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Raman Study of Hydro-Cancrinite Compressed in an Aqueous Medium at High Pressures and Temperatures

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Abstract—In situ Raman spectroscopy is used to study the behavior of synthetic carbonate–aluminosilicate hydro-cancrinite $Na_6Ca_2[(OH,CO_3)_2 Al_6Si_6O_{24}]\cdot 2H_2O$ compressed in an aqueous medium up to 1.6 GPa at 500°C. It is found that hydro-cancrinite retains its crystal structure up to 1.5 GPa and 300°C. It then amorphizes as the temperature rises, partially dissolves, and decomposes into two main products: nepheline and a scheelite-like compound.

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INTRODUCTION

Hydro-cancrinite $Na_6Ca_2[(OH,CO_3)_2Al_6Si_6O_{24}]\cdot 2H_2O$ is a rare mineral—a feldspathoid of complex carbonate-aluminosilicate composition [1]. Cancrinite, an anhydrous form of the mineral, was found for the first time in South Ural in 1839. The name of the mineral was proposed by geologist Gustav Rose, to honor Russian Finance Minister Count Egor Frantsevich Cancrin (1774–1845). Cancrinite is a framework mineral of oversaturated Na-alkaline and strongly SiO_2-undersaturated igneous rocks (nepheline syenites). Synthetic cancrinite is considered a promising piezooptical material [1].

Hydro-cancrinite emerges in natural processes at relatively low (moderate) pressures (i.e., around 1 bar). Its phase transitions and stability at high or moderate *P–T* parameters remain poorly studied, especially in terms of the effect of penetrating and nonpenetrating media. Under these conditions, the behavior of hydro-cancrinite can be a pattern for carbonate and hydroxyl complexes penetrating into silicate structures at high pressures. Studying the stability of this mineral at high (moderate) *P–T* parameters could clarify the question of its participation in different hydrothermal processes in the Earth's crust and at the initial stage of the subsidence of oceanic plates.

Raman spectroscopy at high *P–T* parameters was used in [2–11] to study the behavior of different minerals in a diamond anvil cell, including zeolites (scolecite, natrolite, tomsonite, NaA zeolite), datolite, phengite, and lawsonite. In some cases, there were phase transitions induced by pressure and heating, superhydration [9, 10] and amorphization [10–12], and the dissolution of minerals in water. In some cases, the mineral decomposed into other compounds that were stabler at high *P–T* parameters.

Cancrinite was not under high *P–T* conditions in situ. Due to the geological and practical importance of the mineral, it is of interest to study the behavior of synthetic hydro-cancrinite in an aqueous medium in the range of *P–T* stability via Raman spectroscopy, in order to identify its polymorphous transitions, superhydration, amorphization, and possible transformation into other minerals.

EXPERIMENTAL

In situ Raman spectroscopy was used to study the behavior of synthetic hydro-cancrinite $Na_6Ca_2[(OH,CO_3)_2Al_6Si_6O_{24}]\cdot 2H_2O$ compressed in an aqueous medium at high *P–T* parameters (up to 1.6 GPa, 500°C) with a μScope diamond anvil cell (DAC) (EasyLab, Great Britain) and a tungsten metal gasket (hole diameter, 200 μm) [2–9]. The Raman spectra were recorded on Horiba Jobin Yvon T64000 spectrometers at the Institute of Physics and LabRam HR800 spectrometers at the Institute of Geology and Mineralogy. The monocrystals of hydro-cancrinite were grown via hydraulic autoclaving, using carbonate-aluminosilicate gel [1]. The temperature was measured by a thermocouple with a contact in the upper diamond anvil cell [4, 11]. The pressure was determined via ruby luminescence using the wavelength of the R1 line [4, 12].

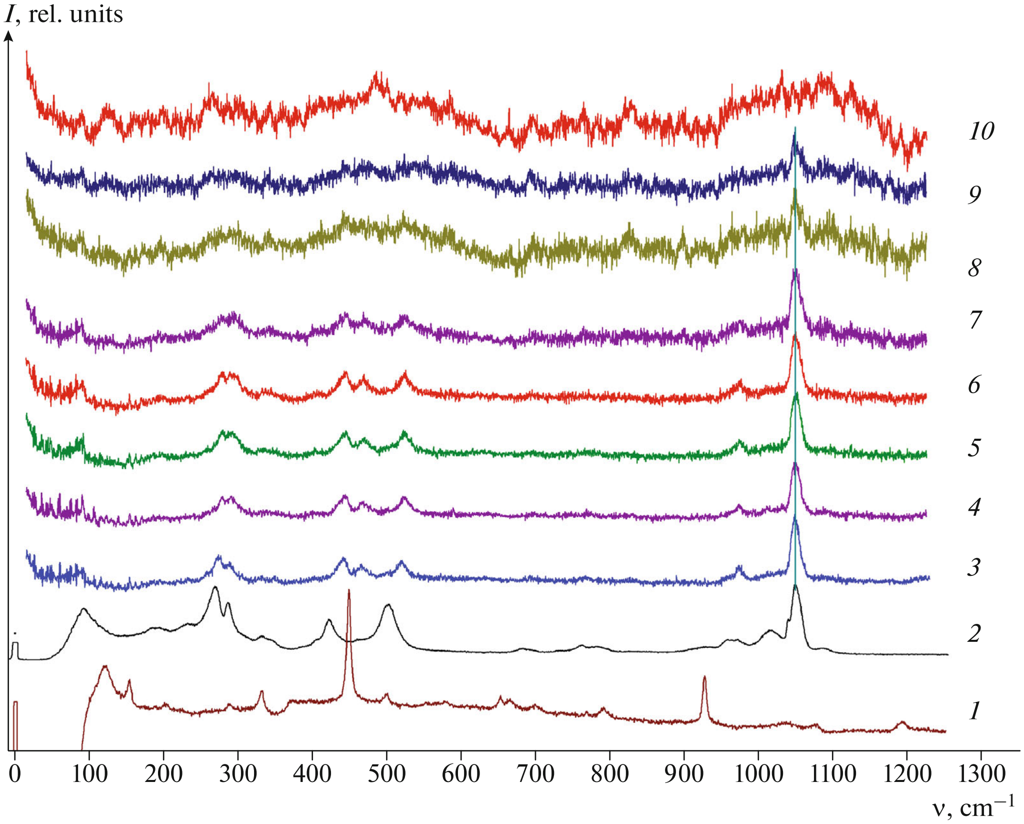

Fig. 1. In situ Raman spectra of hydro-cancrinite $Na_6Ca_2[(OH,CO_3)_2\ Al_6Si_6O_{24}]·2H_2O$ compressed in an aqueous medium at different *P*–*T* parameters (*2*–*10*): (*2*) 10^5 Pa, 23°C; (*3*) 0.11 GPa, 23°C; (*4*) 0.85 GPa, 23°C; (*5*) 0.82 GPa, 95°C; (*6*) 0.91 GPa, 150°C; (*7*) 1.19 GPa, 200°C; (*8*) 1.36 GPa, 250°C; (*9*) 1.58 GPa, 300°C; (*10*) 1.59 GPa, 500°C and (*1*) ex situ spectrum of its products of decomposition recorded in open air at 10^5 Pa, 23°C.

RESULTS AND DISCUSSION

It was found that in an aqueous medium, hydro-cancrinite retains its crystal structure up to 1.5 GPa and 300°C (Fig. 1). The main Rama bands were found to weaken starting at a temperature of 250°C. Wide humps appeared, due to the amorphization of hydro-cancrinite. This led to the emergence of notably wide humps at 400–550 and 1050–1100 cm^{-1} in the Raman spectrum in Fig. 1 (the upper spectrum). A new Raman spectrum appeared when *T* was raised to 500°C. According to our interpretation, it consisted of the spectra of phases 1 and 2, whose ratio of intensity varied in the different segments of the sample. These two phases remained stable during each experiment (5 h) at high *P*–*T* parameters and upon lowering *T* to room temperature and *P* to 1 atm. The Raman bands of both phases were narrow (50% smaller than in the initial mineral) at $T = 23$°C and $P = 1$ atm (Fig. 1). Phase 1 attributed to (Na,Ca)-nepheline $(Na,Ca)AlSiO_4$ had the strongest Raman band at 448 cm^{-1}, near the 466 cm^{-1} band of Na-nepheline $NaAlSiO_4$.

Phase 2 with the main Raman bands at 331 and 927 cm^{-1} was part of the scheelite-type structure. The main Raman bands of scheelite $CaWO_4$ were located at 333 and 912 cm^{-1}, where the latter was more intense. Sodium tungstate dihydrate $Na_2WO_4·2H_2O$ displayed strong bands at 336 and 931 cm^{-1} associated with the characteristic vibrations of the WO_4 tetrahedron, along with the strong broad band of valent OH-vibrations at 3303 cm^1 [13].

Figure 1 shows the strong bands at 331 and 927 cm^{-1} in our Raman spectra (the lower spectrum), while the region of OH-vibrations was covered by strong luminescence that grew along with the wave number. Because of the similarity between the Raman spectrum of phase 2 and the spectrum of tungstate $Na_2WO_4·2H_2O$, we assume that similar tungstate $(Na,Ca)_2WO_4·nH_2O$ of near identical composition (where $n \sim 2$) or its polymorphic phase forms during the decomposition of hydro-cancrinite as a result of the participation of a W-gasket.

Due to the consumption of (Na,Ca) cations for the growth of (Na,Ca) tungstate crystals, there is an excess of the aluminosilicate component, which can form an amorphous or crystalline compound of the Al_2SiO_5-kyanite type, the spectrum of which is shown in Fig. 2 (spectrum *6*). Note that kyanite is a typical product of

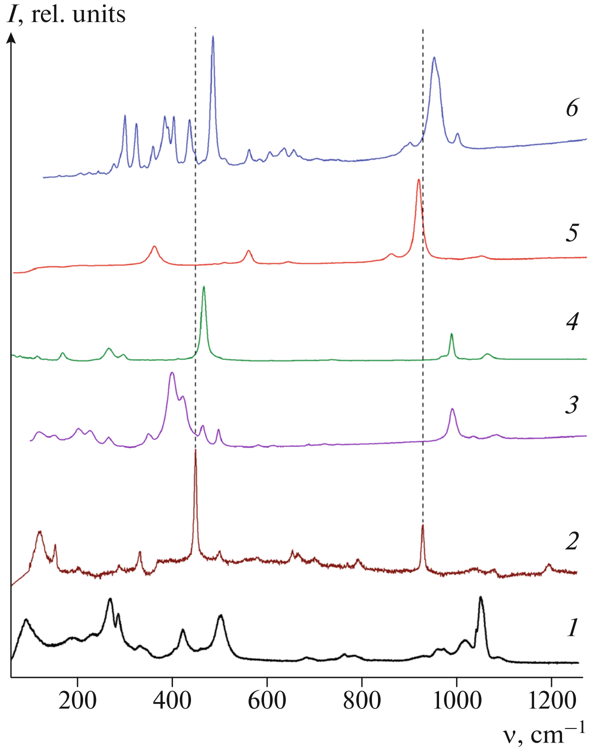

Fig. 2. Raman spectra of hydro-cancrinite, (*1*) for the initial phase and (*2*) for the phase obtained after H*P*–H*T* processing, compared to the spectra of different minerals as potential products of hydro-cancrinite decomposition: (*3*) sodalite, (*4*) nepheline, (*5*) garnet, and (*6*) kyanite.

the decomposition of many hydrated aluminosilicate minerals. Crystalline kyanite was not detected in our experimental products, but this does not preclude the presence of its amorphous form. On the other hand, even though the Raman spectrum of phase 2 is similar to that of garnet, it cannot be garnet, since the latter can only form at high *P*–*T* parameters. Our Raman microprobe analysis revealed no crystalline carbonate phases in the products of hydro-cancrinite decomposition, but this does not preclude their presence in amorphous form.

Hydro-cancrinite retains its initial crystalline phase up to $P = 1.5$ GPa and $T = 300$°C. Upon a further rise in temperature ($T > 300$°C), the mineral amorphizes, partly dissolves, and decomposes into two main products: nepheline and a scheelite-like compound. Nepheline is a typical product of the joint growth or decomposition of anhydrous cancrinite as it grows from a melt (the decomposition of the hydrated mineral was not studied earlier). It turned out that an additional scheelite-like product ($CaWO_4$) emerges with the participation of a metal W-gasket whose partial dissolution leads to the growth of tungstate in the form of thin crystallites, generated first on the cylindrical internal surface of the gasket. The tungstate crystals then grow in number and begin to cover almost the whole volume of the diamond anvil cell, forming a surface layer that impedes Raman microprobe analysis of the internal parts of the sample. Tungstate was also seen form in other aqueous mineral systems when a W-gasket was used in the diamond anvil cell.

CONCLUSIONS

Hydro-cancrinite compressed in an aqueous medium retains its initial phase in the range of *P*–*T* parameters up to 1.5 GPa and 300°C. Upon a further increase in pressure and temperature (up to 1.6 GPa and 500°C) the mineral amorphizes, partly dissolves, and decomposes into several products, two of which were recorded using the Raman technique: nepheline $(Na,Ca)AlSiO_4$ and a scheelite-like compound of projected composition $(Na,Ca)_2WO_4 \cdot nH_2O$. The latter compound resulted from the interaction between hydro-cancrinite and a W-gasket that partly dissolved in an active aqueous medium at high *P*–*T* parameters.

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