Raman spectroscopic study of pressure induced amorphization in Cavansite

T. R. Ravindran\textsuperscript{A*}, A.K. Arora\textsuperscript{A} and G. Parthasarathy\textsuperscript{B}
\textsuperscript{A}Condensed Matter Physics Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
\textsuperscript{B}National Geophysical Research Institute, Hyderabad 500007, India
E-mail: trr@igcar.gov.in

Abstract. High pressure phase transformations in calcium aluminum silicate (cavansite), a rare mineral, are reported up to a pressure of 15 GPa using Raman spectroscopy. Structural transformations are indicated at 1, 4, 6 and 8 GPa followed by amorphization above 15 GPa. The amorphous phase is quenchable to ambient pressure.

1. Introduction
Hydrated calcium vanadium silicate (Ca(VO)Si\textsubscript{4}O\textsubscript{10} \cdot 4H\textsubscript{2}O) - mnemonically known as cavansite - is a rare mineral that crystallizes in an orthorhombic structure with four formula units per unit cell. This brilliant blue (or greenish blue) coloured mineral was first discovered in the year 1960 in Oregon, USA. Excellent crystals of cavansite have been obtained from the zeolite mines at Wagholi, near Pune, India. Its structural, mineralogical and thermal properties have been reported \cite{1,2}. The structure of cavansite consists of silicate tetrahedra linked by vanadyl groups resulting in an infinite framework of vanadium silicates. This open structure is analogous to zeolites and other materials with negative thermal expansion (NTE) that also exhibit pressure induced amorphization \cite{3}. Many complex silicate minerals have been found to turn amorphous at high pressure \cite{4}. Here we report the first high pressure Raman spectroscopic study of cavansite.

2. Experimental
Crystalline samples were obtained from afore mentioned mines at Wagholi. X-ray diffraction pattern recorded at ambient conditions confirmed that the crystals are of good quality. Crystalline fragments of dimensions about 50-100 microns were loaded into a compact, symmetric diamond anvil cell with ruby pressure markers of a few microns size; 4:1 mixture of methanol and ethanol was used as pressure transmitting medium. Pressure measurement and sample spectra were recorded from the same spot without moving the DAC to avoid error in pressure measurement. This was possible because of the small size of the ruby chips and the high intensity of its luminescence signal. Raman spectra were recorded using a Renishaw Invia micro-Raman system with 514 nm laser excitation.
3. Results and discussion:
Cavansite crystallizes in a centro-symmetric orthorhombic unit cell (space group \( D_{2h}^{16} \)) with four formula units per primitive cell. Factor group analysis (Bhagavantam and Venkatrayudu method) results in the following irreducible representation

\[
\Gamma_{\text{Total}} = 46A_g + 41B_1g + 46B_2g + 41B_3g + 41A_u + 46B_1u + 41B_2u + 46B_3u
\]

The first four modes are Raman active, Au are optically inactive and the others are IR active, so there are 174 Raman active and 133 IR active modes expected from the crystal. However, at ambient conditions cavansite exhibits 36 Raman bands, some of which could be overtones and combinations. Less number of modes than predicted by group theory is not uncommon and could be due to accidental degeneracy or low Raman scattering cross section. The modes below 300 cm\(^{-1}\) are lattice modes; those in the region of 500-800 cm\(^{-1}\) are due to Si-O bonds and 900-1000 cm\(^{-1}\) due to V-O bonds. A band about 3546 cm\(^{-1}\) with three shoulders arises from the four molecules of water of crystallization.

As pressure is increased to 1.1 GPa (Figs. 1 - 3) there are qualitative changes in the spectrum: the bands at 90 and 935 cm\(^{-1}\) disappear and the most prominent internal mode at 981 cm\(^{-1}\) undergoes significant softening. Even more dramatic is the appearance of new Raman bands in the region 2800-3400 cm\(^{-1}\), above the second order features of the diamond anvils (not shown in the figure). These new bands - that could be due to hydrogen atoms of water making weak bonds with other atoms such as Si or V - appear at 2856 and 2960 cm\(^{-1}\); the water bands get closer to each other and become less distinguishable from one another. As the pressure is increased to 1.6 GPa the spectral features change again: new modes appears at 337 and 957 cm\(^{-1}\), the water bands around 3544 cm\(^{-1}\) intensify before splitting into three distinct modes at higher pressures. Most of the Raman modes show the usual behavior of hardening as pressure is increased; a few modes such as 236 and 958 cm\(^{-1}\) show softening. Above 14 GPa the lattice modes disappear; internal modes broaden and merge into four broad modes, at 332, 640, 717 and 973 cm\(^{-1}\), indicating a possible transformation into an amorphous state. The transition into the amorphous state is irreversible.

Examination of the \( \omega \) vs. \( P \) plot (fig. 4) shows also the following: There are large changes at 1.1 GPa: there is a down-shift of frequency from 90 to 76 cm\(^{-1}\), 112 to 106 cm\(^{-1}\), and an up shift from 133 to 141 cm\(^{-1}\), and disappearance of the mode at 164 cm\(^{-1}\). Additionally, new modes appear at 2856, 2960, 3236 and 3424 cm\(^{-1}\). At 3 GPa the mode at 600 cm\(^{-1}\) splits into two and a new mode at 964 cm\(^{-1}\) appears. In the pressure range 4-5 GPa, a new mode appears at 453 cm\(^{-1}\) and the modes at 254 and 270 cm\(^{-1}\) merge into a single one at 259 cm\(^{-1}\); as the pressure is increased further, the mode at 215 cm\(^{-1}\) splits into 3-4 modes at 6 GPa; similar splitting of modes occurs at 8 GPa for the 221 cm\(^{-1}\) mode; the mode at 1050 cm\(^{-1}\) disappears between 6 and 7 GPa; a new mode at 1116 cm\(^{-1}\) appears and the slope of the 989 cm\(^{-1}\) mode changes above 8 GPa; all the modes disappear and merge into broad, weak modes about 250, 340, 630, 700 and 925 cm\(^{-1}\) at 15 GPa. These results indicate possible phase transformations around 1, 4, 6 and 8 GPa followed by amorphization above 15 GPa.

Studies of phase transformations of calcium silicates at high pressure are scarce. There are only a few Ca silicates whose high pressure behaviour is well documented. Anorthite (CaAl\(_2\)Si\(_2\)O\(_8\)) disproportionates into a mixture of grossularite (Ca\(_4\)Al\(_2\)-Si\(_3\)O\(_{12}\)) + kyanite (Al\(_2\)SiO\(_3\)) + quartz (SiO\(_2\)) at pressures above 3 GPa [5]. At 15 GPa the quartz component transforms into stishovite (SiO\(_2\)) [6]. A nonquenchable phase was observed at pressures greater than 22 GPa [4]. Both CaSiO\(_3\) • 10% Al\(_2\)O\(_3\) and CaMgSi\(_2\)O\(_6\) • 10% Al\(_2\)O\(_3\) crystallize in a garnet-type structure in the pressure range 100-150 kbar [7]. CaSiO\(_3\) transforms to a cubic perovskite-type structure at about 15 GPa as detected by in situ X-ray diffraction.
Fig. 1. Raman spectra of cavansite at different pressures. Changes are clearly seen around 100, 340, 600 cm⁻¹

Fig. 2. Raman spectra of cavansite at different pressures. Changes can be seen about 935, 950 cm⁻¹
Fig. 3. Raman spectra of cavansite at different pressures. New bands appear about 2856 and 2960 cm\(^{-1}\) at 1.1 GPa; water bands around 3546 cm\(^{-1}\) undergo drastic changes.

Fig. 4. \(\omega\) vs. \(P\) for cavansite. Changes are noticeable at 1, 4, 6, 8 and 15 GPa.
A possible decomposition of cavansite into its isochemical mixed oxides is as follows: \( \text{Ca(VO)Si}_4\text{O}_{10} \Rightarrow \text{CaO} + \text{VO}_2 + 4\text{SiO}_2 \). It can be expected that at high temperature and pressure, cavansite would decompose into these oxides if the combined molar volumes of the daughter phases is lower than the original cavansite. It is possible that amorphization of cavansite takes place at 15 GPa due to insufficient kinetics for decomposition: at a sufficiently high temperature, cavansite may decompose into its daughter phases above (\( \text{CaO}, \text{VO}_2 \) and \( \text{SiO}_2 \)) rather than amorphizing. Since at ambient temperature the mobility of the constituent atoms is not enough for the daughter phases to nucleate and grow, the structure settles into an amorphous state that is of the lowest energy. It is noteworthy that recent, extensive investigations on the structure and chemical composition of cavansite by Ishida et al [8] have revealed that it contains \( \text{H}_2\text{O}^+ \) and \( \text{OH}^- \) species in addition to \( \text{H}_2\text{O} \), and the correct structural formula is \( \text{Ca(VO)(Si}_4\text{O}_{10})(\text{H}_2\text{O})_{4-2x}(\text{H}_3\text{O})_x(\text{OH})_x \) rather than \( \text{Ca(VO)}\text{Si}_4\text{O}_{10}\cdot4\text{H}_2\text{O} \). The latter applies only to pentagonite, a mineral that coexists with cavansite but crystallizes with a different space group motif (\( \text{Ccm}_2 \)) in the orthorhombic structure [2]. The difference between the structures of the two minerals is essentially in the manner in which some of the \( \text{H}_2\text{O} \) units are split as \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) in the lattice. This does not, however, affect the present analysis, since water molecules are not considered in the above decomposition; molecules of water of crystallization do seem to play a role in the phase transformations as seen from the Raman spectra, and this aspect needs further investigation.

References

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