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IR spectroscopic study of the effects of high pressure on zeolites Y, A and sodalite

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In this work, we present the effect of high external pressure on the structures of several representative zeolites: zeolite Y (Na-Y), lithium exchanged zeolite A (Li-A) and sodalite, as studied by IR spectroscopy. Pressure-induced amorphization was observed at 19 and 18 kbar in Na-Y and Li-A, respectively. However, the amorphous phases formed under such pressures seem to be reversible. The structural memory of the glasses might be due to the presence of hydrated charge balancing cations. Sodalite, on the other hand, exhibited no phase change in the pressure range of 0–48 kbar.

Zeolites are aluminosilicates with well defined pore and channel structures. These materials are widely used in industry as ion exchangers, molecular sieves, sorbents and, particularly in the petroleum industry, as catalysts.

The structural stability of zeolites is very important to their applications and their thermal stability has been investigated extensively. Surprisingly, the major unexplored area of synthetic zeolite work at present is the behavior of the zeolite structure under external pressures. To date, there are only a few reports dealing with this issue. These studies have focused mainly on natural zeolites[1] and no systematic studies have been performed. As part of our initiative of studying the effect of high pressure on the zeolitic framework structure, we report here the preliminary results of a high pressure IR study of zeolite Y (Na-Y), lithium exchanged zeolite A (Li-A) and sodalite. Zeolites Y and A are two industrially important materials with low-Si/Al ratios. Sodalite represents a transition between the non-zeolitic felspathoids and the zeolites. Since its structure is closely related to those of zeolites Y and A, it was also examined in the present study. The relationship between the structures and the vibrational spectra of these materials at ambient conditions has been studied extensively.[2] In previous studies, the unit cell parameters of sodalite[1b] and zeolite A (Na-A)[1a] were measured as a function of pressure by X-ray diffraction. While the X-ray diffraction method detects only long range ordering and periodicity, vibrational spectroscopy, on the other hand, can provide complementary information regarding the effects of pressure on short range ordering and local structures of zeolites.

Experimental

Materials

The sodium chlorosodalite, $Na_6(SiO_2)(AlO_2)\cdot 2NaCl$, was synthesized by heating a mixture of kaolin, NaOH and NaCl at 80 °C for 48 h.[3]

Zeolite A (Na-A, Si/Al = 1) was prepared by hydrothermal synthesis from a mixture of molar ratio 2.0 $SiO_2:Al_2O_3:5.0\ Na_2O:150H_2O$ heated at 80 °C for 3.5 h.

Li-exchanged zeolite A (Li-A) was obtained by conventional ion-exchange of Na-A (as synthesized) with an aqueous solution of LiCl as described in the literature.[4]

Zeolite Y (Si/Al = 2.35) was obtained from Strem Chemical Co.

In each case, the sample crystallinity and purity were checked by powder X-ray diffraction measurements (Philips PW1050 powder diffractometer).

High pressure IR experiments

All IR spectra under high pressure (4 cm^{-1} resolution) were recorded on a Bruker IFS48 FT-IR spectrometer equipped with an IR microscope. The diamond anvil cell (DAC) used for the high pressure measurements was obtained from High Pressure Diamond Optics, Inc. The sample and a thin layer of pressure calibrant (0.14 mass% $NaNO_3$ in NaBr, prepared by the method of Klug and Whalley[5]) were placed in the 270 µm hole of a 200 µm thick, stainless-steel gasket located between the parallel faces of the two diamonds. The purpose of the gasket was to ensure that the pressure gradient was as uniform as possible over the sample. The DAC was then mounted on a *X–Y–Z* stage, and the IR beam was focused onto the sample through an IR microscope objective. The pressure in the DAC was determined from the observed wavenumber shift of the asymmetric N—O stretch of the NO_3^- ion. Since the IR microscope is equipped with a NaCl beam splitter, only the spectral region above 600 cm^{-1} could be examined.

Results and Discussion

Zeolite Y (Na-Y)

This represents the first study of zeolite Y under high external pressure. Three framework vibrations were followed as a function of pressure in the region 1400–600 cm^{-1} (Fig. 1A). According to Flanigen *et al.*,[2] the 812 cm^{-1} band is due to the T—O (T = Si, Al) symmetric stretching vibration, whereas the strong band at 1043 cm^{-1} and a medium band at 1176 cm^{-1} can be assigned to T—O asymmetric stretching modes. Below 19 kbar, all three bands shifted to higher energies quickly with increasing pressure (Fig. 2). The relatively large pressure dependence of these modes (see caption of Fig. 2 for $d\nu/dP$ values) indicates that there is a significant reduction in the volume of the crystal. At 19 kbar, the bands initially positioned at 1176 and 812 cm^{-1} suddenly became very broad (Fig. 1B) and the 1176 cm^{-1} band now appeared as a very broad shoulder. Increasing the pressure further resulted in increased broadening of these two bands and their frequencies could not be determined accurately at pressures above 19 kbar. In contrast, the appearance of the band at 1043 cm^{-1} at 19 kbar is much less affected (Fig. 1B). This band does however exhibit a distinct break in its slope of ν *vs.* P plot (Fig. 2). All of these results suggest that there is a phase change occurring at 19 kbar. At 19 kbar, striking changes also occurred in the O—H stretching and bending regions of water molecules located inside zeolitic framework. For instance, three well resolved peaks centered at 3547, 3476 and 3415 cm^{-1} were initially observed at ambient conditions (Fig. 3A). These bands are superimposed on a very

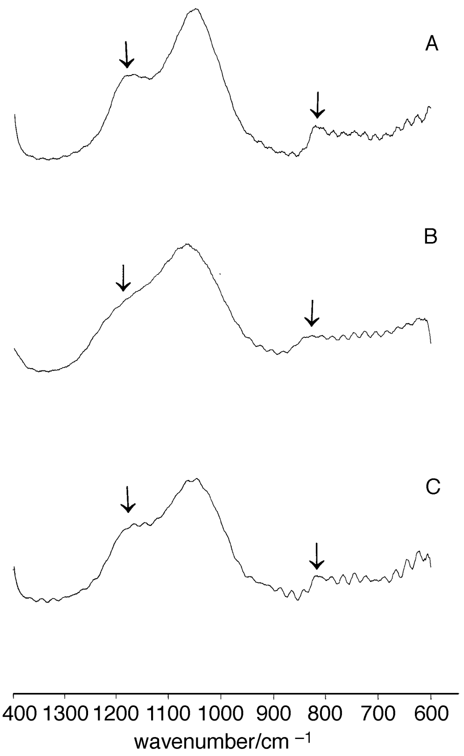

Fig. 1 IR spectra of zeolite Y (Na-Y) framework at (A) 1 bar, (B) 19.3 kbar and (C) 1 kbar after decompression, all in the region 1400–600 cm^{-1}. Bands indicated by arrows are the structurally sensitive vibrations.

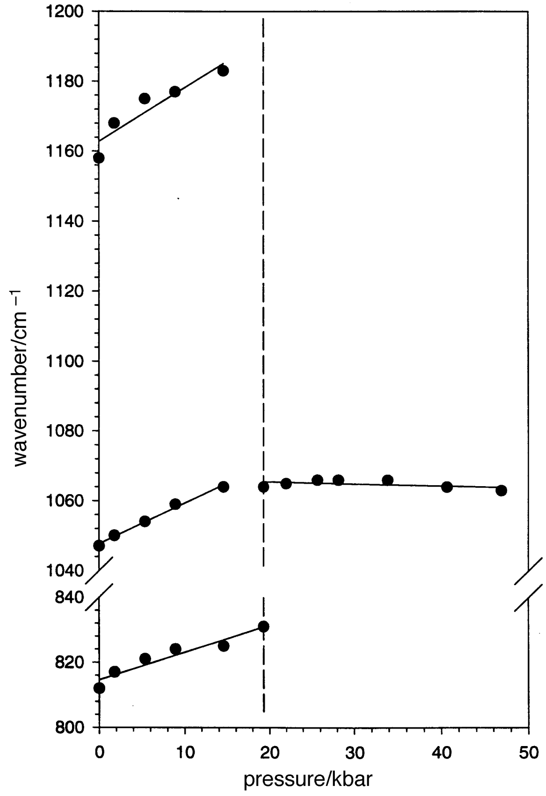

Fig. 2 Pressure dependences of the IR bands due to the zeolite Y framework vibrations. The dν/dP values of 1176, 1043 and 812 cm^{-1} bands in the low pressure phase are 1.5, 1.2, 0.9 $\mathrm{cm}^{-1}\,\mathrm{kbar}^{-1}$, respectively.

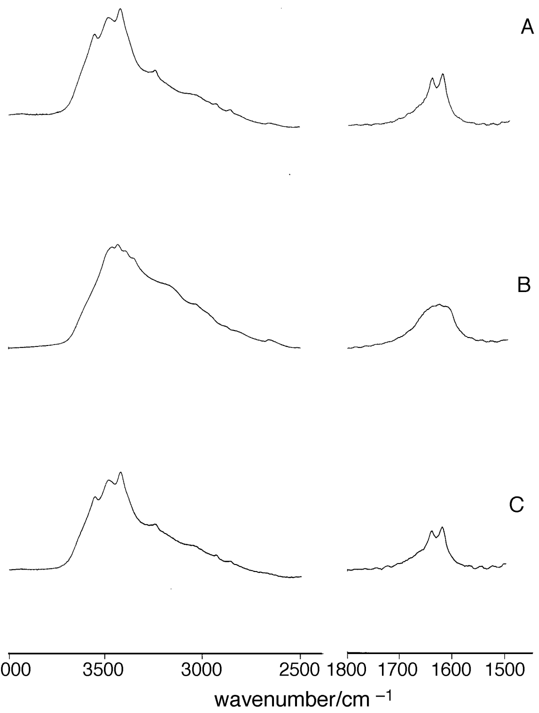

Fig. 3 IR spectra of OH stretching and bending vibrations due to the water molecules located inside the framework at (A) 1 bar, (B) 19.3 kbar and (C) 1 kbar after decompression

broad feature. The three resolved bands may be due to the water molecules associated with sodium ions at different sites within the framework (for hydrated Na-Y, there are four water sites present inside the framework at ambient conditions[6]), whereas the broad profile is presumably due to the water molecules physically absorbed on the surface of the crystal. Below 19 kbar, the frequencies of these bands shifted steadily towards lower energies with increasing pressure (Fig. 4), supposedly due to increased strength of hydrogen bonding under pressure. At 19 kbar, all three bands collapsed to a very broad featureless profile (Fig. 3B). The O—H bending modes

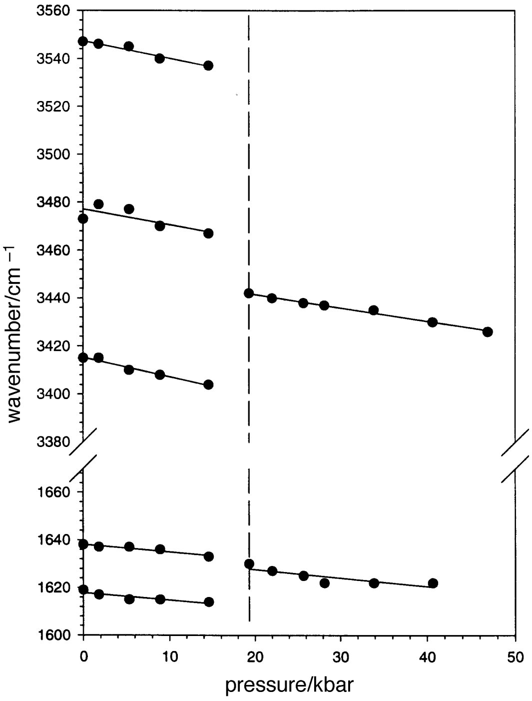

Fig. 4 Pressure dependences of the IR bands due to the water molecules inside the zeolitic framework

exhibited similar behavior with two sharp peaks located at 1637 and 1617 cm^{-1} under ambient conditions (Fig. 3A) which remained very well separated throughout the entire pressure range 1–19 kbar. However, the doublet suddenly collapsed to a very broad singlet at 19 kbar (Fig. 3B). All of these results provide additional evidence that a phase transition had indeed occurred. The discontinuities in v *vs.* P plots at 19 kbar show that the transition pressure is about 19 kbar. Since all observed changes are sudden, the transition must be abrupt.

The nature of the high pressure phase deserves a few words of discussion. The pioneering work by Flanigen *et al.* has shown that in IR spectra some bands are observed for all the zeolite structures and classified as internal tetrahedral (structure insensitive) vibrations, while other bands are inter-tetrahedral (structure sensitive) external linkages.[2] For zeolite Y, the two bands at 1176 and 812 cm^{-1} have been previously assigned to the external linkages of tetrahedra.[2] These inter-tetrahedral bands are very sensitive to the crystallinity of the sample. For example, these external linkage vibrations were used to monitor the extent of thermal decomposition of Na-Y.[2a] It was found that a decrease in the crystallinity of the sample was accompanied by severe line broadening and a decrease in the intensities of these bands. On the other hand, the appearance of the main band near 1043 cm^{-1} remained independent of the crystallinity since it is due to the internal vibration of TO_4 tetrahedra which also exist in amorphous materials. Recently, the decrystallization process of zeolite Y upon mechanical milling has been investigated.[7] The intensity of the structurally sensitive band at 812 cm^{-1} was monitored to follow the changes in crystallinity of zeolite Y upon milling. Based on these studies, the decreased intensity and band broadening of two structurally sensitive modes at 1176 and 812 cm^{-1} of Na-Y in the present study may indicate that zeolite Y had been converted to an amorphous material under a pressure of 19 kbar. The broadness of O—H stretching and bending modes of water molecules in the high pressure phase further support that the nature of the high pressure phase is amorphous because in a glass the water molecules no longer sit at specific positions in cavities and cages which are regularly arranged in the lattice of the starting materials. Similar pressure-induced amorphization has been recently observed in natural zeolites such as scolecite and mesolite.[1e]

Upon reducing pressure, the spectrum looks very similar to that of the original sample at ambient conditions (Fig. 1 and 3), implying that the phase change may be reversible. A study has shown that upon compression, crystalline α-berlinite ($AlPO_4$), which is isomorphous with α-quartz, transforms to an amorphous material.[8] Interestingly, this pressure-induced amorphized $AlPO_4$ is reported to retain a 'memory' of the crystalline structure and to revert back to the original structure and orientation upon releasing the pressure. Recently, Tse *et al.* have studied the effects of pressures on dodecasil-3C and 3R which have cage-like voids and two-dimensional channels, respectively.[9] They found that both tectosilicates transform into glasses under high pressure, but amorphization is fully or partially reversible when organic template molecules are present. In the present study, zeolite Y appears to exhibit similar behavior. It is interesting to compare this pressure-induced amorphization with the crystallization of zeolite directly from the solid gel phase. It has been shown that when the amorphous gel solids of zeolite X (which has exactly the same framework structure as that of zeolite Y but lower Si/Al ratio) were separated from solution, they were able to transform directly to an X-ray crystalline zeolite X.[10] It appears that some amorphous aluminosilicate materials do have the capability of reorganizing themselves to form crystalline zeolitic structures, provided that the composition of the amorphous phase is the same as that of the final materials. It has been suggested that the existence of non-deformable units is essential for reversible amorphization. For instance, PO_4 tetrahedra and organic template molecules were found to act as such units in α-berlinite and clathrasils, respectively.[9,11] For zeolite Y, hydrated sodium ions may play a similar role since it is well known that hydrated alkali-metal ions have some structure-directing ability.[12] If the amorphous material produced from Na-Y under pressure still has a certain extent of short range ordering, the hydrated sodium ions may move back into the original, structurally ordered state with lowest free energy upon decompression and direct the tilted TO_4 tetrahedra back to their original positions.

Lithium-exchanged zeolite A (Li-A)

There are four bands in the ambient spectrum of lithium-exchanged zeolite A in the range 1300–600 cm^{-1} (Fig. 5A). Based on the assignment of Flanigen for Na-A,[2] the bands at 698 and 984 cm^{-1} are assigned to symmetric and asymmetric stretching vibrations, respectively, both of which are due to internal tetrahedra. The bands at 1152 and 1015 cm^{-1} are unique features of Li-A, as no corresponding bands are observed in the spectrum of Na-A, both of which can be assigned to the T—O asymmetric vibrations. The former might be due to the external linkage and the latter an internal tetrahedron. Below 18 kbar, the bands at 689 and 1152 cm^{-1} shifted very quickly to higher energies with increasing pressure (Fig. 6). In contrast, the frequencies of two T—O asymmetric stretching vibrations due to internal tetrahedra are completely insensitive to pressure. At about 18 kbar, all of the peaks suddenly became extremely broad (Fig. 5B). The bands initially centered at 1152 and 698 cm^{-1} almost disappeared into the baseline. The 1015 and 984 cm^{-1} bands collapsed to a very broad profile. As for Na-Y, the observed line broadening may be explained in terms of the formation of an amorphous phase. Upon decompression, the 984 and 1015 cm^{-1} bands narrowed significantly and were once again well separated. The bands at 1153 and 698 cm^{-1} also reappeared (Fig. 5C). All of these results indicate that similar to Na-Y the crystal to glass transition may be reversible. However, the bandwidth of the 698 cm^{-1} band is still much broader than that in the spectrum taken before compression. The intensity of the 1153 cm^{-1} band

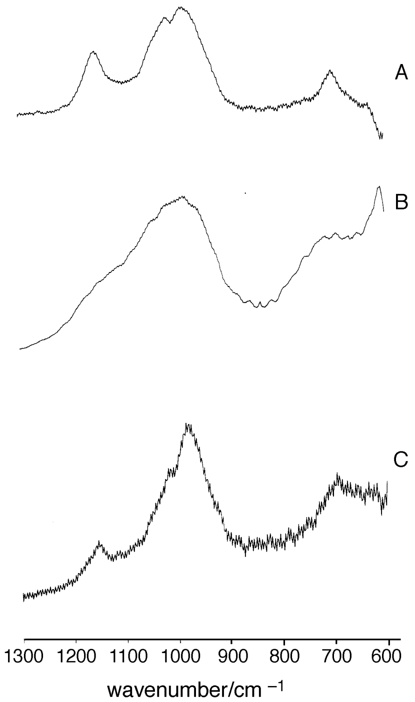

Fig. 5 IR spectra of zeolite A (Li-A) framework at (A) 1 bar, (B) 18.2 kbar and (C) 1 kbar after decompression, all in the region 1300–600 cm^{-1}

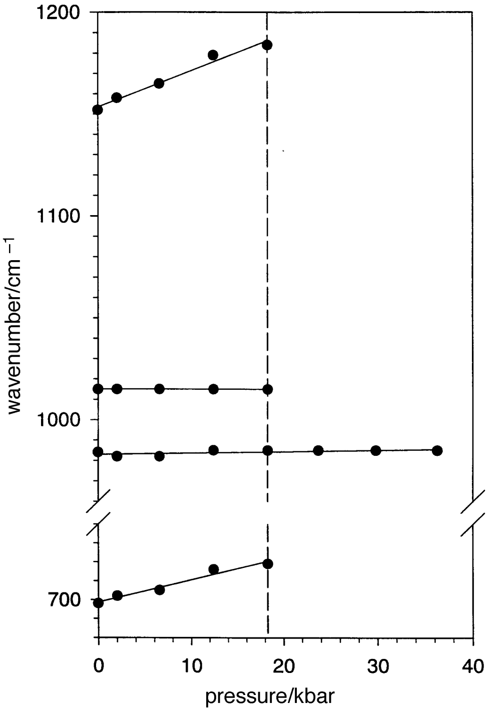

Fig. 6 Pressure dependences of the IR bands due to the zeolite A (Li-A) framework vibrations. The d*v*/d*P* values of 1152, 1015, 984 and 698 cm^{-1} bands in the low pressure phase are 1.8, 0, 0.1 and 1.2 cm^{-1} kbar^{-1}, respectively.

relative to the 984 cm^{-1} main peak is significantly lower than that of the original sample. These differences imply that upon releasing pressure the disordered structure only partially reverted back to the initial crystalline phase. As is the case with sodium ions in Na-Y, the hydrated lithium ions may be responsible for the partially reversible transformation.

Sodalite

The volume change in unit cell of sodalite with pressure has been previously studied in the pressure range 0–26 kbar by X-ray diffraction.[1b] In the present IR study the pressure range was extended to 48 kbar. The pressure dependences of four observed IR fundamentals are shown in Fig. 7. The plots are linear without any obvious breaks throughout the entire 0–48 kbar range indicating the absence of a pressure induced phase transition in sodalite. The associated d*v*/d*P* values are given in the caption of Fig. 7. The positive slopes of *v vs. P* plots suggest that the unit cell dimension of sodalite decreases with increasing pressure. On the basis of XRD data of several dense framework silicates and aluminosilicates, it has been suggested that the principal compression mechanism for sodalite is the reduction in Si—O—Al angles in response to compression of Na—O bonds rather than shortening the T—O distances.[1b] However, in the present study, the observation of positive frequency shifts of T—O stretching modes indicate that a reduction in T—O bond length under pressure may also contribute to the shrinkage of the unit cell. This is because, since most chemical bonds (including the Al—O and Si—O bonds) are anharmonic, the reductions in interatomic distances caused by pressure result in an increase in the vibrational force constants and, consequently, lead to an increase in the frequencies of the vibrational modes (if the T—O bonds were harmonic no pressure shifts should occur).[13]

Information regarding the effect of pressure on Si—O—Al angle can also be obtained from the change in intensity of an IR band near 750 cm^{-1}. By normal mode calculations, Creighton *et al.* have established a linear correlation between the intensity of this IR band and the Si—O—Al angles.[14] In particular, they found that for $M_8[Al_6Si_6O_{24}]Cl_2$ (M = Li, Na, K) and silica sodalite the relative intensity of this peak (the absorbance of 750 cm^{-1} band relative to that of the intense absorption near 1000 cm^{-1}) decreases linearly with a decrease in the Si—O—Al angle. If increasing pressure causes a reduction in the average Si—O—Al angle, a decrease in relative intensity of the 750 cm^{-1} band with increasing pressure should be observed. The experimental data (Fig. 8), however, show that the relative intensity of this band is essentially independent of pressure, implying that the decrease in the Si—O—Al angle upon compression may not be substantial. Thus, the IR results indicate that the reduction in T—O distance may be, at least partially, responsible for the shrinkage of the unit cell under pressure.

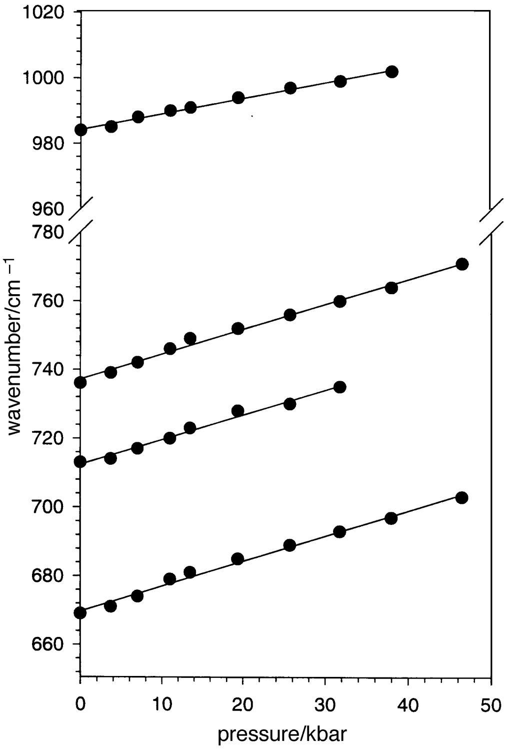

Fig. 7 Pressure dependences of the IR bands of sodalite. The d*v*/d*P* values of 984, 736, 713 and 669 cm^{-1} bands are 0.5, 0.7, 0.7 and 0.7 cm^{-1} kbar^{-1}, respectively.

Summary

The effects of external pressure on zeolites Na-Y and Li-A have been investigated by IR spectroscopy. Pressure-induced amorphization was observed at 19 and 18 kbar in Na-Y and Li-A, respectively. Pressure-amorphized materials seem to show reversible behavior. The structural memory of the glasses

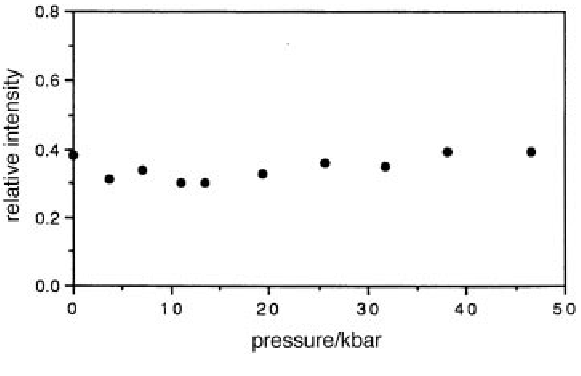

Fig. 8 The plot of the relative intensity of the 750 cm^{-1} band of sodalite *vs.* pressure

might be due to the presence of hydrated charge balancing cations. Sodalite has also been examined under pressure. No phase transition was observed in the pressure range 0–48 kbar. The present work demonstrates that the high-pressure IR spectroscopy is a useful technique in investigation of the effects of pressure on zeolitic frameworks and can provide structural information complementary to that obtained from X-ray diffraction methods.

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