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**THE APPLICATION OF *IN SITU* X-RAY DIFFRACTION
FOR THE STUDY OF MINERAL REACTIONS:
THE FORMATION OF LAWSONITE AT 400°C AND 25 kbar**

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The method of *in situ* X-ray diffraction with the influence of temperature and pressure on the sample was successfully applied in Siberian Synchrotron and Terahertz Radiation Centre on the experimental station *Diffraction in hard X-rays*. High-pressure water-containing lawsonite silicate $\text{CaAl}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ is obtained at 400°C and 25 kbar in a diamond anvil cell during the decomposition of laumontite. *In situ* diffractometry of the reaction products helps to determine parameters of the unit cell of lawsonite and phase composition of $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 400°C and 25 kbar.

Keywords: high-temperature and high-pressure diffractometry, diamond anvil cell, synchrotron radiation, lawsonite.

INTRODUCTION

In situ research of phase transitions and states has a number of advantages over quenching experiments that are usually applied to study minerals. Namely, *in situ* experiments allow studying the structure of crystal compounds at current *P-T* parameters. The structural data (such as lattice parameters) help to calculate coefficients of the equations of state that are necessary for correct simulation of high-temperature and high-pressure processes with crystalline phases. The latter include magnetism and metamorphism (solid-phase transformation of minerals), mathematical simulation of which has gained widespread use lately [1, 2].

Today the main equipment for high-temperature and high-pressure *in situ* experiments is a *diamond anvil cell* (DAC). The anvils are two conical diamonds that transmit compressive force to the area of less than 0.5 mm². Depending on the form of diamonds and compression mechanism, these cells can generate pressure of more than 350 GPa [3]. Temperatures in the DAC can be increased using either resistance heating ($\leq 1000^\circ\text{C}$), or laser focusing on the sample (up to 5500°C) [3]. Due to the diamond transparency for many types of radiation, the DAC may be used in optical studies, IR and Raman spectroscopy, and X-ray fluorescence chemical analysis [4]. However, the most widespread experiment in this field is X-ray diffraction. Specific features of the DAC (small sample volume and limitation of the maximum diffraction angle) set high requirements for sources of X-ray radiation, which usually are high-intensity beams of the synchrotron radiation with a small wavelength ($< 0.5 \text{ \AA}$).

A high-pressure water-containing mineral lawsonite $\text{CaAl}_2[\text{Si}_2\text{O}_7](\text{OH})_2 \cdot \text{H}_2\text{O}$ is selected as a sample, that is formed

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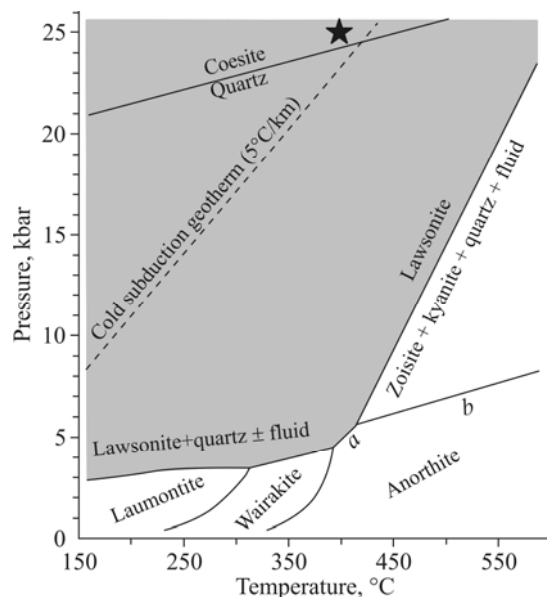
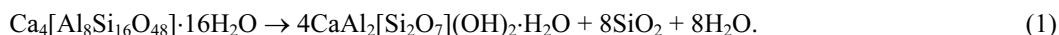


Fig. 1. Mineral equilibria that limit the stability field of lawsonite (grey). Star denotes the conditions of our *in situ* experiment.

during the decomposition of $\text{Ca}_4[\text{Al}_8\text{Si}_{16}\text{O}_{48}] \cdot 16\text{H}_2\text{O}$ laumontite according to the reaction (Fig. 1):



Due to the stability under P – T conditions of the Earth's mantle [5] that are not typical of water-containing minerals, lawsonite has long attracted interest of geologists because of the problem of transporting water to the deep geospheres [6-8].

EXPERIMENTAL

The synthesis of lawsonite and *in situ* X-ray diffraction of CaO – Al_2O_3 – SiO_2 – H_2O at $T = 400^\circ\text{C}$ and $P = 25$ kbar are performed on the equipment of the experimental station *Diffraction in hard X-rays* of Siberian Synchrotron and Terahertz Radiation Centre [9]. A sample of laumontite zeolite from a hydrothermal vein (Nidym river) is used as the original substance. The composition of the sample $\text{Ca}_{3.9}\text{Na}_{0.1}[\text{Al}_{7.9}\text{Si}_{16.1}\text{O}_{48}] \cdot 13.7\text{H}_2\text{O}$ refined by microprobe and thermogravimetric analyses corresponds to the calcium type of this mineral.

Diacell Helios DAC (diameter of the working platform of the anvil ≈ 0.7 mm; $2\theta_{\text{max}} = 25^\circ$) with resistive heating is used to model the subsurface conditions. A slot of 0.35 mm drilled in a nickel-chromium plate INCONEL-718 of 0.13 mm thick is used as a processing chamber. The laumontite powder ground for 1 h is put in the slot, and then the plate is pressed between the diamond anvils. To accelerate the reaction that proceeds through the zeolite amorphisation stage, the experiment is conducted under nonhydrostatic conditions (without the pressure transmitting fluid). The pressure on the anvils is generated by a gas membrane, which is a hollow metal ring that expands when filled with compressed helium. For the pressure in the processing chamber to be 25 kbar the pressure of the membrane should be ≈ 50 atm.

The pressure in the chamber is estimated according to the shift of $R1$ bands in the luminescence spectrum of ruby [10] placed in the cell together with laumontite powder. The luminescence is generated by the semiconductor laser radiation ($\lambda = 532$ nm) and recorded using PRL (BETSA) spectrometer.

The sample is heated to 400°C using an annular resistance heater placed around the anvils. The temperature in the cell is measured with a thermocouple adjacent to one of the anvils near the working platform. To prevent the surface oxidation of diamonds and metal parts during heating an argon hydrogen mixture is used in the cell (1 vol.% H_2). Since an increase in temperature also causes the shift of the luminescence spectrum of ruby, the correction of 6.3×10^{-3} nm/ $^\circ\text{C}$ is used

to accurately measure the pressure [11]. However, the accuracy of the measurement decreases significantly with the increase in temperature due to the expansion and lower intensity of *R1* band as well as superposition of peaks in *R1–R2* doublet.

In situ diffraction starts after the sample is kept at 400°C and 25 kbar for two days. X-ray beam ($\lambda = 0.3685 \text{ \AA}$) reduced by the collimator to 0.2 mm in diameter is centered on the sample using an X-ray sensitive video camera. Diffracted radiation is registered by MAR345 two-dimensional image-plate-detector with 0.1 mm resolution. Altogether 10 powder patterns are made with a 5-hour exposition. After the experiment, NaCl powder is put in the cell to calibrate the sample — detector distance. This calibration helps to eliminate uncertainty in the wavelength.

The powder patterns are processed (integrated) using FIT2D program [12]; to refine the parameters of the lawsonite unit cell and phase composition of the products (1) the profiles obtained are processed using GSAS software [13, 14].

RESULTS AND DISCUSSIONS

The analysis of the powder patterns and the corresponding diffraction profiles (Figs. 2 and 3) shows complete transformation of laumontite zeolite into lawsonite according to the reaction (1) when the sample is kept at 400°C and 25 kbar for two days. An excess of silica is deposited in the form of coesite, a high-pressure modification that is stable under these conditions (Figs. 1 and 3). The profiles made within two days after the exposure do not show any significant changes in the state of the system, which indicates high speed of the reaction (1) at 400°C and 25 kbar.

Along with diffraction of the reaction products (lawsonite and coesite), the powder patterns also demonstrate a number of intense lenticular reflections corresponding to diffraction of the ruby crystal (pressure indicator) in stressed state (Fig. 2). When integrated, these reflections give intense peaks that cannot be accurately described by the profile functions during Rietveld refinement. To eliminate these peaks the reflections need to be eliminated from the integration domain of the powder pattern. The presence of ruby in the sample also affects the phase composition of the system. Reacting with free silica formed according to the reaction (1), ruby generates kyanite, a high-pressure phase (see Fig. 3): $\text{Al}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{Al}_2\text{SiO}_5$. This reaction that deteriorates the properties of ruby as the pressure indicator with the increase in temperature severely limits its application in *in situ* experiments with mineral systems with the excess of silica. An alternative may be rare-earth doped borates [11] displaying greater chemical inertness.

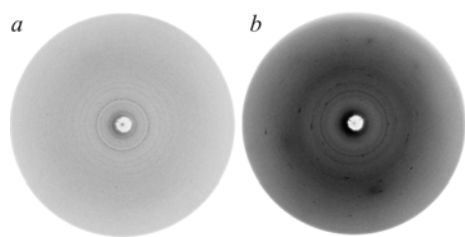


Fig. 2. Powder patterns of laumontite under standard conditions (a) and products of its decomposition at 400°C and 25 kbar (b).

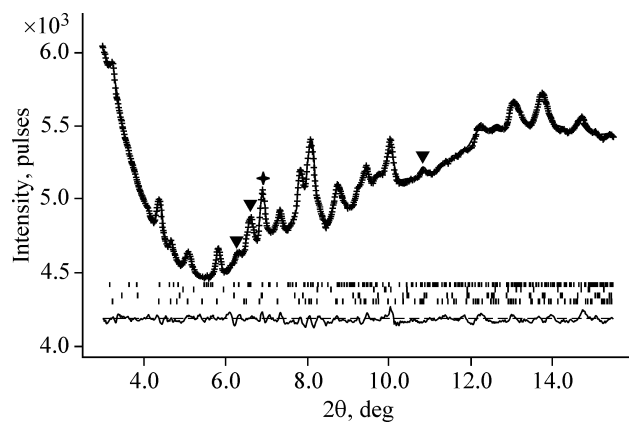


Fig. 3. Refinement results for lawsonite lattice parameters and phase composition of the sample at 400°C and 25 kbar. Independent peaks of coesite and kyanite are marked with a star and triangulars accordingly. Dashes under the profile show the position of reflections of four phases (bottom-up): lawsonite, coesite, corundum (ruby), and kyanite.

The high-quality diffraction profiles obtained at high P – T parameters can be used for full Rietveld refinement to refine the lattice parameters of the basic phase (lawsonite) and determine the proportion of phases in the reaction products. The simulation of the diffraction profile shows that the lawsonite lattice parameters barely change when the profile parameters for the description of the broadened peaks are refined. The obtained values ($a = 5.8060(15)$ Å, $b = 8.788(2)$ Å, $c = 13.084(4)$ Å, $V = 667.6(2)$ Å³, space group $Cmcm$) are similar to the lawsonite lattice parameters under similar P – T conditions previously determined according to the energy-dispersive diffraction data [8].

CONCLUSIONS

The diffraction experiment allows determining the speed of the reaction of lawsonite formation and its lattice parameters at 400°C and 25 kbar. It also helps to reveal the disadvantages of ruby as the pressure indicator at high temperatures and in systems with the excess of SiO₂. This method can be used for *in situ* study of mineral transformations and analysis of the phase structure under high pressure and temperature.

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