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Vibrational Spectrum of Fresnoite ($\text{Ba}_2\text{TiOSi}_2\text{O}_7$) and Isostructural Compounds

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Abstract. Two new isostructural compounds with fresnoite, $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$, have been synthesized and investigated by X-ray diffraction and vibrational spectroscopy. The infrared (IR) and Raman spectra of fresnoite and fresnoite-like pyrosilicates are discussed on the basis of a factor group analysis and with the help of $^{28-30}\text{Si}$ and $^{46-50}\text{Ti}$ isotopic shifts. The short Ti–O bond participates to the $900\text{--}800\text{ cm}^{-1}$ region of the spectrum. However, because of an important mixing with some Si–O stretching modes having the same symmetry properties, no frequency is specifically related to the stretching of this bond. An assignment is also proposed for the remaining Si–O stretching frequencies. The existence or absence of a correlation between short Ti–O distances and high vibrational frequencies is briefly discussed.

Introduction

The structure of fresnoite $\text{Ba}_2\text{TiOSi}_2\text{O}_7$ has been investigated, first by Masse et al. (1967), and later by Moore and Louisnathan (1969). Both papers agree with the existence of Si_2O_7 groups and with a tetragonal pyramidal configuration around the Ti atoms (TiO_5 groups), but disagree with the Ti–O distance related to the oxygen atom located at the apex of the pyramid. This Ti–O distance is normal (1.98 Å) according to the first paper, whereas it is much shorter (1.634 Å) according to the second. It may be noticed that this latter structure determination takes into account a greater number of reflections and leads to lower R values. The choice of the Moore-Louisnathan structure is confirmed by our spectra. In connection with a systematic study of the vibrational behavior of pyro groups (Gabelica-Robert 1980) and of Ti–O bonds (Tarte 1961, 1965; Tarte et al. 1979), we have investigated the vibrational spectrum of fresnoite and of the following isostructural compounds: $\text{Ba}_2\text{V-Si}_2\text{O}_8$ (Feltz et al. 1975a, b), $\text{Sr}_2\text{TiSi}_2\text{O}_8$, and $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (Gabelica-Robert 1980). Our results and interpretations will be compared with those recently published by Blasse (1979).

Experimental

We have prepared $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiSi}_2\text{O}_8$ by conventional solid state reaction techniques, starting from the stoichiometric mixtures of the appropriate oxides or carbonates progressively heated up to $1,200\text{--}1,250^\circ\text{C}$. The same procedure was applied to the germanate, but at a lower temperature ($1,025^\circ\text{C}$). $\text{Ba}_2\text{V-Si}_2\text{O}_8$ was synthesized by heating a mixture of BaSiO_3 and VO_2 at $1,200^\circ\text{C}$ under vacuum.

Table 1. X-ray powder diagrams of $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{TiGe}_2\text{O}_8$

$\text{Sr}_2\text{TiSi}_2\text{O}_8$			$\text{Ba}_2\text{TiGe}_2\text{O}_8$		
<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>
			4.302	3	200
3.820	10	111			
3.718	7	210			
3.203	40	201	3.375	22	201
2.990	100	211	3.148	100	211
2.941	7	220	3.067	6	220
2.632	32	310	2.741	27	310
2.511	28	002	2.682	20	002
2.330	8	311	2.440	4	311
2.307	4	320	2.406	7	320
2.150	4	202	2.281	7	202
			2.205	10	211
2.081	20	400	2.169	6	400
2.018	14	410	2.103	13	410
1.960	8	330	2.044	11	330
1.910	4	222	2.019	4	222
1.872	15	411	1.957	18	411
1.860	10	420–302	1.940	4	420
1.826	15	331			
1.815	15	312	1.915	18	312
1.572	8	412	1.790	5	003
1.552	10	511	1.688	5	402
1.545	5	520	1.654	7	203
1.528	15	213	1.624	26	213
			1.572	4	422
1.447	8	521	1.543	11	521
			1.446	6	600

The X-ray powder diagrams (C.G.R. diffractometer, Co K α radiation) of the two new compounds (Table 1) have a similarity to fresnoite. The parameters of the tetragonal unit cell and their standard deviations were deduced and refined from *d* values:

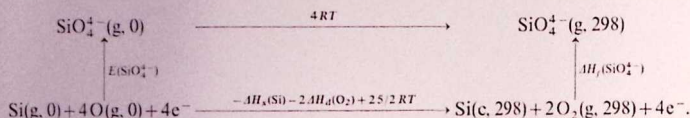
$$\begin{aligned} \text{for } \text{Sr}_2\text{TiSi}_2\text{O}_8 \\ a = 8,321 (7) \text{ \AA} \quad \text{and} \quad c = 5,025 (4) \text{ \AA}, \\ \text{for } \text{Ba}_2\text{TiGe}_2\text{O}_8 \\ a = 8,677 (12) \text{ \AA} \quad \text{and} \quad c = 5,364 (10) \text{ \AA}. \end{aligned}$$

The infrared (IR) and Raman spectra have been registered according to standard techniques (Gabelica-Robert and Tarte 1979a, b).

The magnesium molar sublimation enthalpy $\Delta H_s(\text{Mg})$ and ionization potential $I(\text{Mg})$ amount to 136.4 and 2186.1 kJ mol⁻¹, respectively (Ohashi 1976); by considering Mg²⁺(g) and SiO₄⁴⁻(g) as ideal monoatomic ($C_p=5/2R$) and polyatomic ($C_p=4R$) gases, respectively, the enthalpy of cooling of the system from 298 to 0 K was estimated to be -22.3 kJ mol⁻¹. Using the value $\Delta H_f = -2170.2$ kJ mol⁻¹ for the formation enthalpy of forsterite (Zen and Chernosky 1976), the following result is obtained:

$$\Delta H_f(\text{SiO}_4^{4-}) = -E_{\text{c,oh}} + \Delta H_f - 2\Delta H_s(\text{Mg}) - 2I(\text{Mg}) + 9RT = 2117.6 \text{ kJ mol}^{-1}. \quad (11)$$

It is also interesting to calculate the binding energy $E(\text{SiO}_4^{4-})$ of the SiO₄⁴⁻ ion, i.e., its energy of formation from the gaseous elements at the absolute zero. The suitable thermochemical cycle is:



The sublimation enthalpy of silicon and the dissociation energy of molecular oxygen are $\Delta H_s(\text{Si})=443.5$ and $\Delta H_d(\text{O}_2)=493.3$ kJ mol⁻¹, respectively (Ohashi 1976); then the value of $E(\text{SiO}_4^{4-})$ is computed as follows:

$$E(\text{SiO}_4^{4-}) = \Delta H_f(\text{SiO}_4^{4-}) - \Delta H_s(\text{Si}) - 2\Delta H_d(\text{O}_2) + 17/2RT = 708.6 \text{ kJ mol}^{-1}. \quad (12)$$

Both the $\Delta H_f(\text{SiO}_4^{4-})$ and $E(\text{SiO}_4^{4-})$ values are positive, consistent with the unstable character of the silicate ion in the gaseous state. In principle, by introducing the formation enthalpy of SiO₄⁴⁻ into appropriate thermochemical cycles, the ΔH_f values of several nesosilicates can be calculated, if not known experimentally. On the other hand, the binding energy $E(\text{SiO}_4^{4-})$ obtained here should be compared with values coming from accurate quantum-chemical calculations on the SiO₄⁴⁻ ion; these are very difficult, however, because the binding energy is just a small fraction of the total energy of the ion, which is the direct result obtained, and it is affected strongly by electron correlation, which is usually not taken into account (Johansen 1974).

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Table 2. Description of the stretching vibrations of the pyro groups in the fresnoite structure

Type of vibration	D_{3h} (M.G.)	C_{2v} (S.G.)	C_{4v} (F.G.)	IR-active	Ra-active
$\nu_s(\text{XOX})$	A'_1	A_1	$A_1 + B_2$	A_1	$A_1 + B_2$
$\nu_{as}(\text{XOX})$	A'_2	B_1	E	E	E
$\nu_s(\text{XO}_3)$	A'_1	A_1	$A_1 + B_2$	A_1	$A_1 + B_2$
$\nu'_s(\text{XO}_3)$	A'_2	B_1	E	E	E
$\nu_{as}(\text{XO}_3)$	E	$\begin{cases} A_1 \\ B_2 \end{cases}$	$\begin{cases} A_1 + B_2 \\ E \end{cases}$	$\begin{cases} A_1 \\ E \end{cases}$	$\begin{cases} A_1 + B_2 \\ E \end{cases}$
$\nu'_{as}(\text{XO}_3)$	E'	$\begin{cases} A_2 \\ B_1 \end{cases}$	$\begin{cases} A_2 + B_1 \\ E \end{cases}$	$\begin{cases} - \\ E \end{cases}$	$\begin{cases} B_1 \\ E \end{cases}$

Crystal Structure and Group Theoretical Analysis

Fresnoite and the analogous compounds crystallize in the tetragonal space group $P4bm$ ($=C_{4v}^2$) with two molecular formula in the unit cell.

The knowledge of atomic positions and symmetries [2 Ti, 2 O(4) on sites a (C_{4v}); 2O(1) on sites b (C_{2v}); 4 Ba, 4 Si, 4 O(2) on sites c (C_2); 8 O(3) in general positions] and factor group analysis (Fateley et al. 1971; De Angelis et al. 1972) lead to the following representation for the crystal cell:

$$\Gamma = 11A_1 + 8A_2 + 6B_1 + 10B_2 + 20E.$$

Among these modes, 31 are IR-active ($11A_1 + 20E$) and 47 are Raman-active ($11A_1 + 6B_1 + 10B_2 + 20E$).

Previous studies of akermanite-like and kentrolite-like silicates and germanates containing bent pyro groups (Gabelica-Robert and Tarte 1979a, b) have shown that the approximation of internal modes can apply to the stretching vibrations, but not to the bending vibrations, of the pyro group. However, these conclusions cannot be extended to the fresnoite case without discussion: some of the Ti—O frequencies can be high enough to fall in the range of the Si—O frequencies because of the presence of a highly charged cation and of a short Ti—O bond. Thus, the band assignment in this spectral region is not straightforward, and is further complicated by the possible mixing of Si—O and Ti—O modes. The application of the site group method (Hornig 1948) leads to the number and symmetry species of the normal modes of a molecular X_2O_7 group in the fresnoite structure (Table 2 for the stretching vibrations). For the translations of the Ti atoms, the correlation method leads to the representation: $\Gamma_{Ti} = A_1$ (IR, Ra) + A_2 (inactive) + $2E$ (IR, Ra). The Ti displacement along the z direction (equivalent to a stretching of the short Ti—O bond) belongs to the A species; the Ti displacements in the xy plane, to the E species.

This analysis shows that some vibrations of Si_2O_7 groups belong to the same representations (A_1 and E) as Ti translations, so their mixing is allowed. The answer to this problem is given by the study of isotopic species (Tarte and Preudhomme 1970).

Experimental Results and Interpretations

Spectra of Fresnoite and Related Silicates

The IR (showing the ^{28}Si – ^{30}Si isotopic shifts) and Raman spectra of $\text{Ba}_2\text{TiSi}_2\text{O}_8$ are illustrated in Fig. 1; the IR and Raman data of the pyrosilicates are listed in Table 3. The spectra of the fresnoite-like pyrosilicates are similar to those of the akermanite-

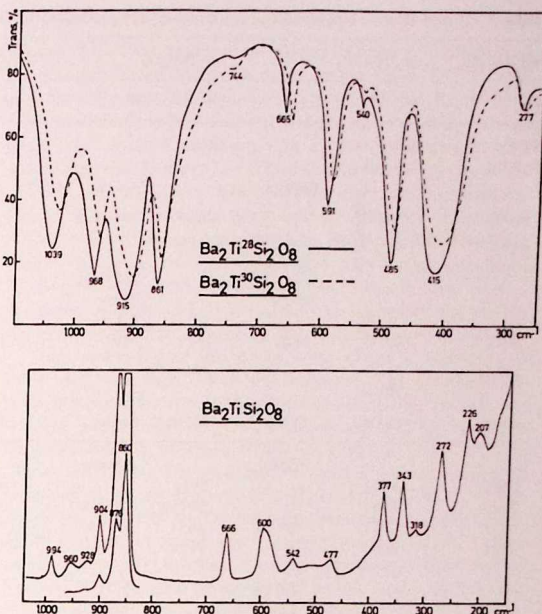


Fig. 1. IR and Raman spectra of fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$); the frequencies are related to the ^{28}Si compound

like ones (Gabelica-Robert and Tarte 1979a), probably because of some analogies between the two structures (same symmetry C_{2v} , similar bond lengths, and bridge angle for the pyro groups). However, a detailed study points out some differences due to the nature of the other groups contained in the structure, especially because of the existence of pyramidal TiO_5 groups in fresnoite and tetrahedral MgO_4 groups in akermanite.

Fresnoite-Stretching Modes

This spectral range is limited, on the low frequency side, by the band observed at 665 cm^{-1} in both IR and Raman spectra. This band exhibits a large ^{28}Si – ^{30}Si isotopic shift; in agreement with previous interpretations (Tarte et al. 1973; Gabelica-Robert et al. 1979a, b), this band may be assigned to the bridge symmetric stretch $\nu_s(\text{SiOSi})$ of A_1 class (in phase vibration of the two pyro groups).

The following IR band at 861 cm^{-1} shows a relatively small ^{28}Si – ^{30}Si isotopic shift (3 cm^{-1}). The corresponding Raman peak is the strongest of the spectrum, which suggests the assignment of this frequency to the A_1 -type $\nu_s(\text{SiO}_3)$ vibration. But this band exhibits also a significant ^{46}Ti – ^{50}Ti isotopic shift, implying the simultaneous participation of the stretching vibration of the short Ti—O bond, which is also of A_1 type. The assignment of this band to a totally symmetric mode is thus confirmed.

The next frequency, a Raman peak at 876 cm^{-1} , shows an analogous Ti isotopic shift (5 cm^{-1}). Because of the relatively high intensity of the peak and the fact that the A_1 -type ν (Ti—O) is the only possible mode of the TiO_5 group in this range, this 876 cm^{-1} peak must be assigned to another A_1 mode. The important ^{28}Si – ^{30}Si isotopic shift (9 cm^{-1}) suggests its assignment to a normal mode including the $\nu_{as}(\text{SiO}_3)$ and the ν (Ti—O) vibrations, both of A_1 class.

The remaining IR bands are necessarily of E class (Table 2).

Table 3. IR and Raman frequencies in the fresnoite-like pyrosilicates ^{28}Si - ^{30}Si and ^{46}Ti - ^{50}Ti isotopic shifts in the spectra of fresnoite

$\text{Ba}_2\text{VSi}_2\text{O}_8$		$\text{Sr}_2\text{TiSi}_2\text{O}_8$		$\text{Ba}_2\text{TiSi}_2\text{O}_8$		$\Delta\nu(\text{Si})$		$\Delta\nu(\text{Ti})$		Assignments
IR	IR	Ra	IR	Ra	IR	Ra	IR	Ra		
1037 s	1050 s		1039 s		9		1		} $2E v_{as}(\text{SiOSi}) + v'_{as}(\text{SiO}_3)$	
1007 sh	1030 sh									$B_1 v'_{as}(\text{SiO}_3)$
		1000 vw		994 vw		—		—	$E v'_s(\text{SiO}_3)$	
966 s	963 sh, b		968 s	960 vw, b	7	—	0	—	$E v_{as}(\text{SiO}_3)$	
917 s	927 s		915 s		12		0		} $2B_2 v_s(\text{SiO}_3) + v_{as}(\text{SiO}_3)$	
				928 vw, b		—		—		$A_1 v_{as}(\text{SiO}_3)$
				904 w		—		0	$A_1 v_s(\text{SiO}_3)$	
		893 w		876 m		~9		5	} $+7(\text{Ti}-\text{O})$	
862 s	862 s	860 s	861 s	860 s	3	2	3	6		
739 vw			744 vw, b		—		—		} ?	
654 m	681 m	684 m	665 m	666 w	11	10	0	0	$A_1 v_s(\text{SiOSi})$	
		628 m		600 w, b		—		—		
588 m	610 s		591 s		8		-1			
539 w	556 w		540 vw	542 vw	4	—	2	—		
482 s	497 s	504 w	485 s	477 vw	6	—	0	—	bending	
420 s	425 s		415 s, b		~10		~0		modes	
	393 s									
		407 vw		377 w		~6		6		
		350 w		343 w		0		0		
279 m	286 w		277 m, b	272 w	~5	—	~0	—		
				318 vw		—		—		
				226 w		—		1		
		250 w		207 vw, b		—		—		

—: The band is too broad or not observed in one of the isotopic compounds

The 915 cm^{-1} band, which exhibits the largest ^{28}Si - ^{30}Si isotopic shift, is assigned to the locally antisymmetric $v_{as}(\text{SiO}_3)$ mode, whereas the 968 cm^{-1} band is assigned to the $v'_s(\text{SiO}_3)$ mode.

The strong absorption band at 1039 cm^{-1} is assigned to a mixing of the $v_{as}(\text{SiOSi})$ (bridge antisymmetric stretch) and $v'_{as}(\text{SiO}_3)$ vibrations, both of class E, as for the akermanite-like pyrosilicates (Gabelica-Robert and Tarte 1979a). This interpretation is supported by the study of silicate-germanate solid solutions:

the $v_{as}(\text{SiOGe})$ vibration has been identified at 955 cm^{-1} (see below)

in a SiO_2 -poor solid solution (5%), which would no longer contain Si_2O_7 groups, a band is still present at 1003 cm^{-1} . This must characterize a vibration of the SiO_3 external group (in a SiGeO_7 group).

The interpretation of the remaining weak Raman peaks is consistent with the previous assignments and the results of group theory (Tables 2 and 3).

Fresnoite-Bending Modes

Between 250 and 600 cm^{-1} , most of the frequencies exclusively characterize bending modes of the Si_2O_7 groups. They show relatively important ^{28}Si - ^{30}Si isotopic shifts (from 4 to 10 cm^{-1}) and, except for the 540 (IR) and 377 (Ra) cm^{-1} frequencies, they are not shifted by the ^{46}Ti - ^{50}Ti substitution.

The spectra of $\text{Sr}_2\text{TiSi}_2\text{O}_8$ and $\text{Ba}_2\text{VSi}_2\text{O}_8$ can be interpreted in the same way. Apart from some small frequency shifts (Table 3), these spectra are nearly identical (in band shapes and relative intensities) to that of fresnoite, and they are not reproduced here.

Table 4. IR and Ra frequencies of $\text{Ba}_2\text{TiGe}_2\text{O}_8$

IR	R
911 m	914 m
891 m	
882 sh	883 sh
843 m	848 s
	814 m
800 s	802 s
757 s	
	748 m
	719 s
	551 m
533 m, b	531 sh
490 m	
	471 w
456 m	453 w
404 sh	405 w
382 m	
	356 w
340 s, b	

Spectra of $\text{Ba}_2\text{TiGe}_2\text{O}_8$

The spectra of $\text{Ba}_2\text{TiGe}_2\text{O}_8$ (Fig. 2) are completely different from those of the isostructural silicates and also from the akermanite-like pyrogermanates, certainly because of the stronger interactions between the vibrations of the Ge_2O_7 and TiO_5 groups.

In the spectral region corresponding to the stretching modes (920 – 530 cm^{-1}) we observe 11 bands, for a total of 12 active modes deduced from the group theory: 11 modes corresponding to the Ge_2O_7 group (Table 2) and the stretching motion of the

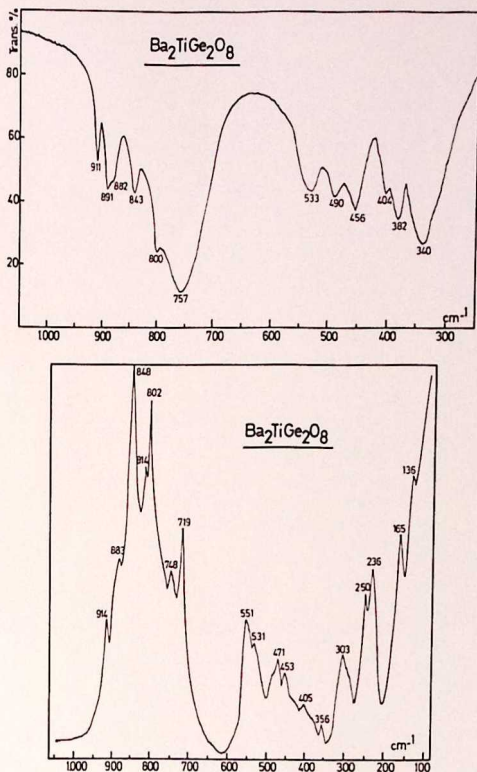


Fig. 2. IR and Raman spectra of $\text{Ba}_2\text{TiGe}_2\text{O}_8$.

Discussion

Blasse (1979) has assigned the strong 860 cm^{-1} Raman peak of fresnoite to the stretching mode of the short Ti—O bond, and the corresponding IR band to Ti—O and Si—O vibrations. This assignment is based on the strong intensity of the Raman peak, and on the comparison with Ti—O frequencies in compounds containing short Ti—O bonds (Blasse and van den Heuvel 1974; Paques-Ledent 1976). No clear explanation is proposed for the 876 cm^{-1} Raman peak, and no reference is made to the short Ti—O distance evidenced by Moore and Louisnathan (1969). It is clear from our results that these assignments must be revised, since both 860 and 876 cm^{-1} bands arise from a simultaneous stretching of Ti—O and Si—O bonds, the mixing of these modes being allowed by the theoretical group analysis.

It is interesting to discuss to what extent a short Ti—O bond leads to a high vibrational frequency. The correlation is well-established for compounds such as NaLnTiO_4 (Blasse and van den Heuvel 1974), Ln_2TiO_5 (Paques-Ledent 1976), and now fresnoite. But the situation is not so clear-cut if we turn to titanite CaTiSiO_5 . The structure of pure, synthetic titanite is characterized by the existence of a short (1.766 \AA) Ti—O bond (Speer and Gibbs 1976). On the other hand, at about 680 cm^{-1} the IR spectrum of titanite (Howie and Woolley 1968; Plyusnina and Zaitseva 1971) exhibits a strong, very broad band that is assigned to a vibration of the Ti—O bonds. This is well below the $900\text{--}800\text{ cm}^{-1}$ range previously observed for short Ti—O bonds, and not much higher than the 600 cm^{-1} value quoted for condensed TiO_6 octahedra with normal Ti—O distances (Tarte 1961, 1965).

We have carried out a systematic study of the vibrational spectrum of both natural and synthetic titanite. A detailed discussion of the results is outside the scope of this paper, and we shall restrict the conclusions to those that are relevant to the problem under consideration: no strong band exhibiting a significant $^{46}\text{--}^{50}\text{Ti}$ isotopic shift is observed in the $1000\text{--}700\text{ cm}^{-1}$ range, either in the IR or in the Raman spectrum. Only one feature, namely the strong, broad IR band centered near 680 cm^{-1} , may possibly be associated to short Ti—O distances. This band has no counterpart in the Raman spectrum and thus, *nothing in the Raman spectrum reveals the existence of a short Ti—O bond*. The vibrational behavior is thus completely different from that observed in fresnoite. It should be immediately pointed out that the structural arrangement of Ti—O bonds is very different in fresnoite and in titanite: in fresnoite, the short Ti—O is 'isolated' in a discrete TiO_3 group; in titanite, this short bond is included in a chain of TiO_6 octahedra (Speer and Gibbs 1976), the oxygen being common to one short and one normal Ti—O bond. We suggest that this arrangement precludes the existence of a vibration that would be really localized on the short Ti—O bond, the chain structure being responsible for some averaging of the vibrational frequencies. Further work on these problems is being carried out in this laboratory.

Conclusions

This vibrational investigation of fresnoite shows that the study of isotopic species is of great help in interpreting the spectrum of pyrosilicates, and to evidence possible Ti—O and Si—O vibrational interactions in the spectrum of titanosilicates. The existence of a short Ti—O bond in a structure may induce high Ti—O vibrational frequencies, but this is not a general rule and depends on the very structure of the compound under consideration.

short Ti—O bond. However, due to the lack of isotopic data, definite assignments are not possible because of the probability of strong mixing between the different types of Ge—O stretching modes and between the Ti—O and Ge—O modes of appropriate symmetry.

We can just assign the 551 and 531 cm^{-1} bands to the two modes (B_2 and A_1 , respectively) associated with the ν_s (Ge—O—Ge) bridge symmetric stretch. These vibrations have been observed near 530 cm^{-1} in the spectrum of akermanite-type germanates (Gabelica-Robert and Tarte 1979a). In these latter compounds, the corresponding antisymmetric motion ν_{as} (Ge—O—Ge) is the highest-frequency band of the spectrum and is located near 860 cm^{-1} . By analogy, the same vibration in the fresnoite lattice should be assigned to one of the IR bands observed in the $915\text{--}880\text{ cm}^{-1}$ region.

Spectra of Solid Solutions $\text{Ba}_2\text{TiSi}_{2-x}\text{Ge}_x\text{O}_8$

Besides Si_2O_7 and Ge_2O_7 groups, such solid solutions generally contain mixed SiGeO_7 groups and thus exhibit new bands, the most characteristic ones being the stretching vibrations of the SiOGe bridge:

1. The ν_s (SiOGe) vibration is identified at 600 cm^{-1} , this value being practically equal to the average between the corresponding SiOSi and GeOGe frequencies.

2. A new band at 955 cm^{-1} , an intermediate frequency between ν_{as} (SiOSi) (1039 cm^{-1}) and ν_{as} (GeOGe) (between 915 and 880 cm^{-1}), is probably the ν_{as} (SiOGe) vibration.

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