 3) Kish graphite. Each sample was compressed in a DAC with/without an ethanol/methanol pressure transmitting medium and rapidly heated to a target temperature using fiber laser (1072 nm). The sample became transparent after laser heating, suggesting that the phase transition of graphite to diamond phase(s). The recovered samples were first examined by Raman spectroscopy for phase identification and then by transmission electron microscopy (TEM) for microtextural observations and electron diffraction analysis.

TEM observation revealed that the transparent area of recovered samples consists purely to mostly of hexagonal diamond with a layered structure similar to that of the graphite starting sample. A trancce amount of cubic diamond also coexists in some cases. The electron diffraction (ED) patterns collected from pure hexagonal diamond synthesized from HOG and HOPG samples are complex and can be interpreted as a superposition of several types of reciprocal patterns in which [100], [002] and [-212] of hexagonal diamond are all arranged in a coaxial relation with graphite [001]. This suggests that the phase transition from graphite to hexagonal diamond proceeds mostly by 1/2(3a)1/2 or 1/(3a)1/2 shifts of graphene layers along graphite [100]. On the other hand, the ED patterns collected from Kish graphite are simple and can be indexed as a single reciprocal lattice where [100] of hexagonal diamond is parallel to [001] of the host graphite. It is likely that the crystallite size of hexagonal diamond synthesized correlates positively to the crystallite size (particularly in the a-axis direction) of initial graphite sources. Furthermore, the variety of the coaxial relation and transition process seems to be originated from the mosaicity (misorientation along c-axis) of the graphite sources.

Keywords: hexagonal diamond, graphite, laser-heated diamond anvil cell, TEM
Structural changes of silicagel by compression

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The structural changes of silica gel by compression

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The structural change in amorphous silica gel (SiO₂ₙH₂O) compressed up to about 1GPa and investigated by X-ray diffraction, Raman and Infrared spectroscopic measurements for elucidate the structural change processes.

Silica gel powder put in an Al alloy tube and compressed with 25kN to 200kN of press loads. Observed X-ray diffraction patterns show typical halo patterns for amorphous materials which have maxima at about 2theta=23degree (FSDP). FSDP shifted to higher angle by compression. Tan and Arndt (1999, J. Non-Cryst., Solids, 82, 117) reported that the shift of FSDP position to higher angle for compressed SiO₂ glass and this caused by decreasing in size of intermediate-range order of silica glass to increase its density.

In Raman spectrum, the 430 cm⁻¹ broad band attributed to Si-O-Si symmetric stretching vibrations became sharp and the average position shifts to high wavenumber by compression. This shows that Si-O-Si angle in SiO4 tetrahedral linkage in SiO₄-X(OH)x decrease. The new band appears at 600cm⁻¹ in 50 kN and the intensity increase in increasing of compression load. This band has been attributed to three-membered rings of SiO₄ tetrahedra. The intensity of 980cm⁻¹ band of silanol groups increases by compression. This fact shows that some silanol groups reacts to dehydrate and form three-membered rings of SiO₄ tetrahedra. However, this dehydration reaction are limited and most H₂O and silanol groups were remained. Because, Raman band around 3500cm⁻¹ associate with H₂O almost remains its intensity after compression.

In IR spectra, the intensity of 800cm⁻¹ band of Si-O-Si bending mode increased by compression. It is consistent with formation of three-membered rings of SiO₄ tetrahedra those were found in Raman study. The FWHM of the 1080cm⁻¹ band increases and the band position shifts to lower wavenumber by compression. These facts show that the deformation of SiO₄ tetrahedron and the average Si-O length increase by compression.
Characterization of sulfur-containing calcite in a travertine carbonate rock

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Since the first documentation by Reeder and Wenk (1979), a number of studies reported weak extra reflections in rhombohedral carbonates in electron diffraction (ED) and referred to them as $c$-reflections. It was suggested that $c$-reflections are formed by the ordering of impurity cations such as $\text{Mg}^{2+}$, $\text{Fe}^{2+}$, and $\text{Mn}^{2+}$ substituting $\text{Ca}^{2+}$ (e.g. Reeder, 1981). Recently we have also found weak extra reflections similar to $c$-reflections in the ED patterns of calcite precipitated in a hot-spring (La Duke) near Yellowstone National Park. The Selected-area ED pattern along the [001] direction indicated that the extra reflections appear holding the three-fold symmetry of calcite. Those weak reflections were found halfway between principal reflections. However, X-ray microanalysis indicated that the amount of impurity cations such as $\text{Mg}^{2+}$ is very small and sulfur (S) is the major impurity element. S/Ca atomic ratio is about 3%. The cell parameters of the La Duke sample were determined by synchrotron X-ray powder diffraction (wavelength = 0.7749 angstrom) and Rietveld refinement. It showed that the \textit{a}-length (4.9757 angstrom) slightly decreased and the \textit{c}-length (17.0998 angstrom) slightly increased compared to the pure calcite ($a = 4.9906$ angstrom, $c = 17.0621$ angstrom), or the \textit{c/a} axial length (3.437) of La Duke calcite is longer than that of pure calcite (3.419). The TG-DTA analysis was performed to find whether the sulfur exists in the calcite crystal or as organic matter. The anhydrite ($\text{CaSO}_4$) was detected at 600 degrees C and the \textit{c}-length has recovered to that of pure calcite, suggesting that sulfur are incorporated in the calcite as a solid solution. XPS analysis was used to determine the chemical species of sulfur. Since the sulfur 2p3/2 peak of La Duke is located at 168.35 eV, the sulfur is involved in the ions of sulfate ($\text{SO}_4^{2-}$). The crystal structure of La Duke calcite has been investigated using a four-circle X-ray diffractometer (Mo, wavelength = 0.71075 angstrom). Weak electron density around the oxygen was found, which may be related to the $\text{SO}_4^{2-}$.

Keywords: calcite, electron diffraction, sulfur, superstructure, travertine
Dendritic magnetite spherules produced by fine particle heating / quenching experiments

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Magnetite is a common accessory mineral in various rocks. Crystal shapes and habits of magnetite show diversity depending on crystallization conditions, especially cooling rate. Characteristic dendritic or skeletal magnetite crystals occur in quench rims of effusive rocks (e.g. Szramek et. al., 2010). The dendritic magnetite also occur in micrometeorites undergone quick heating and quenching at atmospheric entry (e.g. Genge, 2008, 2006, Toppani and Libourel, 2003).

In this study, we constructed a fine particle free fall apparatus in a high temperature furnace and carried out crystallization experiments with quick heating and quenching. In the experiments with volcanic ash particles, we found quite characteristic dendritic magnetite spherules. From the powdered meteorite, we got melted artificial micrometeorites (Gondo and Isobe, 2012).

Experiments were carried out in a vertical tube furnace with CO₂, H₂ and Ar mass flow controllers to control oxygen partial pressure and total gas flow rate. At the top of the furnace, a silica glass tube with an orifice with approximately 0.5mm in diameter was set to keep falling rate of particles. Particles were retrieved in an alumina crucible at the bottom of the furnace tube.

Terminal velocity of silicate particles with 100 micron meters in diameter in Ar gas at 1200 degree C is 18 cm/sec. Gas ascent rate at 1200 degree C is 11 cm/sec in the furnace tube when gas flow rate is approximately 1 l/min at standard condition. The falling speed of the particles with 100 micron meters in diameter, therefore, is reduced to approximately 7 cm/sec. When the highest temperature of the furnace set to 1520 degree C, the falling particles reach 1400 degree C within 2 seconds, keep above 1400 degree C more than 1 second, and are quenched within 1 second. For the fine particles with 100 micron meters in diameter, time scale of thermal equilibrium by radiation is within 1 second.

With this experimental apparatus, we carried out quick heating / quenching experiments of volcanic ash particles from Sakurajima volcano. The volcanic ash particles are sieved to 60 to 160 micron meters in diameter, and contain plagioclase, pyroxene, magnetite and groundmass glass in various proportions. Some particles contain quite high volume fraction of magnetite. After the experiments, more than half of the volcanic ash particles were well melted to show spherical shape. Groundmass glass and plagioclase particles formed clear glass spherules.

From particles with high volume fraction of magnetite, we can see quite characteristic texture in which dendritic magnetite cover almost whole surface of the spherule. Magnetite dendrite crystals with particular crystallographic direction to the spherule surface also occur. We discuss on dendritic magnetite texture with heating / quenching rate of fine particles.

Keywords: magnetite, dendritic crystal, quench texture, fine particles