Phys Chem Minerals (1991) 18:126–130

PHYSICS AND CHEMISTRY OF MINERALS

# Raman Spectra from the $Al_2SiO_5$ Polymorphs at High Pressures and Room Temperature

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Received September 5, 1990 / Accepted March 6, 1991

**Abstract.** Raman spectra of the three $Al_2SiO_5$ polymorphs; andalusite, sillimanite and kyanite were recorded as a function of pressure at room temperature. All the Raman active bands which could be observed from the high-pressure cell showed a linear pressure dependence for each of the three $Al_2SiO_5$ polymorphs and no phase changes were observed over the pressure ranges used in this study. In andalusite and to a lesser extent in sillimanite, vibrations which could be correlated with internal motions of the $SiO_4$ tetrahedra were generally well separated from the lattice modes and showed a greater pressure dependence than that observed for other modes. The distinct pressure dependence of the internal $SiO_4$ modes is less evident in kyanite, probably due to the lack of continuous tetrahedral chains and the fact that the rigid $SiO_4$ tetrahedra now form an integral part of the structural network. At ambient pressure, kyanite also exhibits two fluorescence bands at 705 and 706.2 nm which are due to small amounts of $Cr^{3+}$ in the kyanite crystals. These fluorescence bands showed a non-linear frequency shift as pressure was increased.

## Introduction

The three $Al_2SiO_5$ polymorphs; andalusite, sillimanite and kyanite provide an interesting system where aluminium occurs in three different types of coordination. Octahedral coordination is found in all three polymorphs but aluminium also occurs in tetrahedral coordination in sillimanite and in five-fold trigonal bipyramidal coordination in andalusite. Kyanite is approximately ten percent more dense than the other two, and hence its formation is favoured by high pressures; sillimanite is characteristic of high-grade metamorphic rocks, and hence its formation is favoured by high temperatures; and andalusite is commonly a product of the moderately high-temperature metamorphism, and is the most stable form at ambient conditions.

Room temperature Raman data are presented as a function of pressure up to 104 kbar for andalusite, 153 kbar for sillimanite and 140 kbar for kyanite, respectively. The stability relationships of these three polymorphs have been the subject of several experimental investigations (Richardson et al. 1969; Holdaway 1971; and Salje and Werneke 1982) and cannot yet be considered to have been defined absolutely. Knowledge of the effect of pressure on the Raman spectra of these polymorphs will increase the understanding of bonding and the interatomic forces which affect the stability relations and phase transformations that occur in the $Al_2SiO_5$ system.

## Experimental

The specimen of andalusite was obtained from Kanmantoo, South Australia while the kyanite and sillimanite were obtained from the Harts Range, Northern Territory, Australia. The minerals were checked for homogeneity and purity by obtaining electron probe

**Table 1.** Electron microprobe analyses (oxide wt%) and atomic formula (5 oxygens) of $Al_2SiO_5$ polymorphs

| | Andalusite | | Kyanite | | Sillimanite | |
|---|---|---|---|---|---|---|
| | Wt% | Atoms | Wt% | Atoms | Wt% | Atoms |
| $SiO_2$ | 36.63 | 0.9906 | 36.31 | 0.9928 | 35.79 | 0.9856 |
| $TiO_2$ | <0.02 | | <0.02 | | <0.09 | |
| $Al_2O_3$ | 63.04 | 2.0094 | 61.86 | 1.9931 | 62.03 | 2.0130 |
| $Cr_2O_3$ | <0.03 | | 0.39 | 0.0084 | <0.10 | |
| FeO | 0.17 | 0.0038 | 0.53 | 0.0121 | 0.40 | 0.0092 |
| MnO | <0.02 | | <0.02 | | <0.10 | |
| NiO | <0.03 | | <0.03 | | – | |
| MgO | 0.02 | 0.0009 | <0.02 | | <0.10 | |
| CaO | <0.02 | | <0.02 | | <0.06 | |
| $Na_2O$ | <0.02 | | <0.02 | | <0.14 | |
| $K_2O$ | <0.01 | | <0.01 | | <0.05 | |
| Total | 99.87 | 3.0047 | 99.09 | 3.0064 | 98.23 | 3.0079 |

microanalyses from several regions in each crystal and typical analyses are presented in Table 1.

In the high pressure experiments, a single crystal with dimensions ca. 20 × 30 × 80 μm was placed in the gasket hole (ca. 200 μm in diameter) of a diamond-anvil pressure cell. A small chip of ruby was also placed inside the gasket hole for pressure determination by the ruby fluorescence technique. An ethanol-methanol (1 : 4) mixture was introduced as the pressure-transmitting medium and yielded hydrostatic pressures up to at least 105 kbar, at room temperature.

Raman spectra were typically recorded from 200 to 1150 $cm^{-1}$ on a Microdil 28 Raman microprobe (Liu and Mernagh 1990) using a spectral bandpass of ca. 4 $cm^{-1}$. The samples were examined with approximately 60 mW (at the sample) of 514.5 nm laser excitation from a spectra Physics Model 2020 argon ion laser. An Olympus ULWD 50 × microscope objective was used to focus the laser beam to a spot ca. 2 μm in diameter. Wavenumbers are accurate to $\pm 1$ $cm^{-1}$.

## Results and Discussion

Raman and infrared spectra of andalusite at ambient pressure have been reported by Alvarez and Coy-yll (1978) and Iishi et al. (1979). Those for sillimanite and kyanite at ambient pressure were presented by Salje and Werneke (1982) and McMillan and Piriou (1982), respectively. The Raman spectra recorded at ambient conditions in this study are shown in Fig. 1. They agree well with the previously reported spectra although fewer bands were observed in our spectra as a complete polarization study was not attempted.

### *Andalusite*

The crystal structure of andalusite was refined by Burnham and Buerger (1961) and confirmed by Winter and Ghose (1979) and is composed of chains of edge-sharing $AlO_6$ octahedra parallel to the *c*-axis, which are linked laterally by $SiO_4$ tetrahedra. Aluminium atoms $[Al_{(2)}]$ occupy the large holes between each set of four linking tetrahedra and each have five nearby oxygen atoms. Thus, the andalusite structure can be considered to be composed of $SiO_4$ tetrahedra, $AlO_6$ octahedra, and 5-coordinated $AlO_5$ trigonal bipyramidal groups.

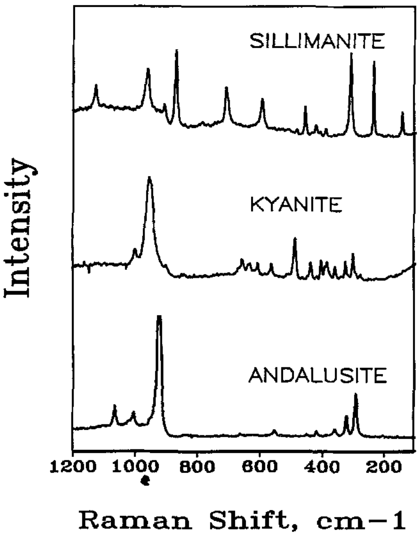

**Fig. 1.** Raman spectra of the three $Al_2SiO_5$ polymorphs; andalusite, kyanite and sillimanite at ambient conditions

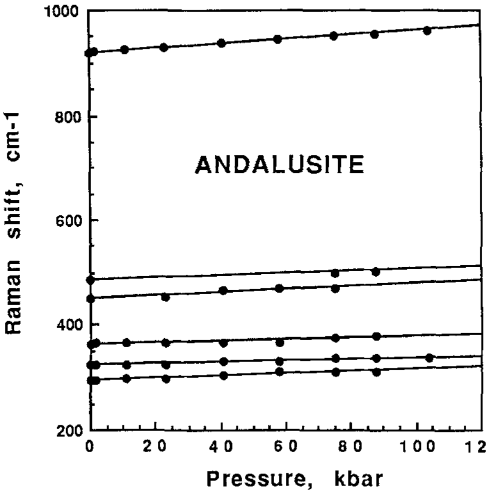

**Fig. 2.** Plot of observed Raman frequencies versus pressure for andalusite

The frequency shift of the Raman bands of andalusite as a function of pressure up to 104 kbar are shown in Fig. 2. Due to the presence of a high fluorescent background in the Raman spectra recorded from the diamond-anvil cell only 6 bands could be reliably measured as a function of pressure. These bands all showed a linear increase in wavenumber with increasing pressure and no phase changes were evident. The pressure dependences and mode-Gruneisen parameters for each of the observed Raman bands are given in Table 2.

The $SiO_4$ vibrations have been observed (Iishi et al. 1979; McMillan and Piriou 1982) to dominate the vibrational spectra of the $Al_2SiO_5$ polymorphs and this implies that the aluminate polyhedra only weakly interact with the silicate tetrahedral vibrations. The high frequency modes of andalusite have been correlated with the $\nu_1$ and $\nu_3$ vibrational modes of the free $SiO_4$ ion (Alvarez and Coy-yll 1978; Iishi et al. 1979). The $A_g$ mode observed at 920 $cm^{-1}$ (at ambient conditions) is the most sensitive to pressure and shifts at approximately twice the rate of the other bands. This band has been attributed mainly to symmetric stretching of all the Si-O bonds of the silicate tetrahedron (Iishi et al. 1979). However, Ralph et al. (1984) have found that the $Si\text{-}O_{(b)}$ bond length decreases with increasing pressure while the shorter $Si\text{-}O_{(c)}$ and $Si\text{-}O_{(d)}$ bonds remain virtually unchanged. The results of the present study also suggest that this band results mainly from the stretching of the $Si\text{-}O_{(b)}$ bond and hence better corresponds to the $\nu_{12}$ vibration described by Iishi et al. (1979). Thus, with increasing pressure the length of the $Si\text{-}O_{(b)}$ bond decreases and this results in a higher vibrational frequency which leads to the observed increase in wavenumber of the 920 $cm^{-1}$ band.

The inverse relationship between temperature and pressure effects on the crystal structure of andalusite

**Table 2.** Pressure dependences and mode-Gruneisen parameters$^a$ of the Raman-active modes of the three $Al_2SiO_5$ polymorphs which could be reliably measured at high pressures

| Andalusite | | | Sillimanite | | | Kyanite$^d$ | |
|---|---|---|---|---|---|---|---|
| $\nu_i^b$ | $d\nu_i/dP^c$ | $\gamma_i^a$ | $\nu_i$ | $d\nu_i/dP$ | $\gamma_i$ | $\nu_i$ | $d\nu_i/dP$ |
| | | | 1126 | 0.42 | $0.62 \pm 0.06$ | | |
| | | | 962 | 0.56 | $0.97 \pm 0.10$ | 952 | 0.36 |
| 920 | 0.42 | $0.72 \pm 0.07$ | | | | | |
| | | | 871 | 0.50 | $0.96 \pm 0.09$ | | |
| | | | 708 | 0.32 | $0.75 \pm 0.07$ | | |
| | | | | | | 669 | 0.20 |
| | | | 594 | 0.25 | $0.70 \pm 0.07$ | | |
| | | | | | | 562 | 0.21 |
| 485 | 0.21 | $0.68 \pm 0.07$ | 483 | 0.56 | $1.93 \pm 0.19$ | 486 | 0.23 |
| 452 | 0.28 | $0.98 \pm 0.10$ | 456 | 0.08 | $0.29 \pm 0.03$ | 437 | 0.27 |
| | | | 421 | 0.21 | $0.83 \pm 0.08$ | 419 | 0.22 |
| | | | | | | 405 | 0.22 |
| | | | | | | 386 | 0.12 |
| 361 | 0.17 | $0.74 \pm 0.07$ | | | | 360 | 0.16 |
| 322 | 0.15 | $0.74 \pm 0.07$ | 311 | $-0.09$ | $-0.48 \pm 0.05$ | 325 | 0.21 |
| 293 | 0.21 | $1.13 \pm 0.10$ | | | | 302 | 0.19 |
| | | | 236 | $-0.13$ | $-0.92 \pm 0.09$ | | |
| | | | 143 | 0.002 | $0.023 \pm 0.002$ | | |

[a] Mode-Gruneisen parameters were calculated using the Reuss bulk moduli from Vaughan and Weidner (1978) and $\gamma_i = (B_o/\nu_i)(d\nu_i/dP)_T$

[b] Initial frequencies ($cm^{-1}$) of the vibrational mode at ambient conditions

[c] Pressure dependences in $cm^{-1}kbar^{-1}$

[d] Mode-Gruneisen parameters could not be calculated for kyanite because the bulk modulus has yet to be determined

has been shown (Ralph et al. 1984) to only be approximately correct. The *c*-axis and the $Al_{(1)}$-$O_{(d)}$ bond deviate most strongly from inverse behaviour. This suggests that the elasticity of andalusite is controlled by the $Al_{(1)}O_6$ octahedra. The data on thermal expansion (Winter and Ghose 1979) and compressibility (Vaughan and Weidner 1978) are in agreement with the measured elastic constants which give $c_{11} < c_{22} < c_{33}$. Iishi et al. (1979) have also found that there are two Raman modes at 1065 and 242 $cm^{-1}$ which have a strong temperature dependence. Ralph et al. (1984) have predicted that with increasing pressure the 1065 $cm^{-1}$ band would remain virtually unchanged while the 242 $cm^{-1}$ would increase in frequency. Unfortunately, these modes could not be observed in the present study but the 962 $cm^{-1}$ band of sillimanite (see below) which is thought to correspond to the 1065 $cm^{-1}$ of andalusite (Salje and Werneke 1982) actually shows the greatest pressure dependence of all the bands. More work on the effect of pressure on these bands of andalusite is required before this problem can be solved but it is clear that the $SiO_4$ modes are well separated from other lattice modes. The $SiO_4$ tetrahedra behave as a rather rigid group but generally the high energy modes show a greater increase in frequency as pressure is increased.

The mode-Gruneisen parameters (see Table 2) calculated from the pressure shifts and the bulk modulus are all similar but show a slight increase towards the lower frequencies. For materials with strong covalent bonding the mode-Gruneisen parameter approaches one (Mernagh and Liu 1991). The mode-Gruneisen parameters for andalusite also give values close to one which is consistent with previous conclusions (Isihi et al. 1979; McMillan and Piriou 1982) that andalusite was best described by covalent $SiO_4$ groups embedded in a more ionic aluminate framework.

## *Sillimanite*

The crystal structure of sillimanite was refined by Burnham (1963a) and confirmed by Winter and Ghose (1979). Sillimanite is characterized by straight chains of edge-sharing $AlO_6$ octahedra parallel to the *c*-axis and in this way it resembles the structure of andalusite. The difference is due to the fact that half of the Al atoms in sillimanite are in 4-fold coordination rather than 5-fold, as in andalusite. Each $AlO_4$ tetrahedron shares three corners with $SiO_4$ tetrahedra, thus forming a unique double chain which is responsible for sillimanite's prismatic habit and its common fibrous character.

An attempt was made to produce sillimanite by heating single crystals of kyanite. However, no sillimanite could be generated even after heating for 10 days at 1200° C and at atmospheric pressure. Raman spectra recorded from the crystals after each heat treatment confirmed the kyanite structure (see below). Previous studies have produced large discrepancies in the position of the kyanite – sillimanite boundary (Richardson et al. 1969; Holdaway 1971; and Salje and Werneke 1982) but these tests also show that the phase transformation is very sluggish at ambient pressure.

Eleven Raman bands of sillimanite could be reliably measured at pressures up to 153 kbar and the results are given in Fig. 3 and Table 2. Once again, no phase changes were observed. The high wavenumber bands

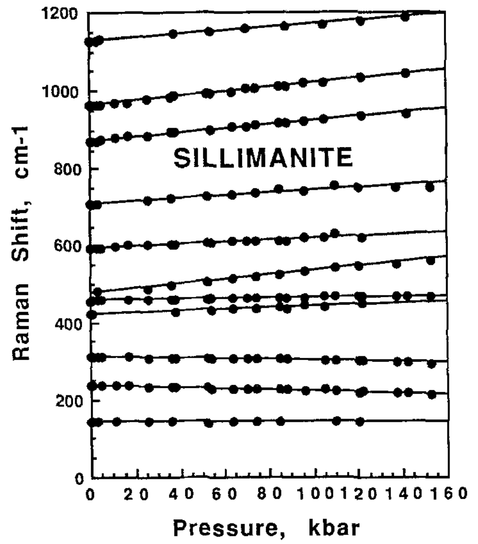

**Fig. 3.** Plot of the observed Raman-active internal and lattice modes of sillimanite as a function of pressure

show a similar and higher pressure dependence than that observed for the other bands of sillimanite. Thus, the internal $SiO_4$ modes are readily distinguishable and the $B_{3g}$ mode at 483 $cm^{-1}$ (under ambient conditions) also shows a similar pressure dependence which indicates that it also corresponds to the $\nu_2$ mode of the free $SiO_4$ ion. The high wavenumber bands are again derived from the $\nu_3$ vibration of the free $SiO_4$ tetrahedron and they can be assigned mainly to Si-$O_{(c)}$ vibrations by using the transformation suggested by Salje and Werneke (1982).

McMillan and Piriou (1982) have suggested that bands in the mid-wavenumber region may be attributed to aluminium – oxygen displacements and have related a band at 700 $cm^{-1}$ in mullite to vibrations of $AlO_4$ tetrahedra. It is difficult to distinguish between the vibrations of the silicate and aluminate tetrahedra of sillimanite in this region but those with lower mode-Gruneisen parameters (see Table 2) are indicative of more ionic bonding and may correspond to vibrations of the aluminate tetrahedra. The double chains of Si and $Al_{(2)}$ tetrahedra, which crosslink the octahedral chains leave open tunnels parallel to the *c*-axis. As the pressure increases, these tunnels permit minor rotations of the chains to occur which leads to a general increase in energy of the tetrahedral vibrations.

The low wavenumber modes show very little pressure dependence and some modes even have a negative slope (see Table 2). These modes are mostly rotational or translational lattice modes and are probably strongly mixed. They are not greatly affected by the rotation of the chains and the corresponding decrease in cell volume which occurs with increasing pressure. The variation in mode-Gruneisen parameters for sillimanite (see Table 2) show that aluminium displacements are having a greater effect on the vibrational spectra and that the $SiO_4$ tetrahedra are not as rigid or structurally isolated as in the case of andalusite.

Order-disorder phenomena in the Al-Si tetrahedra of sillimanite may also effect the Raman spectra and generally causes a broadening of the bands with increasing disorder. However, the relatively sharp Raman bands (see Fig. 1) and the chemical analysis given in Table 1 indicate that the sillimanite used in this study has low levels of Al/Si disorder. It is interesting to note that the andalusite to sillimanite transformation requires exchange of half the $Al_{(2)}$ and Si atoms which perhaps explains the common metastable coexistence of these polymorphs (Kwak 1971).

### *Kyanite*

Kyanite has the smallest unit cell volume of all the $Al_2SiO_5$ polymorphs which is, in part, due to the fact that its structure is based on cubic, close-packed oxygens. Once again, there are chains of $AlO_6$ octahedra which are linked together by the remaining Si, Al and O ions (Burnham 1963b; Winter and Ghose 1979). The aluminium ions are coordinated by 6 oxygen ions and the silicon atoms lie between 4 oxygens which results in independent $SiO_4$ tetrahedra.

Eleven Raman active bands were also observed for kyanite at pressures up to 140 kbar. No phase changes were observed and the frequency dependence as a function of pressure is shown in Fig. 4 and Table 2. Since kyanite is triclinic, it is not possible to directly compare its spectrum with those for the orthorhombic polymorphs. However, the highest wavenumber mode (at 952 $cm^{-1}$ under ambient conditions) once again shows a slightly greater frequency dependence than that for the remaining bands and hence, is likely to be an $SiO_4$ tetrahedral vibration.

The other Raman active modes all show remarkably similar pressure dependences (see Table 2). Since there are no continuous tetrahedral chains parallel to the *c*-axis in kyanite, there is no rigid constraint to compression or expansion in this direction. The $SiO_4$ tetrahedra now form an integral part of the structural network in kyanite and the uniform pressure dependences for most

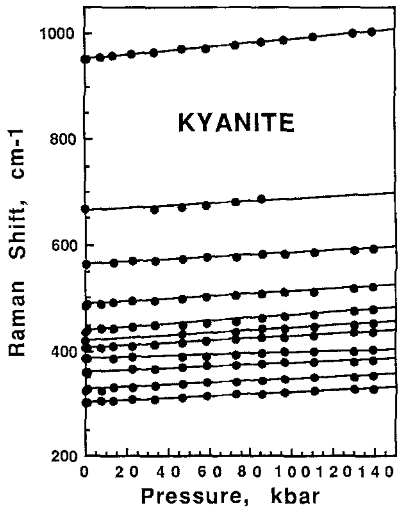

**Fig. 4.** Plot of the observed Raman modes versus pressure for kyanite

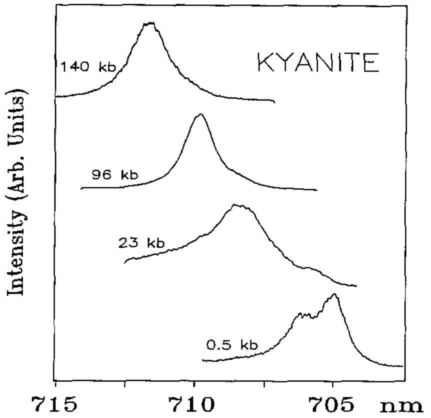

**Fig. 5.** The profile of the fluorescence bands of kyanite as a function of pressure

of the observed modes indicate that the silicate tetrahedra remain relatively rigid with most contraction occurring within the $AlO_6$ octahedra. Therefore, the volume decrease with increasing pressure is more uniformly distributed throughout the crystal which agrees well with the results of Winter and Ghose (1979) who observed a more uniform thermal expansion in kyanite. These two observations suggest that the inverse volume relationship between pressure and temperature, previously observed for andalusite (Ralph et al. 1984), may actually hold true for the case of kyanite.

It is also interesting to note that kyanite exhibits a double fluorescence peak at 705.0 and 706.2 nm at ambient pressure as shown in Fig. 5. These bands are attributed to the small amounts of $Cr^{3+}$ present in our sample (see Table 1) and are probably generated by a mechanism similar to that responsible for the well known ruby fluorescence bands of corundum which have been extensively studied (Barnett et al. 1973).

As pressure is applied to the kyanite crystal the higher frequency band gradually decreases in intensity and merges with the low frequency band which rapidly increases in intensity. During the merger of the two bands the bandwidths are quite broad but at pressures above 50 kbar a single band is observed with a weak shoulder on the high frequency side (see Fig. 5). This band is also sensitive to the onset of non-hydrostatic conditions above about 105 kbar and the *full width at half maximum* (FWHM) increases from approx. 25 $cm^{-1}$ at 96 kbar to 32 $cm^{-1}$ at 140 kbar. In contrast to the case for corundum, the fluorescence bands of kyanite have a non-linear pressure dependence. Thus, these fluorescence bands are not as useful for pressure determinations due to the broadness of the bands, especially at low pressures, and their non-linear pressure dependence.

*Acknowledgements.* We thank R.G. Warren, M.B. Duggan, J.D. Reid and the Bureau of Mineral Resources Museum for providing the crystals used in this study. We are indebted to N. Ware for electron microprobe analyses of the samples. TPM publishes with the permission of the Executive director of the Bureau of Mineral Resources.

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