A new high-pressure phase transition in anorthite (CaAl₂Si₂O₈) revealed by Raman spectroscopy

Isabelle Daniel
Laboratoire de Sciences de la Terre, ENS Lyon and Université Claude Bernard Lyon I (URA 726),
46 allée d'Italie, 69364 Lyon cedex 07, France

Philippe Gillet
Laboratoire de Sciences de la Terre, ENS Lyon and Université Claude Bernard Lyon I (URA 726),
46 allée d'Italie, 69364 Lyon cedex 07, France;
and Institut Universitaire de France

Subrata Ghose
Mineral Physics Group, Department of Geological Sciences, University of Washington, Seattle, Washington 98195, U.S.A.

Abstract

The pressure dependence of the anorthite Raman spectrum has been investigated to 11.4 GPa at room temperature using a single crystal in a diamond-anvil cell. We observe a first-order phase transition on increasing pressure at 2.6 GPa, which is consistent with the $P\bar{1}$-$I\bar{1}$ transition reported in previous X-ray diffraction experiments. Changes in the Raman spectrum also reveal an additional displacive reversible phase transition to a new phase at 10 GPa. Still not fully characterized, the new phase contains much shorter T-O bond lengths, indicating a major change in the compression mechanism above 10 GPa.

Introduction

Phase transitions in feldspars have been extensively studied, including the high-temperature phase transition in anorthite (CaAl₂Si₂O₈), the calcic end-member of the plagioclase solid-solution series. Under ambient conditions, the structure of anorthite is triclinic, space group $P\bar{1}$ (Kempster et al., 1962; Megaw et al., 1962; Wainwright and Starkey, 1971). On increasing temperature, Brown et al. (1963) first reported that anorthite undergoes a displacive phase transition at 623 K (now known to be at 514 K) to a structure with $I\bar{1}$ symmetry. Since then, numerous investigations using a variety of experimental and theoretical techniques have been carried out on the high-temperature $P\bar{1}$-$I\bar{1}$ transition. Its thermodynamic character has been shown to be tricritical in samples with high degrees of Al-Si order (Redfern and Salje, 1987, 1992). A fluctuation-induced transition mechanism has been proposed, in which the high-temperature $I\bar{1}$ state is considered to be a dynamic average of small $P\bar{1}$-type domains (or clusters) (Ghose et al., 1988; Van Tendeloo et al., 1989). Angel (1988) discovered that on increasing pressure at room temperature a $P\bar{1}$-$I\bar{1}$ phase transition also occurs at 2.6 GPa. Single-crystal in situ X-ray diffraction studies have shown that this transition is first order in well-ordered anorthite (Angel, 1992). The high-pressure, low-temperature and high-temperature, low-pressure phase boundaries have very different Clapeyron slopes (Hackwell and Angel, 1995), possibly indicating different mechanisms for the high-temperature and high-pressure transitions. In this paper, we report the results of in situ high-pressure Raman spectroscopic studies of

anorthite. The high-pressure $P\bar{1}$-$I\bar{1}$ transition is described at 2.6 GPa, as is a new phase transition occurring at about 10 GPa.

Experimental methods

The sample used for this work is natural anorthite from Toal della Foja, Val di Passa, Monzoni, Italy (NMNH no. B19995), used earlier by Van Tendeloo et al. (1989) in a TEM study and by Ghose et al. (1993) in a neutron diffraction study. Microprobe analysis indicated that the crystal is pure anorthite (An₁₀₀). A centimeter-size crystal was doubly polished to a thin section of ~30 μm thickness and ~100 μm diameter; chips were cut from it for Raman measurements.

High-pressure experiments were performed in a diamond-anvil cell, using low-fluorescence type IIa diamonds with 600 μm culets. The sample chamber consisted of 200 μm diameter holes drilled in a preindented stainless steel plate about 100 μm thick. A 4:1 methanol-ethanol mixture was used as a pressure medium to achieve a hydrostatic environment. Pressure was determined by the calibrated shift of the R₁ fluorescence line of ruby.

Raman spectra were recorded in a backscattered geometry, with a Dilor XY double substractive spectrograph with premonochromator (1800 g/mm holographic gratings), equipped with confocal optics before the spectrometer entrance and an EGG CCD detector. A microscope with a Mitutoyo 50× long-working distance objective was used to focus the incident laser beam (514.5 nm line of an Ar⁺ laser) into a 2 μm spot and to collect the Raman signal.
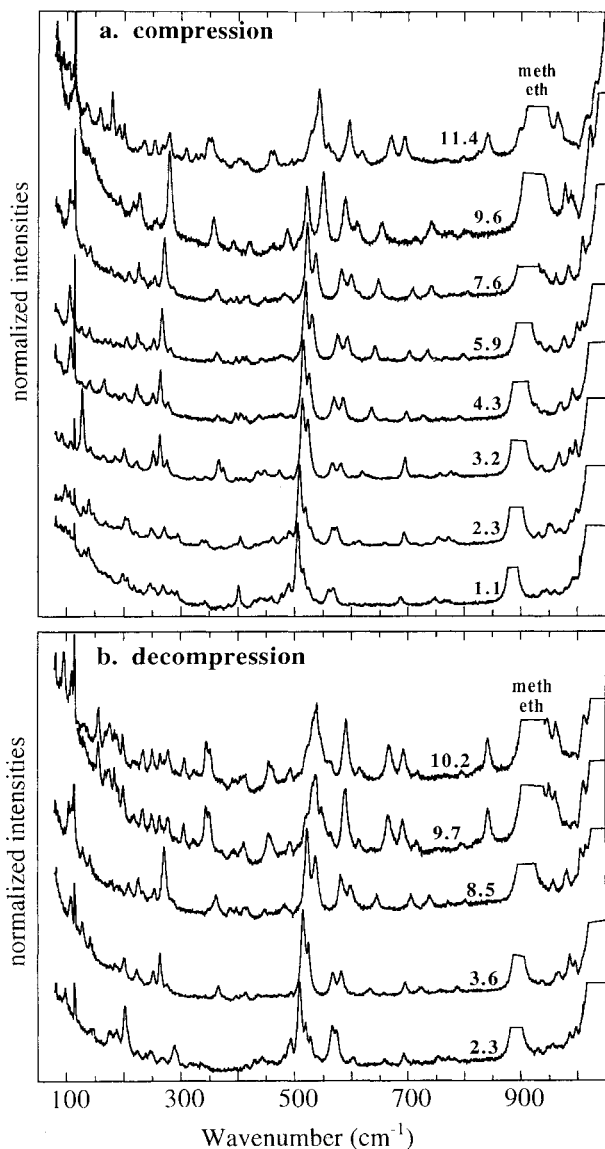
Fig. 1. Pressure evolution of the anorthite Raman spectrum during compression (a) and decompression (b). All spectra intensities have been normalized to the highest intensity in the 500 cm⁻¹ region. Pressures are indicated in gigapascals. The broad bands for which intensity has been cut belong to the Raman spectrum of the methanol-ethanol mixture used as a pressure medium.

Fig. 2. Raman spectra of anorthite across the $P\bar{1}$-$I\bar{1}$ transition. The bold arrows point to new peaks characteristic of the high-pressure $I\bar{1}$ phase, whereas the light arrows show the peaks that disappear at the transition and are intrinsic to the $P\bar{1}$ phase. The asterisks identify the Ar plasma line at 116 cm⁻¹.

RESULTS

For primitive anorthite ($P\bar{1}$) with $Z = 8$, factor-group analysis predicts $156A_g$ (Raman active) + $156A_u$ (IR active) optic modes. The room-pressure Raman spectrum of Val di Passa anorthite, although well ordered (Ghose et al., 1993), displays only 50 bands with frequencies that correlate well with previously published results (White, 1975; Sharma et al., 1983; Matson et al., 1986; Daniel et al., 1995). The observation of fewer bands than the pre-
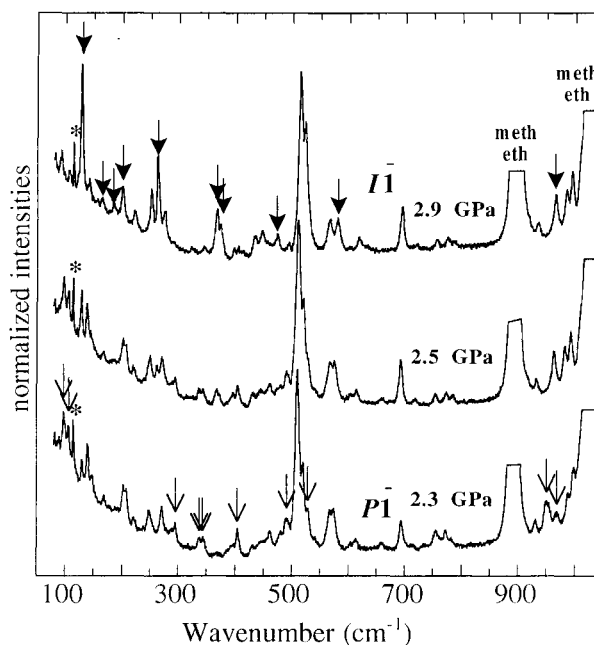
dicted number of modes may be due to accidental degeneracies or weak intensities.

A series of Raman spectra were collected during compression up to 11.4 GPa and during decompression (Fig. 1). On increasing pressure, between 2.3 and 2.9 GPa there are important but progressive changes in the Raman spectra. Intense peaks grow between 2.5 and 2.9 GPa, whereas others, decreasing in intensity between 2.3 and 2.5 GPa, disappear above 2.5 GPa (Fig. 2). The pressure at which these changes occur is in agreement with the $P\bar{1}$-$I\bar{1}$ transition pressure (2.61 ± 0.06 GPa) reported for pure, well-ordered anorthite by Angel and Ross (1988). On decreasing pressure, the phase transition occurs in the same way without any noticeable hysteresis. With increasing pressure further above the transition up to 9.6 GPa, modes related to the $I\bar{1}$ phase shift to higher frequencies. An abrupt change occurs in the Raman spectrum with increasing pressure between 9.6 and 10.3 GPa, indicating a phase change within this pressure range (Fig. 3). Most of the Raman bands are affected by this transition. These changes in the Raman spectra were observed also in complementary experiments using Ar as the pressure medium, suggesting that the transition is not induced by nonhydrostatic stresses developed in alcohol in this pressure range. On decompression, the transition appears to be fully reversible with a slight hysteresis. The $I\bar{1}$ Raman spectrum is restored between 9.7 and 8.5 GPa (Fig. 1b).

DISCUSSION

High-pressure behavior of $P\overline{1}$ anorthite

Upon increasing pressure up to 2.3 GPa, Raman bands shift toward higher frequency without any major change in the spectrum. This is in good agreement with the anorthite structure refinements at 10^5 Pa and 2.5 GPa by Angel (1988). Compression within this pressure range is essentially accommodated by reduction of Ca-O bond distances caused by small flexing of the T-O-T bond angles between essentially rigid tetrahedra.

$P\overline{1}$-$I\overline{1}$ transition

In the 600–800 cm^{-1} region of the Raman spectrum, where bands are due to Al-Si vibrations within the tetrahedral units, no changes occur through the transition, indicating that the tetrahedral units are not affected (Fig. 2). This is consistent with the structural analysis of Angel (1988), in which it was found that there were no significant changes in the average T-O distance or O-T-O bond angles at the transition.

In the Raman spectrum, the transition is marked by a reduction in the number of Raman peaks attributed to symmetric stretching vibrations of the T-O-T bonds [ν_s(T-O-T)] in the 500 cm^{-1} region, confirming the increased symmetry of the $I\overline{1}$ structure. Only the two most intense peaks (513 and 522 cm^{-1} at 2.9 GPa) are still present above the critical pressure. This agrees well with the interpretation of Angel (1988) that the phase transition may be described as a tilting of essentially rigid tetrahedra, marked by a significant change in the T-O-T bond angles involving O atoms at the $m00$ and $mz0$ positions of the $P\overline{1}$ structure at room pressure.

In the high-frequency region of the spectrum, modes are assigned to antisymmetric stretching motions within the T-O-T bonds [ν_s(T-O-T)]. We observe the growth of a unique peak at 962 cm^{-1} (at 2.5 GPa) at the expense of peaks at 954 and 968 cm^{-1} (at 2.3 GPa), which disappear. The 998 and 988 cm^{-1} bands decrease in frequency across the transition.

The low-frequency part of the spectrum, related to lattice modes, is the most strongly affected by the transition. The peaks located at 128, 262, 366, and 373 cm^{-1} above the transition start growing in intensity at 2.5 GPa and become prominent at 2.9 GPa. New peaks are distinguished at 163, 184, and 262 cm^{-1} only above 2.9 GPa. At the same time, some peaks of the $P\overline{1}$ Raman spectrum disappear, e.g., 97, 106, 294, 336, 342, and 404 cm^{-1}, whereas some others decrease in frequency.

High-pressure behavior of $I\overline{1}$ anorthite

The major changes occurring in the Raman spectrum of $I\overline{1}$ anorthite above 2.9 GPa involve the frequency shifts of most of the bands toward higher frequencies. This is the case for all peaks except at 366 cm^{-1} (at 2.9 GPa), which decreases to 356.5 cm^{-1} at 9.6 GPa. The partial softening of the 366 cm^{-1} peak indicates that this mode s probably coupled with some parameters driving the
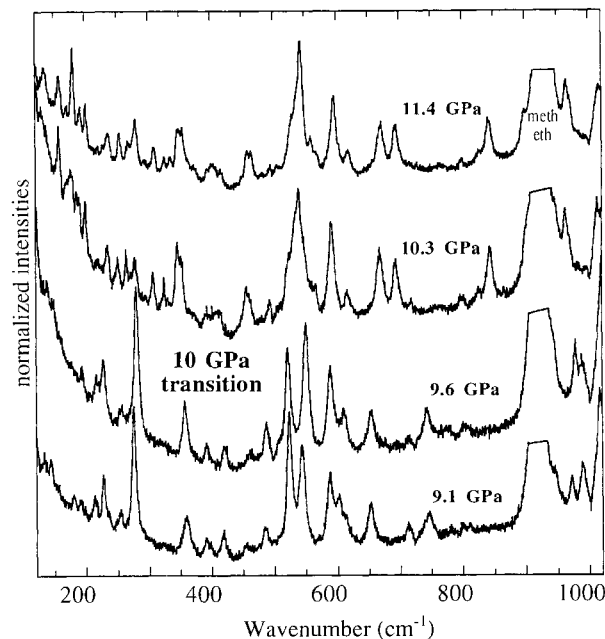

Fig. 3. High-pressure Raman spectra of anorthite showing evidence of a new phase above 10 GPa. Almost all the peaks are affected at the transition. These spectra were recorded with increasing pressure; the transition is fully reversible as shown in Fig. 1b.

phase transition. Noticeable changes in the relative intensities of some bands are also observed between 3.2 and 4.3 GPa, but they are not coupled to any change in the frequency shift of these modes. The 516 cm^{-1} peak, preserved across the $P\overline{1}$-$I\overline{1}$ transition, shows an anomalous behavior when approaching 9.6 GPa (Fig. 4). It shifts rapidly to higher frequencies, reaches 550 cm^{-1} at 9.6 GPa, and becomes more intense than the 506 cm^{-1} peak (at 1.1 GPa); the latter decreases slightly in frequency just below the transition. Such a behavior of the ν_s(T-O-T) modes indicates that, upon compression, some of the T-O-T bond angles decrease considerably, whereas others are relatively insensitive to pressure, leading to a strong distortion of the aluminosilicate framework.

A new transformation at 10 GPa in anorthite

Increasing the pressure from 9.6 to 10.3 GPa induces significant changes in all regions of the spectrum. The major change involves the ν_s(T-O-T) modes, located at 521 and 550 cm^{-1} just below the transition. They collapse to form a broad band centered at 540 cm^{-1} with shoulders at 524 and 560 cm^{-1} that could be interpreted as residuals of the two original peaks. This implies a major change in the T-O-T angle distribution and a different type of distortion of the aluminosilicate framework at pressures above 10 GPa. Changes also affect modes assigned to vibrations of Al and Si atoms within the tetrahedral units. The bands located at 653 and 742 cm^{-1} (9.6 GPa) vanish at the transition, and the bands that

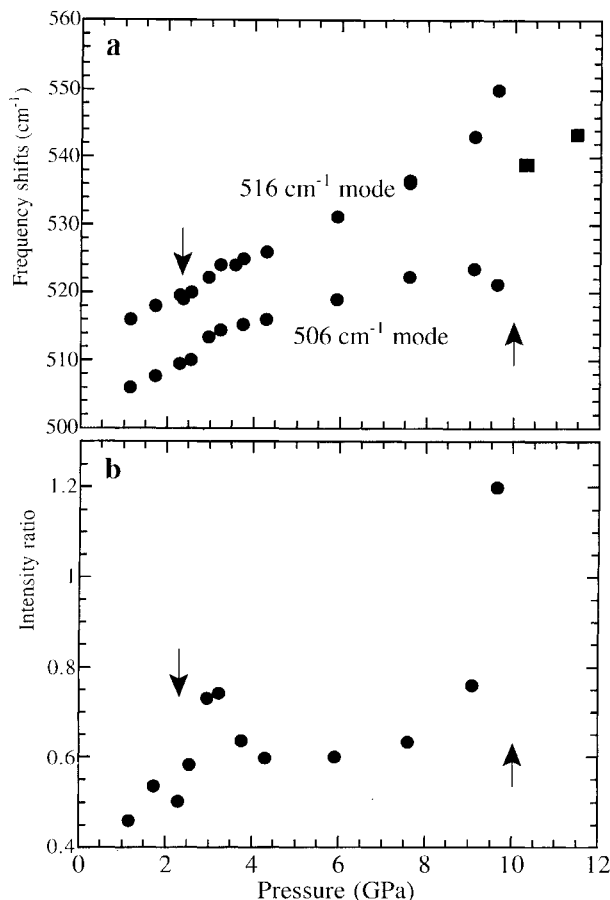Fig. 4. Pressure dependence of the 506 and 516 cm^{-1} Raman mode frequencies (**a**) and of the relative intensities between the 506 and 516 cm^{-1} lines (**b**).

appear in replacement are located at higher frequencies, 667, 694, and 843 cm^{-1} (10.3 GPa), suggesting a significant shortening of the T-O bond lengths. In the low-frequency part of the spectrum, numerous new peaks grow above the transition pressure, and the peaks characteristic of the $I\bar{1}$ phase are lost, indicating that significant changes also occur in the lattice vibrations involving Ca.

ACKNOWLEDGMENTS

REFERENCES CITED

Angel, R.J. (1988) High-pressure structure of anorthite. American Mineralogist, 73, 1114–1119.
——— (1992) Order-disorder and the high-pressure $P\bar{1}$-$I\bar{1}$ transition in anorthite. American Mineralogist, 77, 923–929.
Angel, R.J., and Ross, N.L. (1988) The high pressure phase transitions in anorthites: Consequences for the phase relations of plagioclase. Eos, 69, 498.
Brown, W.L., Hoffman, W., and Laves, F. (1963) Über kontinuerliche und reversible Transformation des Anorthits (CaAl$_2$Si$_2$O$_8$) zwischen 25 und 350 °C. Naturwissenschaften, 50, 221.
Daniel, I., Gillet, P., McMillan, P.F., and Richet, P. (1995) An in-situ high-temperature structural study of stable and metastable CaAl$_2$Si$_2$O$_8$ polymorphs. Mineralogical Magazine, 59, 25–34.
Ghose, S., Van Tendeloo, G., and Amelinckx, S. (1988) Dynamics of a second-order phase transition: $P\bar{1}$ to $I\bar{1}$ phase transition in anorthite, CaAl$_2$Si$_2$O$_8$. Science, 242, 1539–1541.
Ghose, S., McMullan, R.K., and Weber, H.-P. (1993) Neutron diffraction studies of the $P1$-$I1$ transition in anorthite, CaAl$_2$Si$_2$O$_8$, and the crystal structure of the body-centered phase at 514 K. Zeitschrift für Kristallographie, 204, 215–237.
Hackwell, T.P., and Angel, R.J. (1995) Reversed brackets for the $P\bar{1}$ $\rightleftharpoons$ $I\bar{1}$ transition in anorthite at high pressures and temperatures. American Mineralogist, 80, 239–246.
Kempster, C.J.E., Megaw, H.D., and Radoslovich, E.W. (1962) The structure of anorthite, CaAl$_2$Si$_2$O$_8$: I. Structure analysis. Acta Crystallographica, 15, 1005–1017.
Matson, D.W., Sharma, S.K., and Philpotts, J.A. (1986) Raman spectra of some tectosilicates and of glasses along the orthoclase-anorthite and nepheline-anorthite joins. American Mineralogist, 71, 694–704.
Megaw, H.D., Kempster, C.J.E., and Radoslovich, E.W. (1962) The structure of anorthite, CaAl$_2$Si$_2$O$_8$: II. Description and discussion. Acta Crystallographica, 15, 1017–1035.
Redfern, S.A.T., and Salje, E. (1987) Thermodynamics of plagioclase: II. Temperature evolution of the spontaneous strain at the phase transition in anorthite. Physics and Chemistry of Minerals, 14, 189–195.
——— (1992) Microscopic dynamic and macroscopic thermodynamic character of the $P\bar{1}$-$I\bar{1}$ phase transition in anorthite. Physics and Chemistry of Minerals, 18, 526–533.
Sharma, S.K., Simons, B., and Yoder, H.S. (1983) Raman study of anorthite, calcium Tschermak's pyroxene, and gehlenite in crystalline and glassy states. American Mineralogist, 68, 1113–1125.
Van Tendeloo, G., Ghose, S., and Amelinckx, S. (1989) A dynamical model for the $P\bar{1}$-$I\bar{1}$ phase transition in anorthite, CaAl$_2$Si$_2$O$_8$: I. Evidence from electron microscopy. Physics and Chemistry of Minerals, 16, 311–319.
Wainwright, J.E., and Starkey, J. (1971) A refinement of the structure of anorthite. Zeitschrift für Kristallographie, 133, 75–84.
White, W.B. (1975) Structural interpretation of lunar and terrestrial minerals by Raman spectroscopy. In C. Karr, Jr., Ed., Infrared and Raman spectroscopy of lunar and terrestrial minerals, p. 325–358. Academic, New York.