

An in-situ high-temperature structural study of stable and metastable $\text{CaAl}_2\text{Si}_2\text{O}_8$ polymorphs

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Abstract

High-temperature Raman spectroscopy and optical microscopic observations have revealed a new metastable polymorph of $\text{CaAl}_2\text{Si}_2\text{O}_8$ composition, which brings to four the number of known crystalline phases in this system. Similar to the metastable monoclinic pseudo-orthorhombic and pseudo-hexagonal phases, the new polymorph nucleates prior to anorthite, at around 1545 K, and its pseudo-liquidus temperature is 1700 ± 10 K. It can also be formed from the transformation of the pseudo-hexagonal phase at 1050 K. The actual structure of this new crystalline form is unknown, but its Raman spectrum indicates that it is most likely a 6-membered aluminosilicate framework. We have obtained all three metastable phases as pure single crystals using wire loop heating techniques, and have studied their structures via Raman spectroscopy up to their metastable melting points or transformation temperatures.

KEYWORDS: plagioclases, anorthite polymorphs, metastable nucleation, Raman spectroscopy, high temperature.

Introduction

TRICLINIC anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, is the calcic end member of the plagioclase series. Because of the importance of feldspar phase relations for understanding magmatic crystallization processes, the stable melting relations of anorthite have been extensively investigated. In an experimental study, Davis and Tuttle (1952) identified two additional, metastable, polymorphic forms of $\text{CaAl}_2\text{Si}_2\text{O}_8$ as synthetic run products, with hexagonal and orthorhombic morphologies (Fig. 1). The crystal structures of these are different from that of anorthite (Takéuchi

et al., 1973; Ito., 1976). The space groups are monoclinic $C2$ for the pseudo-hexagonal polymorph, and monoclinic $P2_1$ for the pseudo-orthorhombic polymorph. The nucleation, growth kinetics and relationships between the stable and metastable polymorphs of $\text{CaAl}_2\text{Si}_2\text{O}_8$ were investigated in detail by Abe *et al.* (1991).

In the present study, we have used a newly developed furnace technique (Mysen and Frantz, 1992; Richet *et al.*, 1993), which allows us to heat the sample up to 2000 K, and permits both visual observation and *in-situ* characterization of the sample by Raman spectroscopy. In the course of our

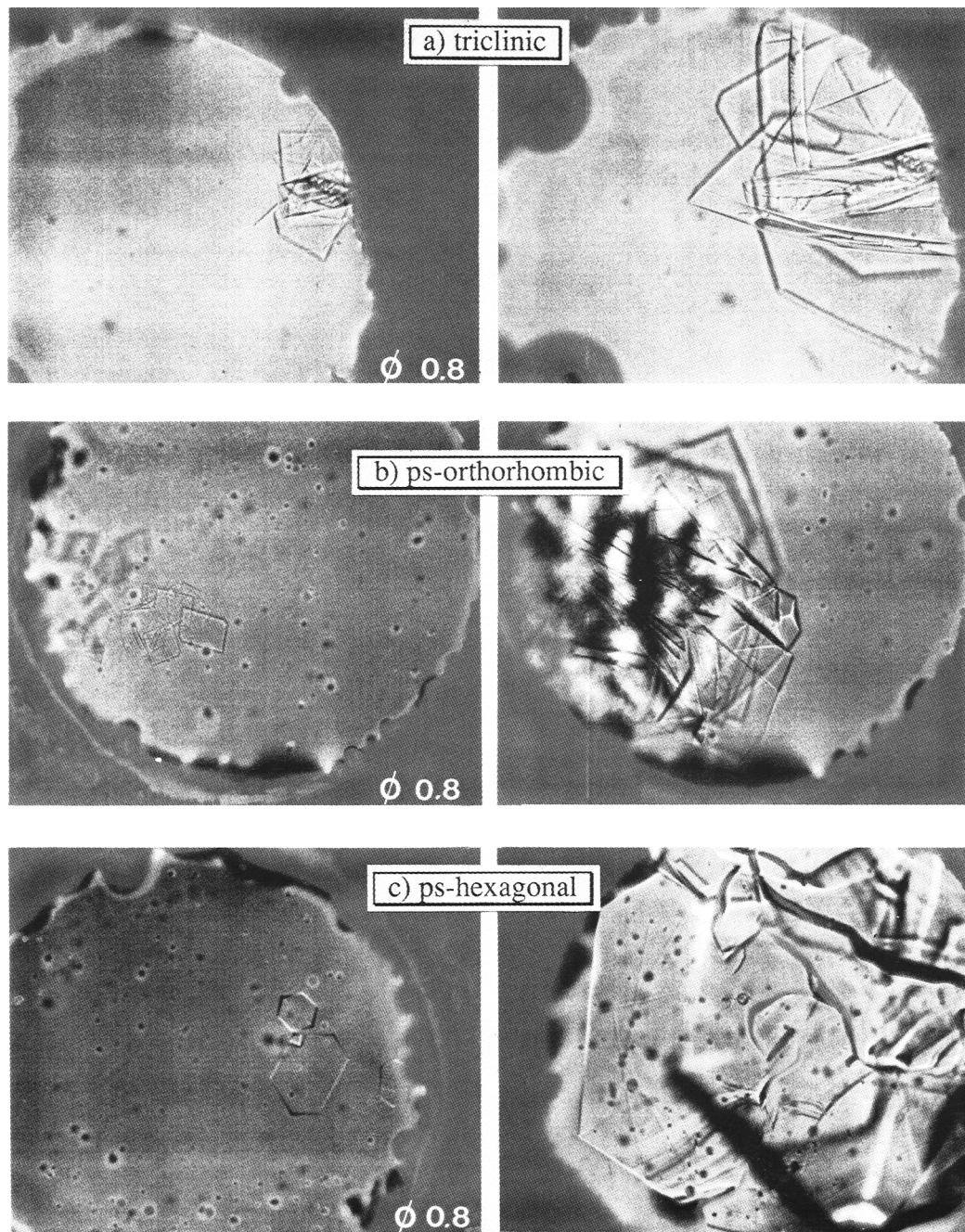


FIG. 1. Characteristic morphologies of crystals growing in the $\text{CaAl}_2\text{Si}_2\text{O}_8$ melts: (a) triclinic at around 1820 K, (b) pseudo-orthorhombic at around 1680 K, (c) pseudo-hexagonal at around 1660 K. The diameter of the hole in the Pt/10%Ir wire is 0.8 mm.

experiments on supercooled CaAl₂Si₂O₈ liquid, crystallization of four different phases was observed. Three corresponded to the stable triclinic form and the known metastable pseudo-orthorhombic and pseudo-hexagonal forms. A new metastable polymorph of currently unknown structure was also observed. The Raman spectra of the four CaAl₂Si₂O₈ polymorphs are reported as a function of temperature, up to their melting or transformation points.

Experimental techniques and samples

The furnace used is a simplified version of that described by Mysen and Frantz (1992). It consists of a Pt/10%Ir wire connected to a 0–10 V, 0–75 A power supply. In order to have a symmetrical and reproducible temperature, the wire is flattened to 500 μm between two cylindrical sapphires, and a 0.8 mm hole is drilled at the centre of the flattened area (Richet *et al.*, 1993). The sample is placed over the drilled hole and melted, so that at the onset of melting the liquid enters the hole and is maintained in it by surface tension. The starting material was the synthetic An₁₀₀ glass prepared by Richet and Fiquet (1991) which was heated and subsequently quenched in the furnace.

Temperatures are obtained by calibrating the furnace power, using a series of known melting point compounds up to 2000 K. Intermediate temperatures are obtained by a numerical interpolation between the known melting points. The melting temperatures are reproducible to within 10 K. The temperature stability is good: for example, in this study, it was possible to maintain a small crystal in equilibrium with its melt for several hours. When solid phases (glass or crystals obtained from complete crystallization of the melt) are heated, a small temperature gradient, lower than 10 K/mm, exists in the furnace (Richet *et al.*, 1993).

With the microscope of the Raman spectrometer, the experimental set-up allowed both viewing of the sample and *in-situ* characterization by Raman spectroscopy. Raman spectra were obtained using a Dilor[®] XY double subtractive spectrograph with premonochromator (1200 g. mm⁻¹ holographic gratings), equipped with confocal optics before the spectrometer entrance, and an EGG CCD detector. The 488 nm line of a Spectra Physics[®] Ar⁺ laser was used for sample excitation. Long-working distance objectives (Leitz[®] UTK 40 and Nikon[®] 20X) were used. The laser spot size at the sample was on the order of 2 μm . The confocal system was important for discriminating against blackbody radiation emitted by the sample and the furnace at high temperature. Above 1300 K the thermal emission of the sample becomes quite intense at these wavelengths, and is superimposed on the Raman spectrum.

The confocal hole is then progressively closed to minimize the recording of the thermal emission from the sample, away from the source of the Raman scattering.

Growth of the different polymorphs

From studies of melting and crystallization relations of anorthite, different metastable polymorphs with CaAl₂Si₂O₈ composition are observed to nucleate in addition to the stable triclinic phase (Davis and Tuttle, 1952; Takéuchi and Donnay, 1959; Takéuchi *et al.*, 1973; Smith and Brown, 1988). The three known polymorphs (triclinic, monoclinic pseudo-orthorhombic and pseudo-hexagonal) are easily identified optically by their growth habits (Abe *et al.*, 1991) (Fig. 1).

In this study, single crystals of triclinic anorthite were obtained by heating a polycrystalline sample to the stable melting point (1830 K). When all but a few crystallites of the sample had melted, the temperature was slowly reduced to induce the growth of crystals of the triclinic phase from the seed crystals (Fig. 1a). The triclinic symmetry of this phase was apparent from its characteristic crystal morphology (Abe *et al.*, 1991) and confirmed by its Raman spectrum (Fig. 2a).

The pseudo-orthorhombic phase was obtained by rapidly (in a few seconds) heating CaAl₂Si₂O₈ glass to 1225 K, and then annealing it at that temperature for 2–5 minutes. The rapid heating results in a slight overshoot of the glass transition temperature, established by slower cooling of a liquid sample (Fig. 3). The characteristic crystal morphology (Fig. 1b) and the metastable melting point of this metastable phase (1693 \pm 15 K) are in agreement with the observations of Abe *et al.* (1991). The same procedure as for the triclinic phase was then used to obtain and quench a few large crystals, by heating to the metastable melting point, then isolating and growing some crystal nuclei.

The pseudo-hexagonal phase described by Abe *et al.* (1991) was grown by rapidly heating anorthite glass to temperatures between 1275 and 1625 K. The effects of rapid heating will be quickly lost in the supercooled liquid regime, as the relaxation time becomes on the order of seconds or shorter. However, the rapid heating allows different nucleation and growth kinetics to be sampled, compared with the stable triclinic phase. The symmetry of the pseudo-hexagonal phase is evident from the crystal morphology (Fig. 1c) and the metastable melting point (1673 \pm 10 K) is also in agreement with Abe *et al.* (1991). Once more, this phase could be grown and quenched to room temperature.

Re-heating of the pseudo-hexagonal phase leads to a reversible transformation to a previously unknown

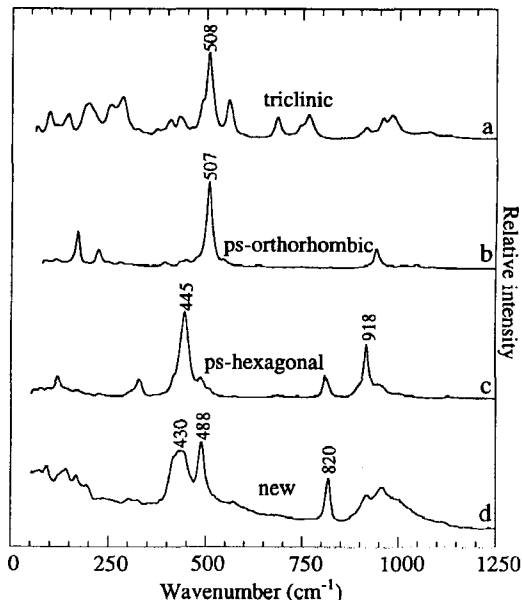


FIG. 2. Raman spectra of the polymorphs of $\text{CaAl}_2\text{Si}_2\text{O}_8$ at ambient conditions: (a) anorthite (triclinic), (b) monoclinic pseudo-orthorhombic phase, (c) monoclinic pseudo-hexagonal phase, (d) new phase. The frequencies (cm^{-1}) are indicated for the strongest Raman peaks.

metastable polymorph, at approximately 1050 K for heating times on the order of minutes. The new phase can be quenched to room temperature by rapid cooling. This new metastable phase can also be produced directly, by rapidly heating $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass to 1545 K, in a few seconds.

Nucleation of corundum (Al_2O_3) or mullite ($2\text{SiO}_2-3\text{Al}_2\text{O}_3$), as reported by Abe *et al.* (1991) was never observed in our high-temperature studies.

These metastable phase relations are summarized in Fig. 3. Triclinic anorthite is the thermodynamically stable phase over the temperature range studied. The glass and supercooled liquid, with a glass transformation range near 1160 K for the heating and cooling rates in these experiments, have higher free energies than the metastable crystalline phases, up to their metastable melting points. The pseudo-hexagonal phase has the lowest melting point, so its $G(T)$ curve crosses that of the supercooled liquid above the crossing points for the pseudo-orthorhombic and new metastable phases. The melting points of these last phases are indistinguishable (1693 K, 1700 K), within the uncertainty of our experiments. The pseudo-orthorhombic phase is observed to crystallize from the supercooled liquid in the region of T_g , suggesting that this phase has the highest free energy

of the metastable crystals at this temperature, consistent with Ostwald's step rule. Because the heating rate in these crystallization experiments was on the order of seconds rather than minutes, we have indicated a likely overshoot of T_g on heating in Fig. 3. However, the pseudo-orthorhombic polymorph has a higher melting point than the pseudo-hexagonal phase, so that their $G(T)$ curves must cross. This crossing is likely in the range 1250–1300 K, because the pseudo-hexagonal phase crystallizes from the supercooled liquid above approximately 1275 K. The 'new' polymorph is obtained reversibly from the pseudo-hexagonal phase by heating above 1050 K, so that their $G(T)$ curves (related by a first-order transition) must cross near this temperature, with the hexagonal phase more stable below this temperature (Fig. 3).

Structures of the different polymorphs

Triclinic anorthite, with space group $P\bar{1}$ is composed of 4-membered-rings of Si and Al tetrahedra (Smith and Brown, 1988). The pseudo-orthorhombic form, with space group monoclinic $P2_1$, has the same 4-membered framework but differs from anorthite by the mode of linkage between the 4-membered-rings (Takéuchi *et al.*, 1973). The pseudo-hexagonal phase, with space group monoclinic $C2$, has a quite different structure and is composed of double hexagonal sheets of tetrahedra cross-linked by Ca atoms (Smith and Brown, 1988).

Similar polymorphism is also known in the Ba-feldspars. $\text{BaAl}_2\text{Si}_2\text{O}_8$ exhibits at least four polymorphs (Lin and Foster, 1968; Pentinghaus, 1980). Monoclinic celsian is stable from room temperature up to 1865 K, where it transforms reversibly to β -hexacelsian with hexagonal symmetry. The latter is the stable form of $\text{BaAl}_2\text{Si}_2\text{O}_8$ which nucleates above 1865 K and it persists metastably on cooling below 1865 K, down to 575 K. On cooling through 575 K, there is a displacive transition to orthorhombic α -hexacelsian. Paracelsian is another monoclinic phase of $\text{BaAl}_2\text{Si}_2\text{O}_8$ and may be the stable low-temperature polymorph in the dry system $\text{BaAl}_2\text{Si}_2\text{O}_8$ (Pentinghaus, 1980). Cymrite ($\text{BaAl}_2\text{Si}_2\text{O}_8 \cdot n\text{H}_2\text{O}$) also has a monoclinic pseudo-hexagonal symmetry, and is composed of 6-membered rings of Al and Si tetrahedra (Drits *et al.*, 1975).

These observations can be used to constrain the structure of the unknown phase in the $\text{CaAl}_2\text{Si}_2\text{O}_8$ system, from its observed Raman spectrum.

Raman spectra at ambient conditions

The Raman spectra of the $\text{CaAl}_2\text{Si}_2\text{O}_8$ polymorphs at ambient conditions are shown in Fig. 2. These spectra

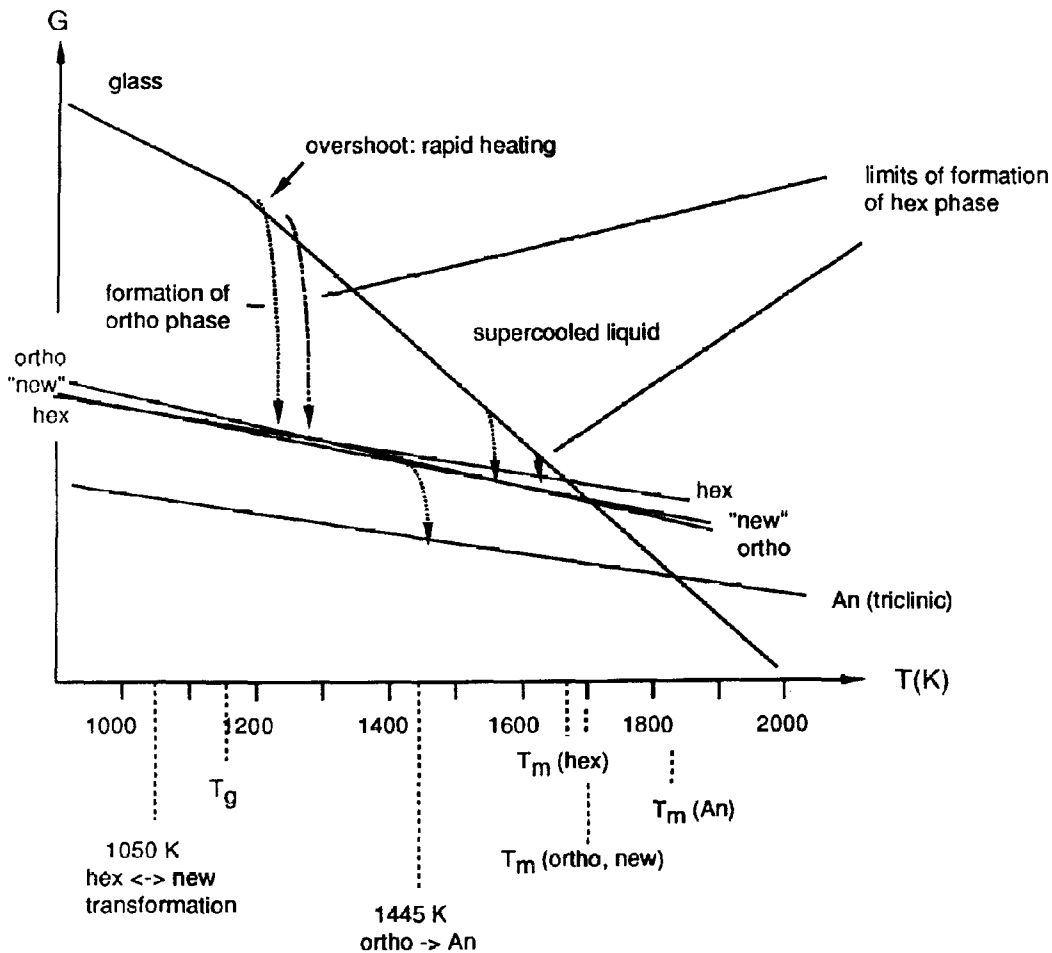


FIG. 3. Proposed metastable phase relations in the CaAl₂Si₂O₈ system at high temperature, constructed using the observed metastable and phase transition temperatures, as discussed in the text.

permit an unambiguous distinction between the different polymorphs, complementary to the optical observations. Differences between the Raman spectra of the polymorphs can be briefly outlined by taking anorthite as a reference (Table 1).

The Raman spectrum of triclinic anorthite (Fig. 2a) is in agreement with results of previous work (McMillan *et al.*, 1982; Sharma *et al.*, 1983; Matson *et al.*, 1986). The assignment of the Raman modes of anorthite has been extensively discussed by Sharma *et al.* (1983).

The Raman spectra of plagioclase feldspars, including the end-members albite and anorthite, are characterized by strong bands at around 500 cm⁻¹, which are assigned to symmetric stretching vibrations of the T-O-T bond [$\nu_s(T-O-T)$]. In general, the weaker high frequency modes between 900 and 1200

cm⁻¹ are assigned to antisymmetric stretching motions within the T-O-T linkages [$\nu_{as}(T-O-T)$]. The highest frequency bands in this range can be attributed primarily to $\nu_{as}(\text{Si-O-Si})$, and the bands at lower frequency to $\nu_{as}(\text{Si-O-Al})$ modes (Iishi *et al.*, 1971). As discussed by Sharma *et al.* (1983), the width, position and relative intensity of these high-frequency modes are indicative of the degree of Al/Si order. The bands in the 600–800 cm⁻¹ region are due to Al or Si vibrations within tetrahedral units, within the fully-polymerized crystalline network. The modes between 80 and 400 cm⁻¹ are related to lattice modes and involve complex bending and twisting motions of the tetrahedra and rings.

Fewer modes are observed for the pseudo-orthorhombic and pseudo-hexagonal polymorphs than for the triclinic form (Fig. 2), as expected by

TABLE 1. Raman frequencies (cm^{-1}) of the $\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8$ crystalline polymorphs

triclinic An #	triclinic An *	orthorhombic form	hexagonal form	new form
63 m			62	
88 m	99 m	88 w	77	77 (sh)
139 m	148 m	113 m	96	92 s
			120 m	
			133 s	131 s
182 m	199 m	171 s	141 (sh)	144 (sh)
200 (sh)	210 (sh)		168 m	169 w
		223 s	197 (sh)	197 w
253 m	259 m	248 (sh)	225 m	
273 m	274 (sh)	279 w		243 m
281 m	286 s		303 (sh)	301 m
316 vw	325 w		329 s	324 m
369 vw	373 vw			
400 w	405 m	394 m		
427 w	430 m	435 (sh)	419 (sh)	417(sh)
	442 (sh)	448 m	445 vs	430 vs
484 (sh)	490 (sh)	479 (sh)	486 m	488 vs
503 vs	508 vs	508 vs	507 w	
553 m	560 s	545 (sh)		
590 vw	598 (sh)		574 w	575 w
620 vw	626 w	635 w		
681 m	685 s		685 m	686 m
741 (sh)	745 (sh)	747 w		
756 w	766 s			
		823 w	809 s	820 s
	900 (sh)		899 (sh)	
908 w	914 m	920 (sh)	916 s	918 s
949 w	959 s	941 s	944 (sh)	958 (sh)
974 m	982 s	975 w		
998(sh)			994 w	987 (sh)
	1018 w	1016 w		
1044 (sh)		1045 m		
1072 (sh)	1079 w	1085 w		
1124 w	1128 w		1128 w	1130 m

Notes: # denotes the data from Sharma *et al.* (1983), and * the present data.
abbreviations: v, very; w, weak; m, medium; s, strong; sh, shoulder.

the higher symmetry of the former. The dominant band occurs at 508 cm^{-1} in anorthite, and 507 cm^{-1} in the pseudo-orthorhombic form. The similar frequency of this $\nu_s(T-O-T)$ mode in anorthite and in the orthorhombic form can be related to their similar 4-membered-ring frameworks. This is consistent with the Raman spectrum of monoclinic celsian, for which the strongest band appears at around 510 cm^{-1} (Graham *et al.*, 1992).

The principal Raman band of the pseudo-hexagonal phase occurs at 445 cm^{-1} . Following

Sharma *et al.* (1983), this can be assigned to a $\nu_s(T-O-T)$ stretching in the 6-membered rings present in this structure. Cymrite ($\text{BaAl}_2\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$), which has a pseudo-hexagonal structure with 6-membered rings of Al and Si tetrahedra (Drits *et al.*, 1975), shows a similar intense band at around 400 cm^{-1} (Graham *et al.*, 1992).

The different $\text{CaAl}_2\text{Si}_2\text{O}_8$ phases also differ in the high-frequency region of their Raman spectra. The spectrum of anorthite contains bands of medium intensity in the $700\text{--}800\text{ cm}^{-1}$ region whereas these

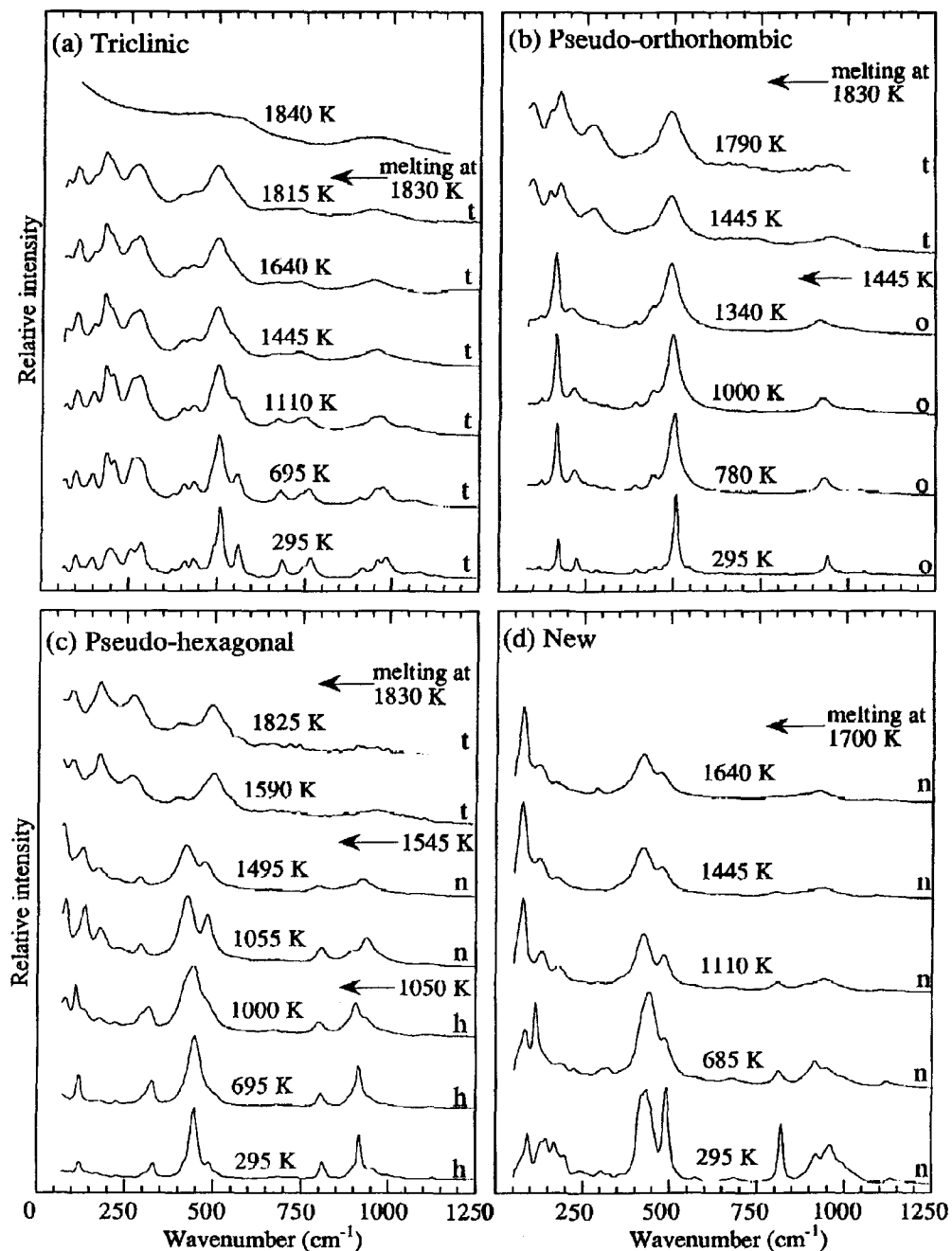


FIG. 4. Evolution of the Raman spectra of the CaAl₂Si₂O₈ polymorphs with increasing temperature. (a) The triclinic anorthite (t) remains stable upon heating and melts at 1830 K. (b) The monoclinic pseudo-orthorhombic polymorph (o) transforms at 1445 K into the triclinic phase (t) which melts at 1830 K. (c) The monoclinic pseudo-hexagonal polymorph (h) transforms successively into a new metastable phase (n) at 1050 K and finally into the triclinic phase (t) at 1545 K. (d) The new metastable polymorph (n) remains metastable up to its pseudo-liquidus temperature (1700 K).

are absent or extremely weak in the pseudo-hexagonal and pseudo-orthorhombic forms. The pseudo-hexagonal form differs from the other polymorphs by the presence of a strong, sharp band at 918 cm^{-1} .

The room temperature Raman spectrum of the 'new' metastable polymorph (Fig. 2d) is characterized by a group of three intense bands between 400 and 500 cm^{-1} . The strongest band at 430 cm^{-1} can be assigned to a $\nu_s(T-O-T)$ stretching in 6-membered rings of Si-Al tetrahedra, analogous to the 445 cm^{-1} band of the pseudo-hexagonal form. The 488 cm^{-1} band could indicate the presence of 4-membered rings in the structure. The spectrum of this polymorph also contains a strong and sharp band at 820 cm^{-1} , analogous to a weaker feature observed in the spectrum of the pseudo-hexagonal form.

Raman spectra and phase changes upon heating

After the different phases were quenched to ambient temperature, they were subsequently reheated. The Raman spectrum of each form was recorded from 295 K up to their respective melting points.

As shown in Fig. 4a, the stable triclinic polymorph does not show any phase transformation upon heating, until it melts at 1830 K. The main changes concern the negative frequency shifts of the Raman modes with increasing temperature, and an increase in the linewidths.

The pseudo-orthorhombic phase remains metastable up to $1445 \pm 10\text{ K}$ where it transforms into stable anorthite (Fig. 4b). The temperature of this phase change did not appear to depend on the dwell time of the experiments (1–30 minutes).

The changes in the spectrum of the pseudo-hexagonal form with increasing temperature are more complicated (Fig. 4c). On initial heating, it transforms rapidly and reversibly at $1050 \pm 10\text{ K}$ into the 'new' metastable phase which exhibits a Raman spectrum very different from those of the three known (triclinic, pseudo-orthorhombic and pseudo-hexagonal) polymorphs. The crystal structure of this new phase has not yet been determined, but its spectrum contains two intense bands (at around 400 and 500 cm^{-1}) which could be related to the existence of both 6 and 4-membered rings in the structure. Further heating of this new phase to higher temperature leads to a transformation into stable triclinic anorthite.

In some runs, the new metastable polymorph also crystallized from the supercooled liquid, and could be quenched to room temperature. It did not transform into anorthite upon re-heating (Fig. 4d); its metastable melting point has been measured to be $1700 \pm 10\text{ K}$.

Conclusions

In complete agreement with Abe *et al.* (1991), the present study confirms that anorthite never nucleates as the first phase from a supercooled melt of the same composition, even at 1350 K, where the incubation time has been measured to be the shortest for the nucleation of anorthite (Uhlmann, 1983). A metastable pseudo-orthorhombic phase nucleates first below 1250 K, whereas the pseudo-hexagonal form nucleates between 1275 and 1625 K. An additional metastable polymorph, first described in this study, nucleates at around 1545 K. The pseudo-liquidus temperature of this new phase was determined to be $1700 \pm 10\text{ K}$. Its Raman spectrum in the $400\text{--}600\text{ cm}^{-1}$ region indicates that the structure of this new phase likely consists of a 6-membered aluminosilicate framework, similar to that of the pseudo-hexagonal form.

Three candidates may be proposed as probable causes of the metastable nucleation of $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Sunagawa, 1992). First, heterogeneous nucleation at the contact with the heater, or at the surface of the liquid could be responsible for the nucleation of the metastable phases. However, both in our experiments and those of Abe *et al.* (1991), no preferential nucleation was observed either at the surface of the liquid or at the contact with the heating wire, even if the growth of large crystals from crystallites occurs preferentially in the vicinity of the wire, just below the melting point temperature (Fig. 1). As a consequence, it is unlikely that a heterogeneous nucleation process can be invoked to explain the metastable crystallization. A second reason for preferential nucleation of the metastable phases might be a slower growth rate of the stable phase compared with the metastable phases. However, Abe *et al.* (1991) have demonstrated that the growth rate of triclinic anorthite is at least one order of magnitude faster than those of the pseudo-orthorhombic and pseudo-hexagonal polymorphs nucleated at the same experimental temperature. The final possibility arises because smaller free energy differences (both bulk and interfacial terms) exist between the metastable phases and the supercooled liquid at the same temperature compared to that between triclinic anorthite and the liquid (Abe *et al.*, 1991). This constitutes an expression of Ostwald's step rule, which states that the first phase encountered during a series of metastable phase transformations is that closest in free energy to the initial material. This principle has been invoked to construct the proposed metastable phase relations in Fig. 3.

In this study, we have demonstrated the utility of the wire loop heating stage, coupled with optical observation and *in-situ* high-temperature Raman spectroscopy as a simple and powerful tool for investigating stable and metastable phase changes in mineralogy.

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