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A high-pressure cubic-to-tetragonal phase-transition in melanophlogite, a SiO_2 clathrate phase

Mario Tribaudino [a,*], G. Diego Gatta [b], Yongjae Lee [c]

[a] *Dipartimento di Scienze della Terra, Università di Parma, Parco Area delle Scienze 157/A, 43100 Parma, Italy*
[b] *Dipartimento di Scienze della Terra, Università di Milano, Via Botticelli 23, 20133 Milan, Italy*
[c] *Department of Earth System Sciences, Yonsei University, Seoul 120749, Republic of Korea*

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ABSTRACT

The crystal-structure and the high-pressure behavior of a natural cubic melanophlogite (Sp. Gr. *Pm*3*n* at room-conditions), a type-I SiO_2 clathrate containing only methane as guest gas, was investigated by X-ray single-crystal diffraction at room-conditions and *in situ* high-pressure synchrotron powder diffraction with a diamond anvil cell and methanol:ethanol:water = 16:3:1 (MEW) mixture and silicon-oil (Si-oil) as pressure transmitting media up to about 6 GPa.

A cubic-to-tetragonal phase-transition was observed at $P \geqslant 1.14$ GPa, in both MEW and Si-oil runs. The tetragonal polymorph is stable up to the highest pressure in the run with MEW, but it switches back to cubic symmetry at $P > 3.12$ GPa in Si-oil. The different elastic behavior is ascribable to the non-hydrostatic conditions in Si-oil medium at $P > 1$ GPa.

The elastic behavior of melanophlogite was described fitting the *P*–*V* data with a Birch–Murnaghan Equation-of-State, showing similar bulk modulus values for the low-pressure cubic and high-pressure tetragonal phases [*i.e.* $K_{0,\text{L-cub}} = 23.4(2.4)$, $K_{0,\text{tetr}} = 22.2(9)$].

The spontaneous strain for the cubic-to-tetragonal transition is almost completely governed by a compression along the *c* axis, with negligible contribution along *a*. An inverse behavior is found with respect to the tetragonal-to-cubic high-temperature phase-transition previously described for Mt. Hamilton melanophlogite. A Landau fit of the spontaneous strain (ε_{ss}), related to the order parameter (*Q*) of the transition as $\varepsilon_{ss} \propto Q$, showed a first-order character of the *P*-induced phase-transition and a $P_c = 1.2(3)$ GPa. Symmetry breaking spontaneous strain prevails respect to the volume strain, which is however present and significant.

1. Introduction

The clathrate family is a widely studied group of microporous materials, in which cages can be filled by different elements and molecules. The clathrate structure-topology is found in several materials, among which H_2O and Si, but also by the SiO_2 molecule, as in the rare mineral melanophlogite. Melanophlogite is isotypic with "gas hydrate I" [1,2], and is formed by a framework of corner sharing SiO_4 tetrahedra. Two types of cages are present, respectively [5^{12}] and [$5^{12}6^2$], where the superscripts give the number of pentagonal and hexagonal faces making up the cages. In melanophlogite, gaseous phases like CH_4, CO_2, N_2 or H_2S have been found [3–5]; H_2O was never found, a clear evidence of the hydrophobic character of melanophlogite [6]. The ideal formula for melanophlogite is, including potential filler of the cages, $46SiO_2 \cdot 2M^{12} \cdot 6M^{14}$, being M the guest gases in the 12 and 14 coordinated cages; the gas substitution is as high as 8% in weight [7], making therefore melanophlogite a potential carrier for greenhouse gas sequestration or storage of CH_4. Gaseous molecules can be removed by heating, to obtain a guest-free melanophlogite [8].

In spite of the potential interest of melanophlogite, few structural studies are available [4,9,10], devoted only on two samples with different content of guest gases. Melanophlogite occurs with two different structures at room-conditions, with space group *Pm*3*n* or *P*4$_2$/*nbc*. The tetragonal phase can be derived by distortion of the cubic one, but with doubling of the *a* (and *b*) parameter. At room temperature, most melanophlogite samples are tetragonal; the tetragonal-to-cubic transition was observed at 65 °C in the most studied sample of melanophlogite from Mt. Hamilton [11,12]. However, the recently discovered melanophlogite from Varano Marchesi is cubic [4]. Structural and chemical analysis did not reveal substantial differences in the silicate framework with the high-temperature cubic structure of Mt. Hamilton melanophlogite [11], but the extra-framework molecules are different: in the Varano Marchesi sample only CH_4 was found, whereas in the Mt. Hamilton there are also CO_2 and N_2 [3,4]. Following Gies [9] it appears, therefore, that the difference in symmetry is due to

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[*] Corresponding author. Tel.: +39 0521 905340; fax: +39 0521 905305.
E-mail address: mario.tribaudino@unipr.it (M. Tribaudino).

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different interaction of the guest molecules in the cages with the tetrahedral framework.

Studies on the behavior of melanophlogite at non-ambient conditions are also scarce [8,11,13]. The cubic-to-tetragonal phase-transition with temperature was first reported by Gies [9], but structural investigation and discussion of the transition mechanisms was later reported by Nakagawa et al. [11], based on *in situ* X-ray single-crystal diffraction. The authors found a *T*-induced first-order transition, very close to tricritical in character.

The high-pressure behavior of melanophlogite was investigated by *in situ* synchrotron powder diffraction with a diamond anvil cell [8,13]. Xu et al. [13] used a sample from Mt. Hamilton after removing the gaseous content, and using a mixture of amorphous boron and epoxy resin as pressure medium, NaCl as pressure marker and an energy dispersion detection system. The high-pressure experiment was performed up to 12 GPa, but at 3 GPa the sample underwent almost complete amorphization. The sample was reported as tetragonal at room pressure. However, due to the low quality of the energy-dispersive diffraction pattern at high-pressure, the diffraction data were refined with a cubic unit-cell [13]. A bulk modulus of 26 GPa was determined [13].

Yagi et al. [8] investigated up to 24 GPa the tetragonal melanophlogite from Fortullino [1], with different pressure media and using guest-free and guest-bearing melanophlogites. Sample amorphization was observed at different pressures as function of the *P*-medium. The sample loaded in the diamond anvil cell without pressure medium got readily amorphous, whereas in the run with He as *P*-medium the diffraction peaks were visible up to 24 GPa. In the gas-bearing melanophlogite, a bulk modulus of 24 GPa was found. In the guest-free melanophlogite, the bulk modulus varies from 14 to 56 GPa, depending on the pressure medium. It is higher in He, in which also an isostructural phase-transition occurs at 11–17 GPa. The higher bulk modulus and the presence of a phase-transition in guest-free melanophlogite was related to the entrance of He in the cages: in guest-bearing melanophlogite the penetration of the *P*-medium molecules was hindered as the cages were already occupied. Although it was stated that Fortullino sample is tetragonal [1], the refinements were performed in cubic symmetry [8].

From the above investigations, it appears that the non-ambient behavior of a real cubic melanophlogite (at room-conditions) has yet to be examined; moreover a precise determination of unit-cell parameters at high-pressure is needed to understand the compressional behavior and to show phase-transitions which may have been possibly overlooked in the previous studies.

On this basis, the aim of the present study was the investigation of the high-pressure behavior of a cubic melanophlogite from Varano Marchesi by synchrotron X-ray powder diffraction with a diamond anvil cell. The sample selected for the high-pressure experiments was previously characterized by X-ray single-crystal diffraction. The high-pressure experiments were then performed using two different pressure media: methanol:ethanol:water = 16:3:1 mixture (MEW) and silicon-oil (Si-oil, dimethylpolysiloxane).

2. Experimental

2.1. X-ray single-crystal diffraction at 0.0001 GPa

X-ray single-crystal and powder diffraction investigation were performed on few grains taken from Varano Marchesi melanophlogite, from the same sample used by Tribaudino et al. [4]. The single-crystal Raman spectroscopy investigation showed only methane as cage-molecules [4]. Moreover, the lack of birefringence, the analysis on the intensity of equivalent reflections, and the lack of superstructure cell-doubling reflections (along the *a* and *b* axes) in transmission electron microscopy, prompted for a cubic symmetry [4].

Single-crystal X-ray diffraction investigation was performed on a transparent fragment ($200 \times 180 \times 130\ \mu m^3$), taken from the same bunch of the powder for subsequent high-pressure investigation. Intensity data were collected with an Xcalibur-Oxford Diffraction diffractometer equipped with CCD at the Earth Sciences Dept. – University of Milano, using graphite-monochromatized Mo*K*α-radiation, and operated at 50 kV and 40 mA. A combination of ω and φ scans was used in order to maximize the reciprocal space coverage and redundancy, fixing a scan width of 0.4°, an exposure time of 20 s/frame, and a crystal-detector distance of 80 mm. The crystal was found to be metrically cubic (with the deviation from isometry $<1.5\sigma(l_i)$, where l_i are the unrestrained unit-cell lengths), with $a = 13.4092(4)$ Å and $V = 2411.1(3)$ Å^3, and the reflection conditions were consistent with space group $Pm3n$. As reported by Tribaudino et al. [4], very faint superstructural reflections were observed, whose the intensities were $I < 1.5(I)$ (background) and $I < 2\sigma(I)$, and thus not significant. The Bragg reflections were then integrated, and Lorentz-polarization and analytical absorption corrections by Gaussian integration based upon the physical description of the crystal, using CrysAlis-Oxford Diffraction package [14], were performed. The discrepancy factor between symmetry-related diffraction intensities (in Laue class $m\overline{3}m$) was $R_{int} = 0.042$ (Table 1). Weighted full-matrix least square anisotropic refinement was performed using SHELX-97 software [15] over 9775 reflections up to $2\theta = 70°$; the atomic scattering curves were taken from the *International Tables for X-ray Crystallography* [16]. The structure was refined starting from the atomic coordinates, site occupancies and displacement parameters reported in Tribaudino et al. [4]. The first refinement cycles were performed assuming the cages as completely empty, obtaining a residual in the electron density map of 2.9 e$^-$/Å^3 at the 5^{12} site, and of 1.4 e$^-$/Å^{3}at the $5^{12}6^2$ site. These residuals are lower than those found in Tribaudino et al. [4], which were 4.6 and 2.0 e$^-$/Å^3, respectively. The refined site occupancy, assuming that the extra-framework sites were occupied only by methane [4], is 61(2) for the [5^{12}] and 74(2)% [$5^{12}6^2$] for the sites, to be compared with 71(3) and 91(4)% previously found [4]. The decrease is significant, and it is possibly due to a loss of gaseous cage-content. The sample of melanophlogite used in this study and that used by Tribaudino et al. [4] were collected in an unexposed location at the same time, but the data collection and structure refinement reported in this study were performed two years later. A loss of cage-molecules with time, as already observed in melanophlogite [17], might have occurred. After the inclusion of extra-framework gas molecules in the structure refinement, the residuals in the difference-Fourier function of the electron density became featureless (<0.4 e$^-$/Å^3). The coordinates and anisotropic displacement parameters of all atoms were refined, down to an agreement factor $R_4\sigma(F) = 4.7\%$. Site coordinates, displacement parameters, bond-distance and angles of the silicate framework are in agreement with those previously published (Tables 1 and 2). A list with atom coordinates and displacement parameters is deposited and available from the authors.

2.2. Synchrotron powder diffraction experiments

H*P*-synchrotron X-ray powder diffraction experiments were performed at the 5 A beamline at Pohang Accelerator Laboratory (PAL). A monochromatic synchrotron beam of 0.6888 Å in wavelength and 200 μm in diameter was provided by a sagitally-focusing monochromator and mirrors. The H*P*-experiment was performed using a Merrill–Bassett type diamond anvil cell (DAC), equipped with two type-I diamonds anvils [19] (culet face diameter: 500 μm) and tungsten-carbide supports. Using the anvils, a