

Pressure-induced band splitting in infrared spectra of sanidine and albite

R. COUTY AND B. VELDE

Laboratoire de Geologie, ER 224 CNRS
Ecole Normale Supérieure
46 rue d'Ulm, 75230 Paris, France

Abstract

Convergence was noted in the infrared spectra of sanidine and albite under pressure (up to 40 kbar). Sanidine spectra showed new bands while certain bands were lost in albite spectra. The new, pressure-induced bands in sanidine spectra are related to changes in the position of the alkali ion in the structure as it influences the oxygens of the tetrahedral network. Both pure Si-O and Si,Al-O related stretch modes are affected. Deformation of the coordination polyhedra of the alkali ions and change in the symmetry of the site, through tilting of the Si,Al tetrahedra, are responsible for the observed changes in infrared spectra under pressure. Small positive shifts of the bands for stretch and bending modes show that the tetrahedra are themselves little deformed by these pressures.

It is deduced that site ordering of Al and Si ions is not the principle reason for band multiplicity in the 1000 and 750 cm^{-1} regions of feldspar spectra. The similarity of spectra for the two feldspars (mono- and triclinic) at 40 kbar suggests that the two structures converge at high pressures and low temperatures.

Introduction

An immense amount of work has been done on the structure, chemistry, spectroscopy, and geologic occurrence of feldspars. The complexity of these minerals has fascinated geologists and mineralogists for many years. Of special interest is the site ordering of the substitution Al for Si in the framework because very much of the subtlety of feldspar mineralogy is related to this phenomenon. Feldspars were used to study the effect of ordering in infrared spectra at an early stage (Laves and Hafner, 1956; Hafner and Laves, 1957). More recent work (Megaw, 1974 and Hazen, 1976) indicates that the triclinic to monoclinic transition could be due to causes other than ordering of Al on specific sites in the feldspar structure, at least in sanidine. In fact the structural form (symmetry) of sanidine can be changed by varying temperature and pressure. The present study provides data on the effect of pressure on infrared spectra of a sanidine in order to better interpret the infrared spectra of the feldspars.

Experimental procedures

Infrared spectra were made in the 1400–400 cm^{-1} range using a Nicolet 5DX FTIR machine equipped with a DTGS detector and a KBr window. Low noise levels were achieved by taking 1000 background scans and 3000 sample scans. The maximum absorbance was slightly below 2. Reproducibility (estimated by taking several spectra of the same sample) was found to be $\pm 2 \text{ cm}^{-1}$. Spectra were smoothed on a 17 point interval using the program provided by Nicolet.

The pressure was attained using a diamond cell of our design where the pressure is applied to the cell using a hydraulic press. Measurements of the pressure in the sample chamber were made using the fluorescence shift of a ruby crystal included in the

sample chamber. The pressure was transmitted to the feldspar sample by a mixture of KBr and CsI. Samples were rerun several times near 22 kbar with reasonably reproducible results (band positions within 5 cm^{-1}). Initial spectra were reproduced after maintaining the sample under pressure for several days. Spectra of ruby fluorescence taken at 45 kbar (Fig. 1) show little change in shape, line broadening and definition compared with one atmosphere data which indicates that the pressure applied by the diamonds to the gasket and KBr assembly is transmitted hydrostatically to 45 kbar. We believe that the method gives reproducible results which represent near isostatic pressure conditions in the pressure chamber.

Two minerals were studied. One was a sanidine from Puy de Dome, France with the formula



as determined by electron microprobe. Infrared spectroscopy and X-ray diffraction indicate that the sample is disordered (Hafner and Laves, 1957; Smith, 1974). This is expected because the feldspar is from an explosive tuff with a composition well between the Na and K endmembers. An albite from the French Alps was studied. It was a nearly pure sodic endmember,



with a high degree of ordering using the criteria mentioned above. This sample was heated at 1000°C for three days in order to establish the initial effects of temperature on the infrared spectra of the mineral. For comparison, a spectrum of albite composition glass was made (supplied by G. Brown, Stanford University, made by Corning Glass Corp.).

Observations

Figure 2 shows the spectra of the three materials made at one atmosphere conditions. The spectra can be divided

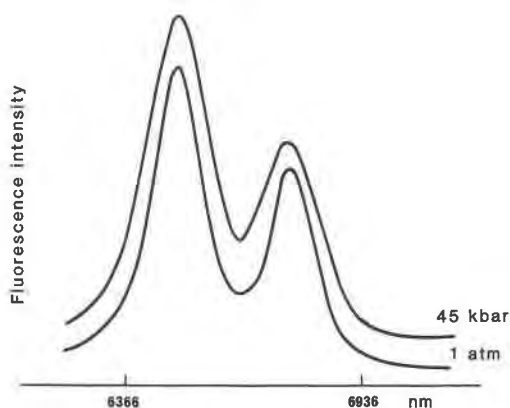


Fig. 1. Ruby fluorescence spectra for one atmosphere and 45 kbar samples showing a very low deformation of the band shape. This indicates that the transmission of the pressure into the KBr pressure medium was nearly isostatic at the pressures used.

into four major zones: I—bands near 1000 cm^{-1} , II—bands near 750 cm^{-1} , III—bands centered around 600 cm^{-1} and IV—bands near 450 cm^{-1} that approach the lower limits of the detector. Obviously the bands in zones I, II and IV are found in all samples whereas the bands in zone III are unique to crystalline material.

As pressure is applied to sanidine, band position increases and new components appear (Fig. 3). The effect of pressure on the bands in zones I and II in the spectra

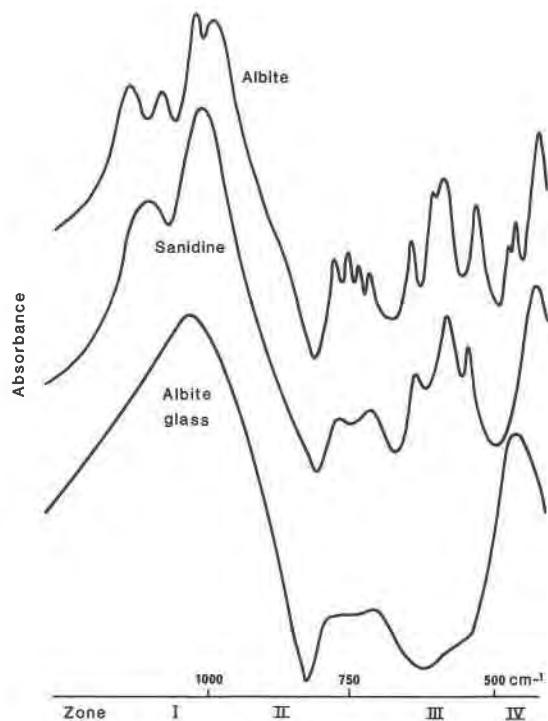


Fig. 2. Absorption spectra of albite and sanidine used in the experiments under atmospheric conditions. Albite glass is shown as a comparison in the sequence of less order in the (Si,Al)-O polymer network.

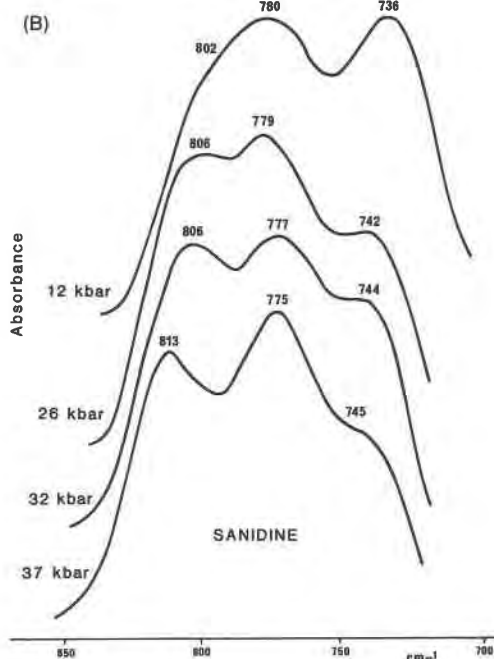
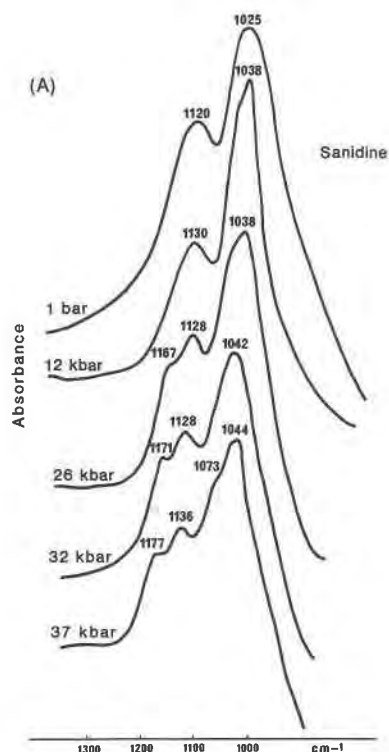


Fig. 3. (a) Absorption spectra of zone I (Fig. 2) bands essentially (Si,Al)-O stretching modes, for sanidine at various pressures. (b) Absorption spectra for sanidine under pressure in zone II.

of the sanidine specimen is seen in Figure 3. Band shifts are generally small and when there is no problem of band splitting, derivatives of less than $0.6\text{ cm}^{-1}/\text{kbar}$ could be measured. Except possibly for the 780 cm^{-1} band there

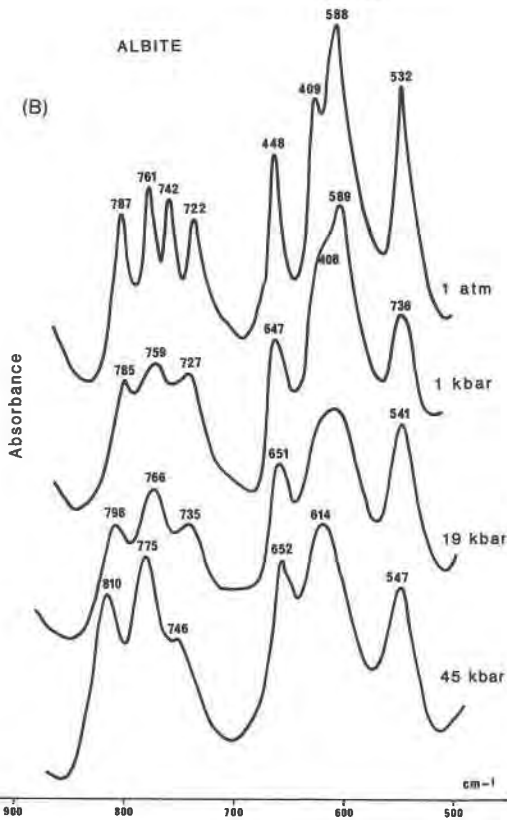
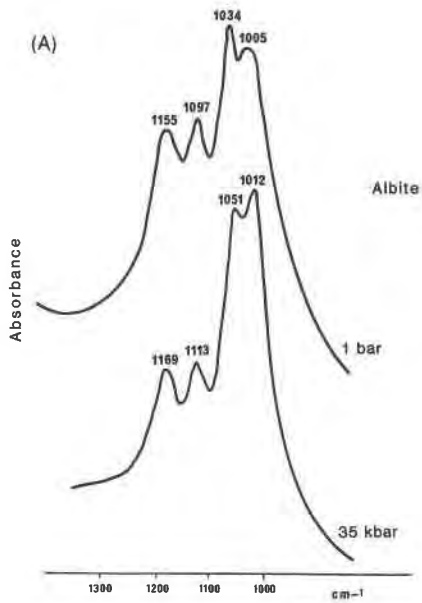


Fig. 4. (a) Absorption spectra for albite at low and high pressure for zone I. (b) Absorption spectra for albite in zones II and III.

is no indication of negative shifts with pressure that could be associated with a reconstructive phase transition. Similar results were found for the albite sample (Fig. 4). In general the spectra of the two minerals converge in appearance at high pressure (Fig. 5).

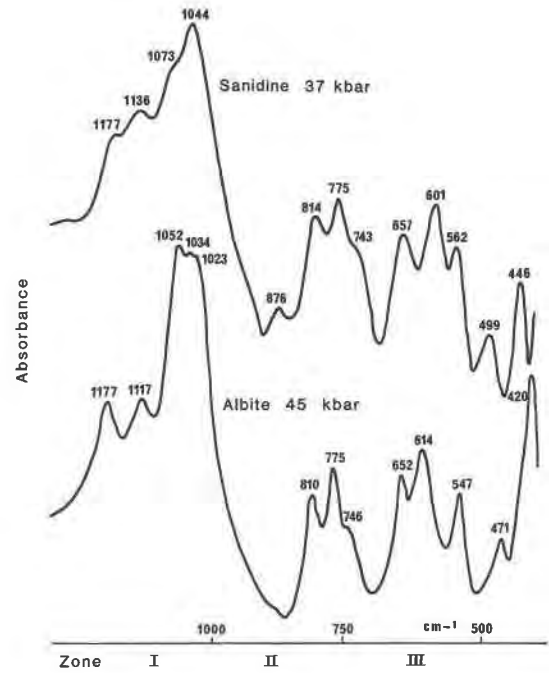


Fig. 5. Comparison of high pressure absorption spectra for sanidine and albite.

Low pressure sanidine has two bands in zone I, two bands in zone II and three bands in zone III. Low pressure albite has twice the number of bands in zones I and II and four bands in zone III. As pressure increases, the sanidine changes into a four band structure in zone I, a three band structure in zone II and remains a three band structure in zone III. Albite attains a similar spectrum at high pressure. The pressure derivatives of the different bands in the two crystalline feldspar species are similar (Table 1).

Spectra of heat-treated albite are similar to those of sanidine (Fig. 6) as has been reported previously (Hafner

Table 1. Pressure derivative in $\text{cm}^{-1}/\text{kilobar}$

Zone	sanidine		albite	
	cm^{-1}	$d\nu/dP$	cm^{-1}	$d\nu/dP$
I			1155	0.5
			1095	0.5
			1034	0.5
			1005	0.5
II	774	0.5	787	0.5
			761	0.3
III	637	0.0	648	0.4
			588	0.3
IV	541	0.4	532	0.3

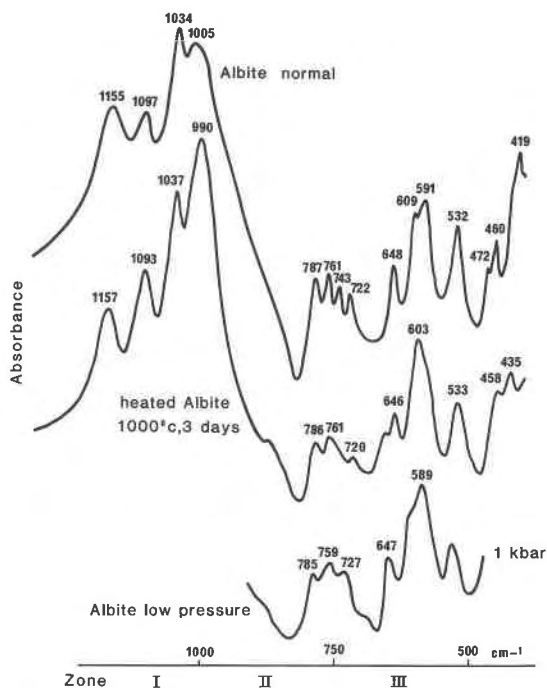


Fig. 6. Comparison of ordered albite, heated albite (3 days, 1000°C) and a low pressure (about 1 kbar) albite spectrum. Note the rapid change in the bands of zone II.

and Laves, 1957; Martin, 1970). Depending upon the study, the bands in zone I change more or less rapidly than those in zone II. The spectra of fully heated and disordered albite given by the cited authors are similar to the spectrum of sanidine given in Figure 2. This comparison shows the similarity of the effects of heating and pressure on the infrared spectra of alkali feldspars.

In summary, the spectra of albite (ordered sites) and sanidine (random site occupancy) show a strong convergence with pressure and temperature. This result confirms the data concerning the X-ray diffraction studies which indicate a convergence of symmetry types at high temperatures.

Discussion

Attributions of the bands observed have been made in previous studies. Iiishi et al. (1971) established that the zone I (1000 cm^{-1}) involves tetrahedrally coordinated ion-oxygen stretch vibrations. Specifically, bands at 1032 and 990 cm^{-1} in ordered albite are affected by the substitution of Al by Ga. The same type of substitution effected changes in the position of bands at 740 and 720 cm^{-1} (zone II). The frequency was displaced by 22 cm^{-1} in zone I and 51 in zone II. Substitutions of Ge for Si revealed a similar relation for the remaining bands in the two regions. Thus the Si and Al-related bands are easily distinguished. Iiishi et al. (1971) attribute the bands in the 750 cm^{-1} zone to tetrahedral-tetrahedral ion vibrations and to O-Si,Al-O bending in zone III (600 cm^{-1}).

This last region is the least affected by changes in temperature and pressure.

The most important observation to be made for the experimental data is that the change in the number of bands for sanidine under pressure cannot be attributed to site ordering. Certainly the energy necessary to displace the Al and Si ions in the polymer network is too great at 20°C for such an effect to be seen in the experiments performed here. Megaw (1974) has argued that the difference in cell dimension due to Si-Al ordering is not great enough to account for the change in dimension in going from monoclinic to triclinic feldspar structures so that a rotation or tilting of the individual structural units (tetrahedra) could change the symmetry of the alkali feldspar structure. The new bands apparently at 1170 and 1070 cm^{-1} under pressure for sanidine can thus be interpreted as a re-organization of the feldspar structure through tetrahedral tilting. The loss of the band at 742 cm^{-1} in albite under pressure and the appearance of a new band at 810 cm^{-1} in sanidine could also be due to this accommodation of the structure.

For silicates, the tetrahedral dimensions are generally considered to be little affected by pressure (Hazen and Finger, 1982). In contrast, the coordination polyhedra around the alkali ions are greatly affected by pressure or by changes in the structural state (tri- or monoclinic) of the alkali feldspars. The symmetry of this site changes in the mono- to triclinic transition. Thus, a rotation of the tetrahedra will change the oxygen-alkali ion distances but not those of Si-O. This is manifested in the appearance of the new bands of the sanidine spectra. In order to see if the change in (Na,K)-O distance is the cause of the new bands, one can look at the spectra of feldspars with different cations in this site such as albite and microcline in order to identify the alkali-sensitive bands. Spectra found in Iiishi et al. (1971) show the following relations:

microcline	1010	1053	1097	1139 cm^{-1}
albite	1005	1034	1092	1155 cm^{-1}

The new bands which appear under pressure in the sanidine spectra are those which are the most affected by the alkali cation present. These bands, attributed to vibrations of Si,Al-O ions must then involve the oxygens closest to the alkali cations. Since one of these bands (1034 cm^{-1}) is associated with Al in the structure and the other (1155 cm^{-1}) with Si, the tetrahedral tilt which occurs with pressure must affect the Al- as well as Si-O vibrations in the silica polymer. This last band (1155 cm^{-1}) appears to have a doublet component in the highest pressure spectrum for albite.

Albite has four bands in zone II which are attributed to Si-Si and Si-Si(Al) vibrations by Iiishi et al. (1971) or to a combination of Si(Al)-O and Si-O-Si vibration modes with the first types being slightly predominant according to von Stengle (1977). The zone is represented by four bands in albite with the two of lowest wave number being associated with Al as demonstrated by Ga for Al substitution (Iiishi et al., 1971). At pressures below 45 kbar

three bands occur. At higher pressure, we infer that only two bands will occur in both feldspars as suggested by the albite spectra at 45 kbar. This relation is the reverse of that found for the Si-O stretch bands at 1000 cm^{-1} . The bands in zone II are not affected by the substitution of potassium for sodium (Iiishi et al., 1971). Therefore the behavior observed for these bands under pressure could be expected to differ from the Si-O stretch bands. The multiplicity of the bands in zone II and their change under pressure cannot be due to a site ordering of Al and Si in the polymer structure.

The zone III bands (near 600 cm^{-1}), not found in the spectra of amorphous material, are assigned to O-Si-O vibrations by von Stengle (1977) as well as by Iiishi et al. (1971). According to other authors, using Raman spectra of glasses (Galeener, 1982; Sharma et al., 1981), the position of zone III bands should be sensitive to the bond angle of the O-Si-O units. According to Hazen and Finger (1982) pressure should affect the bond angle of the O-Si-O units in feldspars radically. The similarity of the measurable pressure derivatives of the bands in zone III and other zones suggests either that bond angle does not affect the vibrations in zone III of the feldspar spectra or that the bond angle is not changing as rapidly as other factors in the structure which affect the spectra. In glass, the bands in zone III are conspicuously absent. In fact, the band involving the O-Si-O vibrations is located toward 500 cm^{-1} in the glass and by analogy should be in the region below 450 cm^{-1} in the crystal structures. It is not possible to interpret changes in the vibrational modes responsible for the bands near 600 cm^{-1} given the present information. However, as in other zones, there is a distinct loss of one band in this region in the albite structure and again a convergence at high pressures for both feldspars.

For the most part, changes in the spectra of the feldspars sanidine and albite are gradual as pressure increases. One abrupt change is the early loss of the 743 cm^{-1} band in albite with pressure as well as in the initial stages of heating. According to Hazen (1976), the phase transformation of sanidine (monoclinic) to a new structure (triclinic) will occur at pressures below 10 kbar at room temperature for the composition of our sample. Therefore, the pressure spectra of our samples are made on crystals which already have a triclinic symmetry. Thus the gradual changes seen in the spectra must be explained by continuing tetrahedral rotation and the consequent change in the symmetry of the alkali ion coordination polyhedra. The infrared spectra show a gradual increase in the intensity of the new bands as pressure increases on the sanidine structure. We can interpret this observation as the effect of a gradual increase in the number of alkali ions which take up a triclinic position in the structure due to tetrahedral tilting as pressure increases according to the description given by Megaw (1974). The sanidine includes a mixture of K and Na ions which will not behave in exactly the same manner due to a difference in their ionic size, and hence the change in symmetry will be spread over a pressure range. The effect of pressure, changing the number of bands

due to a change in the symmetry of certain sites, cannot be associated with the Al,Si ordering which is generally assumed to be the cause of band multiplicity in these structures (Hafner and Laves, 1957; White, 1974). Our data supports Megaw's concluding remark "the study of feldspars is thus not primarily linked with the study of Al/Si distribution."

Conclusions

From the data presented here we observe the following:

1. The infrared spectra of sanidine (disordered) and albite (ordered) evolve toward the same appearance under increasing pressure which suggests very similar structures.
2. The general effect of pressure is to shift all bands observed to higher wave numbers (i.e., increased energy due to decreasing bond lengths in the tetrahedral units).
3. Increasing pressure produces new bands in the 1000 cm^{-1} region of the disordered mineral and decreases the number of bands in the 750 cm^{-1} and 600 cm^{-1} region of the ordered mineral.

One can tentatively conclude from these observations that the multiplicity of the bands in the 1000 cm^{-1} region is not necessarily due to a site ordering effect (i.e., specific configuration of tetrahedral ions) but rather one which involves the general environment of the oxygens of the Si,Al tetrahedra. This is seen by the effect of pressure on sanidine which simulates this ordered environment. The change in the symmetry of the alkali ion sites must be used to explain the multiplicity of peaks in the high-pressure sanidine spectrum. Such a deduction leads one to question how heating changes the albite sample so that its infrared spectrum imitates that of a disordered feldspar. Possibly heating increases the cell dimension of the feldspar which in turn changes the environment of the silica tetrahedra rather than the site occupancies of the feldspar tetrahedral units.

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