

Vibrational spectrum of akermanite-like silicates and germanates

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(Received 28 April 1978)

Abstract—The i.r. and Raman spectra of $A_2^{II}B^{III}X_2O_7$ pyro-silicates and -germanates having the akermanite, or an akermanite-like, structure are reported and interpreted with the help of a group theoretical analysis, and ^{24}Mg - ^{26}Mg and ^{28}Si - ^{30}Si isotopic shifts.

The stretching vibrations of the Si_2O_7 or Ge_2O_7 groups are generally free from interactions with the lattice frequencies, whereas some of the bending vibrations of these groups are strongly mixed up with vibrations of the $B^{III}O_4$ tetrahedra. The existing data on the vibrations of these tetrahedral groups have been confirmed and extended. The X-O-X bridge frequencies of the pyro groups have been identified; the value of the bridge angle deduced from these frequencies is in satisfactory agreement with the literature values obtained by X-ray diffraction.

INTRODUCTION

The vibrational spectrum of silicates and germanates with the akermanite structure has already been investigated [1, 2], mainly by comparison of the spectra of isomorphous compounds and their solid solutions [1]. Some assignments, however, remained tentative, and we have reinvestigated this problem, taking advantage of the possibilities offered by the isotopic substitutions ^{28}Si - ^{30}Si and ^{24}Mg - ^{26}Mg .

EXPERIMENTAL

The following compounds were prepared according to literature data [3-9]: $Ca_2B^{III}Si_2O_7$ ($B^{III}=Be, Mg, Zn, Co$); $Sr_2B^{III}Si_2O_7$, $Sr_2B^{III}Ge_2O_7$ and $Ba_2B^{III}Ge_2O_7$ ($B^{III}=Mg, Zn, Co, Fe, Mn$); $Ba_2B^{III}Si_2O_7$ ($B^{III}=Fe, Mn$). Mn and Fe compounds were synthesized under vacuum. The purity of all compounds was checked by X-ray diffractometry. Infrared (Beckman IR-12; KBr discs) and Raman spectra (CODERG PHO double monochromator; He-Ne laser) were recorded as usual.

CRYSTAL STRUCTURE AND GROUP THEORETICAL ANALYSIS

The crystal structure is well known and has been confirmed by recent works [10, 11]. The structure is tetragonal, space group $P\bar{4}2_1m$ (D_{2d}^3), $Z=2$. In view of the general formula $A_2^{II}B^{III}X_2O_7$ ($X=Si, Ge$), these compounds may be classified as pyro-silicates (or -germanates) with "isolated" pyro groups. Since, however, the X_2O_7 and BO_4 tetrahedra are sharing some oxygen atoms, the structure may be alternatively described by layers of composition $[(BX_2O_7)^{4-}]_n$ connected by the large A^{II} cations in eightfold coordination. The knowledge of the atomic positions and symmetries (Table 1) and the factor group analysis [12, 13] lead to the following representation (for the crystal cell):

$$\Gamma = 10A_1 + 6A_2 + 7B_1 + 10B_2 + 18E$$

Now, we may tentatively apply the following usual approximations.

(1) The separation of the vibrations into internal modes of the X_2O_7 group, and external modes (Table 2).

(2) For the internal modes, the separation into stretching and bending modes:

$$\Gamma^{\text{stretching}} = 3A_1 + A_2 + B_1 + 3B_2 + 4E \quad (7 \text{ i.r.} + 11 \text{ Raman})$$

$$\Gamma^{\text{bending}} = 4A_1 + 3A_2 + 3B_1 + 4B_2 + 6E \quad (10 \text{ i.r.} + 17 \text{ Raman})$$

vibrations of the so-called bridge X-O-X and vibrations of the terminal pyramids XO_3 .

Table 1. Position and symmetry of the sites occupied in the akermanite structure

Atoms	Position	Symmetry
$4A^{II}$	e	C_s
$2B^{III}$	a	S_4
4X	e	C_s
2O(1)	c	C_{2v}
4O(2)	e	C_s
8O(3)	f	C_1

Table 2. Normal modes for the $A_2^{II}B^{III}X_2O_7$ unit cell

Symmetry classes Type	A_1 (Raman)	A_2 (in)	B_1 (Raman)	B_2 (i.r., Raman)	E (i.r., Raman)
Total modes	10	6	7	11	19
Acoustical				1	1
Translational	3	1	2	3	6
Rotational		1	1		2
Internal	7	4	4	7	10

As far as this separation is justified, the vibrational behaviour of the X-O-X bridge is interesting from two points of view: (i) The Raman and i.r. activity of the two stretching modes (symmetric and antisymmetric) of the bridge depends on the configuration (linear or bent) of

the bridge [14]; (ii) The frequency difference $\nu_{as} - \nu_{sym}$ between these modes increases with the X-O-X bridge angle [15].

Before discussing these points, we must first investigate the validity of these approximations by appropriate experimental techniques, essentially the study of isotopic species.

RESULTS AND INTERPRETATIONS

Silicates $Sr_2B^{11}Si_2O_7$ and isotopic data

The i.r. and Raman data are collected in Tables 3 and 4. The isotopic shifts observed in the i.r. spectrum of $Sr_2MgSi_2O_7$ are illustrated in Fig. 1. Owing to their weakness, the Raman spectra exhibit a limited number of peaks.

in the 1100–650 cm^{-1} region (Table 4), against seven predicted i.r. active fundamentals. But we have good reasons to believe that the weak band near 708 cm^{-1} should be assigned to an impurity: its relative intensity is not reproducible from sample to sample; this intensity drops to nearly zero if a small excess of MgO is added to the reacting mixture; and this band is completely missing in all other silicates of the same family. The very nature of this impurity is still unknown.

The remaining bands may be assigned to vibrations of either the X-O-X bridge, or the terminal XO_3 pyramids (Table 5). The bridge symmetric stretch $\nu_{sym}(XOX)$ has been widely investigated [14–19], and the corresponding band is observed in the 730–630 cm^{-1} region. Thus the bands observed at 671 (i.r.) and 653 (R) cm^{-1} may be assigned with confidence to this type of vibration. This assignment is strongly supported

Table 3. Infrared and Raman frequencies in the compounds $Sr_2B^{11}Si_2O_7$

$Sr_2MgSi_2O_7$		$Sr_2ZnSi_2O_7$		$Sr_2MnSi_2O_7$		$Sr_2CoSi_2O_7$	$Sr_2FeSi_2O_7$	Assignments
i.r.	Raman	i.r.	Raman	i.r.	Raman	i.r.	i.r.	
1017 sh		1017 sh		1022 sh		1020 sh	~ 1015 sh	$\nu_{as}(SiOSi) + \nu_{as}(SiO_3)$
1004 s		1005 s		1008 s		1002 s	1002 s	
	{ 984 sh 975 w		995 w		991 w			$\nu_{as}(SiO_3) + \nu_{as}(SiO_3)$
965 s			966 s		968 s		963 s	
925 s								$\nu_{as}(SiO_3)$
{ 904 sh	901 s							$\nu_{sym}(SiO_3) + \nu_{as}(SiO_3)$
		902 s	901 s	907 s	904 s	897 s	911 s	
840 s	838 vw	830 s	839 w	832 s	819 w	827 s	837 s	$\nu_{sym}(SiO_3)$
708 w								$\nu_{sym}(SiO_3)$
671 m		668 m		664 m		668 m	667 m	impurity
	653 m	650 s		649 s				$\nu_{sym}(SiOSi)$
								$\nu_{sym}(SiOSi)$
{ 620 m		{ 600 m		597 m		{ 605 m	595 m	$Si_2O_7 + BO_4$
{ 600 sh		{ 578 sh				{ 577 sh		
	590 vw		596 m		590 vw			Si_2O_7
567 m	568 vw				531 vw	530 w, b		$MgO_4 + Si_2O_7$
		530 w, b	533 w			480 s	485 s	ZnO_4, CoO_4, MnO_4
475 s, b	475 vw	483 s	476 w	482 s		450 s	450 s	Si_2O_7
	450 vw		447 w					
		454 s		443 s				$ZnO_4, MnO_4, CoO_4, FeO_4$
394 s								MgO_4
358 w								
		334 m		334 m		335 m	334 m	$ZnO_4, MnO_4, CoO_4, FeO_4$
		314 w				312 w		
	315 m	314 s		307 w				Si_2O_7
300 m								MgO_4
265 m		267 m		275 m		271 m	275 m	Si_2O_7

A look at the frequencies of the isotopic species of $Sr_2MgSi_2O_7$ (^{28}Si - ^{30}Si and ^{24}Mg - ^{26}Mg : Table 4) shows that the spectrum may be divided into 2 parts: (1) a higher frequency region (1100–650 cm^{-1}), characterized by more or less important mass effects of Si, but no mass influence of Mg: these bands correspond to stretching vibrations of the Si_2O_7 group, with no significant contribution of the external modes. (2) A lower frequency region (620–250 cm^{-1}) where both Si and Mg cations may exhibit mass effects. Such bands must be assigned to Si_2O_7 bending vibrations, MgO_4 vibrations (or Mg translations), or some mixing of these vibrations.

Stretching vibrations of the Si_2O_7 group

The i.r. spectrum of $Sr_2MgSi_2O_7$ exhibits eight bands

by the large ^{28}Si - ^{30}Si isotopic shift (10 cm^{-1} : Table 4) associated to this type of vibration, and which is similar to that already observed for $K_2Pb_2Si_2O_7$ [16] and $Pb_2In_2Si_2O_9$ [14]. The occurrence of two distinct frequencies comes from the presence, in the unit cell, of 2 Si_2O_7 groups, thus giving rise to in-phase (A_1) and out-of-phase (B_2) vibrations.

For the silicates, the bridge antisymmetric stretch is generally assigned to the highest observed frequency which, in favourable cases such as $K_2Pb_2Si_2O_7$ [16], $Sc_2Si_2O_7$ [17], $Ba_3Nb_6Si_4O_{26}$ [18] or $Pb_2M_2^{11}Si_2O_9$ [14], is well separated from the lower frequency bands assigned to vibrations of the terminal SiO_3 pyramids. This is no longer true here, with two overlapping bands near 1000 cm^{-1} ; one of these bands appears as a shoulder, and the ^{28}Si - ^{30}Si isotopic shift cannot be

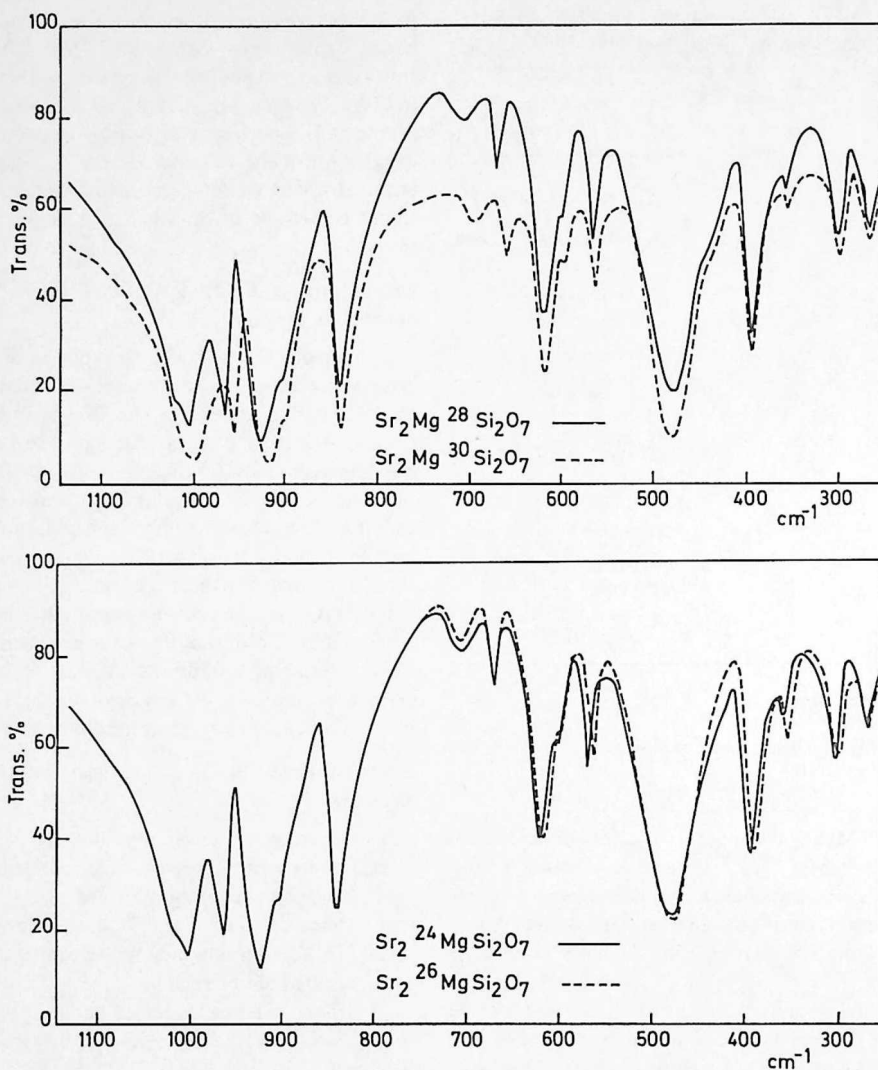


Fig. 1. ^{28}Si - ^{30}Si and ^{24}Mg - ^{26}Mg isotopic shifts in the i.r. spectrum of $\text{Sr}_2\text{MgSi}_2\text{O}_7$.

measured, whereas the other band exhibits a rather moderate isotopic shift (5 cm^{-1}): this is the expected order of magnitude for the bridge antisymmetric stretch. Nevertheless, since the isotopic behaviour of the shoulder remains unknown, it is impossible to decide which of these bands may be assigned to the bridge antisymmetric stretch, the other band being assigned to some vibration of the terminal SiO_3 group. Moreover, this discrimination is perhaps not justified, since some mixing between these two types of vibration is quite possible.

The remaining frequencies must be assigned to vibrations of the terminal SiO_3 pyramids and may be distributed into modes which are: (i) symmetric or antisymmetric with respect to the local ternary axis of the SiO_3 group; (ii) in-phase or out-of-phase. The assignments proposed in Tables 3 and 4 are based on the vibrational behaviour of "isolated" SiO_4 tetrahedra: as a general rule, the antisymmetric vibrations should

lead to higher frequencies, and larger isotopic shifts, than the symmetric ones. Since these assignments are tentative, they will not be discussed at length, but the strong band near 840 cm^{-1} deserves special attention, since an equivalent band (with a similar frequency and a very small isotopic shift) has already been observed in a series of various pyrosilicates: $\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26}$ [18], $\text{Pb}_2\text{M}_2^{11}\text{Si}_2\text{O}_9$ [14] and $\text{M}^{11}\text{Pb}_8(\text{Si}_2\text{O}_7)_3$. This band is assigned to the symmetric, out of phase, stretch of the SiO_3 groups, a type of vibration which should give a relatively low frequency, and a small ^{28}Si - ^{30}Si isotopic shift.

The extension of these assignments to all the compounds of this family is straightforward (Table 3).

Lower frequency bands ($620\text{--}250\text{ cm}^{-1}$)

According to the isotopic shifts (Table 4), these vibrations may be roughly distributed into 3 types: (1) Bending motions of the Si_2O_7 groups; (2) Stretching

Table 4. Infrared and Raman spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7$: ^{24}Mg - ^{26}Mg and ^{28}Si - ^{30}Si isotopic shifts

$\text{Sr}_2\text{MgSi}_2\text{O}_7$		$\Delta\nu(\text{Mg})^*$		$\Delta\nu(\text{Si})^\dagger$		Assignments
i.r.	Raman	i.r.	Raman	i.r.	Raman	
1017 sh		0		‡		$\nu_{\text{as}}(\text{SiOSi}) + \nu_{\text{as}}(\text{SiO}_3)E$
1004 s		0		5		
	984 sh		0	‡		$\nu_{\text{as}}(\text{SiO}_3) + \nu_{\text{as}}(\text{SiO}_3) A_1 + B_1$
	975 w		0	4		
965 s		0		11		$\nu_{\text{as}}(\text{SiO}_3)E$
925 s		0		10		$\nu_{\text{sym}}(\text{SiO}_3) + \nu_{\text{as}}(\text{SiO}_3) B_2$
904 sh		0		~4		
	901 s		0		5	$\nu_{\text{sym}}(\text{SiO}_3) A_1$ ou B_2
840 s	838 vw	0	‡	2	‡	$\nu_{\text{sym}}(\text{SiO}_3)E$
708 w		0		10		impurity
671 m		0		10		$\nu_{\text{sym}}(\text{SiOSi}) B_2$
	653 m		0		10	$\nu_{\text{sym}}(\text{SiOSi}) A_1$
620 s		4		3		$\text{Si}_2\text{O}_7 + \text{MgO}_4$
600 sh		3		2		$\text{Si}_2\text{O}_7 + \text{MgO}_4$
	590 vw		0		4	Si_2O_7
567 m	568 vw	6	‡	3	‡	$\text{MgO}_4 + \text{Si}_2\text{O}_7$
475 s, b	475 vw	0	‡	0	‡	Si_2O_7
	450 vw		0		3	Si_2O_7
394 s		6		1		MgO_4
358 w		6		1		MgO_4
	315m		0		0	Si_2O_7
300 m		6		0		MgO_4
265 m		0		0		Si_2O_7

* $\Delta\nu(\text{Mg})$: $\nu(^{24}\text{Mg}) - \nu(^{26}\text{Mg})$ † $\Delta\nu(\text{Si})$: $\nu(^{28}\text{Si}) - \nu(^{30}\text{Si})$

‡The band is too broad or is not observed in one of the two isotopic compounds.

motions of MgO_4 tetrahedra or, alternatively, translations of the Mg^{2+} cations (a choice between these descriptions is meaningless as far as we have no knowledge of the oxygen displacements); (3) Complex vibrations involving the participation of both Si and Mg atoms.

This behaviour may be extended to the spectra of the similar Zn, Co, Mn and Fe compounds: the bands with no Mg mass effect (SiO_3 bending) are hardly displaced

in the spectra of the other compounds, whereas all the bands exhibiting a significant ^{24}Mg - ^{26}Mg isotopic shift are also more or less strongly shifted towards lower frequencies when Mg is replaced by a heavier cation (Table 3). It is perhaps worth while to mention that the assignment of the 567 and 394 cm^{-1} bands to MgO_4 tetrahedra had already been deduced from the vibrational behaviour of $\text{Sr}_2(\text{Mg}_{1-x}\text{Zn}_x)\text{Si}_2\text{O}_7$ solid solutions [1].

Other silicates $\text{Ca}_2\text{B}^{\text{II}}\text{Si}_2\text{O}_7$ and $\text{Ba}_2\text{B}^{\text{II}}\text{Si}_2\text{O}_7$ with akermanite structure

Apart from $\text{Ca}_2\text{BeSi}_2\text{O}_7$, the spectra of these compounds are quite similar to those of the corresponding Sr compounds, except in the low frequency region (below 400 cm^{-1}), where the band-to-band correspondence is not always clear: it is possible that the large bivalent cation (Ca, Sr, Ba) is participating to some extent to low frequency vibrations, although we were unable to find out frequencies which would be specifically related to these cations. The spectrum of $\text{Ca}_2\text{BeSi}_2\text{O}_7$ is different, as expected from the small mass and ionic radius of Be: some mixing of Si_2O_7 and BeO_4 stretching vibrations should occur; and the possible replacement of Si by Be in the Si_2O_7 group [20] is a further cause of spectral modifications.

Silicates $\text{Ba}_2\text{B}^{\text{II}}\text{Si}_2\text{O}_7$ not having the akermanite structure

The structure of these compounds ($B^{\text{II}} = \text{Mg, Zn, Co}$) is still unknown; however, their vibrational spectra and X-ray powder diagrams are not very different from those of akermanite; the coordination of the small B^{II} cation should be tetrahedral and both structures should be related.

The most striking analogies between the spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Ba}_2\text{MgSi}_2\text{O}_7$ (Tables 4 and 6) are as follows:

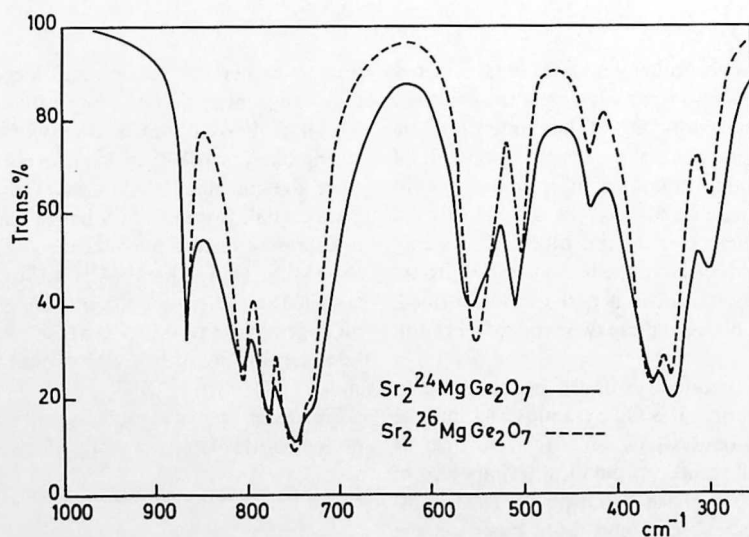
Fig. 2. Infrared spectrum of $\text{Sr}_2\text{MgGe}_2\text{O}_7$ showing the ^{24}Mg - ^{26}Mg isotopic shifts.

Table 5. Stretching modes of the X₂O₇ groups in the akermanite structure

Description	C _{2v} (site group)	D _{2d} (factor group)	i.r.	Raman
<i>v</i> _{sym} (XOX)	A ₁	A ₁ + B ₂	B ₂	A ₁ + B ₂
<i>v</i> _{sym} (XO ₃)	A ₁	A ₁ + B ₂	B ₂	A ₁ + B ₂
<i>v</i> ' _{sym} (XO ₃)	B ₁	E	E	E
<i>v</i> _{as} (XOX)	B ₁	E	E	E
<i>v</i> _{as} (XO ₃)	A ₁	A ₁ + B ₂	B ₂	A ₁ + B ₂
	B ₂	E	E	E
<i>v</i> ' _{as} (XO ₃)	A ₂	A ₂ + B ₁	—	B ₁
	B ₁	E	E	E

Table 6. Infrared and R spectra of Ba₂MgSi₂O₇ and Ba₂ZnSi₂O₇; ²⁸Si-³⁰Si isotopic shifts in Ba₂MgSi₂O₇

Ba ₂ MgSi ₂ O ₇		Ba ₂ ZnSi ₂ O ₇		Δ <i>v</i> (Si)		Assignments
i.r.	Raman	i.r.	Raman	i.r.	Raman	
997 s, b	970 m	990 s, b	978 m	~10	16	<i>v</i> _{as} (SiOSi) + <i>v</i> _{as} (SiO ₃)
962 s		962 s, b		0	—	<i>v</i> (SiO ₃)
{ 927 s	931 w	913 s		12	—	
{ 848 sh	896 s		894 s	—	6	
	857 w				2	
835 s		827 s		2	6	<i>v</i> _{sym} (SiOSi)
	826 m		823 m		10	
	656 s		652 s		6	
638 m		635 m		6	—	
	602 w			—	—	Si ₂ O ₇
568 m		547 s		5	—	Si ₂ O ₇ + BO ₄
	560 m		563 m	—	—	Si ₂ O ₇
		513 m		—	—	ZnO ₄
	500 w		477 w	—	—	Si ₂ O ₇ + BO ₄
{ ~472 sh	471 w	469 s	462 w	—	—	Si ₂ O ₇
{ 463 s		453 s		2	—	Si ₂ O ₇
	447 m			—	—	?
425 m				1	—	MgO ₄
374 m				0	—	?
	336 w		350 w	—	—	MgO ₄
324 w				0	—	ZnO ₄
	290 m		294 m	—	—	Si ₂ O ₇
	280 m		281 m	—	—	ZnO ₄

The occurrence of some bands of the Si₂O₇ group with nearly the same frequency, relative intensity and

²⁸Si-³⁰Si isotopic shift: the strong i.r. bands near 925 (*v* SiO₃) and 840 cm⁻¹ (*v*_{sym} SiO₃) and the Raman band near 653 cm⁻¹ (*v*_{sym} Si-O-Si).

The occurrence, near 570 and 400 cm⁻¹, of bands which are clearly related to vibrations of MgO₄ tetrahedra and are accordingly shifted towards lower frequencies in the Zn, Co...compounds.

Nevertheless, significant differences are also observed: some bands, apparently similar as far as frequency and intensity are concerned, exhibit completely different isotopic shifts and thus cannot be assigned to the same vibrations (e.g. the strong i.r. band near 965 cm⁻¹); likewise, the i.r. band assigned to the B₂ bridge symmetric stretch is lowered from 671 (Sr₂Mg) to 638 cm⁻¹ (Ba₂Mg), whereas the corresponding A₁, Raman-active, band remains practically unshifted at 653-656 cm⁻¹.

Germanates Sr₂B¹¹Ge₂O₇

These spectra are quite similar to those of the corresponding silicates (Table 7, Fig. 2).

Bridge antisymmetric stretch

This is assigned to the highest-frequency i.r. band (870-850 cm⁻¹). This is slightly lower than the values corresponding to a linear Ge-O-Ge bridge [16-18], but quite similar to the frequencies observed in the case of Pb₂M¹¹Ge₂O₉ compounds, with a bent bridge [14].

Bridge symmetric stretch

The fairly strong Raman peak near 520 cm⁻¹ is assigned to the bridge symmetric stretch of A₁ class, whereas the corresponding B₂ mode is represented by the 557 cm⁻¹ i.r. band. However, this latter band cannot be assigned to a pure Ge₂O₇ vibration, because of the ²⁴Mg-²⁶Mg isotopic shift (3 cm⁻¹), which evidences some mixing with a MgO₄ vibration; this mixing is also proved by the frequency lowering observed when passing from the Mg to the Zn, Co, ... compounds

Table 7. Infrared and Raman frequencies in the germanates Sr₂B¹¹Ge₂O₇; ²⁴Mg-²⁶Mg isotopic shifts in Sr₂MgGe₂O₇

Sr ₂ MgGe ₂ O ₇		Sr ₂ ZnGe ₂ O ₇		Sr ₂ CoGe ₂ O ₇	Sr ₂ MnGe ₂ O ₇	Sr ₂ FeGe ₂ O ₇	Δ <i>v</i> (Mg)		Assignments
i.r.	Raman	i.r.	Raman	i.r.	i.r.	i.r.	i.r.	Raman	
869 m		861 m		858 m	862 m	850 m	0	0	<i>v</i> _{as} (GeOGe)
	841 w							0	
807 m	814 m	804 m	800 m	799 m	800 m	797 m, b	2	0	
	798 w							0	<i>v</i> _{sym} (GeO ₃) and <i>v</i> _{as} (GeO ₃)
778 s	778 vs	781 m	777 vs	778 m	777 m	778 m, b	0	0	
			733 w					0	
{ 750 s	748 w, b	725 s	719 w	720 s	727 s	730 s, b	0	—	
{ 733 sh							0	—	
{ 557 m		530 m		533 m	526 m	524 m	3	0	
	522 m		528 m				6	0	<i>v</i> _{sym} (GeOGe) + BO ₄ (B ₂)
511 m								—	<i>v</i> _{sym} (GeOGe) (A ₁)
	476 w							—	MgO ₄
	449 vw	449 vw						—	?
		452 w		455 w	445 w	470 w, b		—	Ge ₂ O ₇
428 w	431 vw	420 w		414 w, b	405 w	400 w, b	1	—	ZnO ₄ , CoO ₄ , MnO ₄ , FeO ₄
	372 vw		371 vw					—	Ge ₂ O ₇
{ 360 s	354 w	{ 350 sh		{ 349 sh	335 s, b	328 s, b	0	—	
{ 342 s		{ 334 s		{ 336 s, b			0	—	
	320 w		311 w				0	0	
297 m	297 w	282 sh		277 sh			0	0	

(Table 7). Such a mixing is not observed, and indeed is forbidden, for the corresponding A_1 , Raman active, vibration, since the B^{II} cations, lying on sites of S_4 symmetry, are not allowed to move during the vibrations of A_1 type. These assignments will be supported by the study of silicate-germanate solid solutions (see below).

GeO₃ stretching vibrations

These bands are located in the 840–700 cm⁻¹ region, but the existing data do not justify a more detailed discussion.

Lower frequency bands (510–250 cm⁻¹)

According to the observed mass effects (Isotopic ²⁴Mg–²⁶Mg, or isomorphic Mg–Zn), these bands may be roughly assigned, either to bending motions of the Ge₂O₇ groups, or to vibrations of the tetrahedral B^{IV}O₄ groups (Table 7).

Solid solutions Sr₂ZnSi_{2-x}Ge_xO₇

Besides Si₂O₇ and Ge₂O₇ groups, such solid solutions generally contain mixed SiGeO₇ groups and thus exhibit new bands, the most characteristic ones being the stretching frequencies of the Si–O–Ge bridge [15, 16, 18, 19]. In the present case, we observe near 930 cm⁻¹ a new i.r. band, whose intensity is maximum for $x=1$. This band is assigned to the antisymmetric stretch of the Si–O–Ge bridge, its value being practically equal to the average between the corresponding Si–O–Si and Ge–O–Ge frequencies.

No new i.r. band corresponding to the Si–O–Ge symmetric stretch has been observed, possibly because of overlapping with the 600 and 578 cm⁻¹ bands of Sr₂ZnSi₂O₇. But a probably* new Raman peak is observed at 600 cm⁻¹: it is assigned to the Si–O–Ge symmetric stretch, with an intermediate frequency between those of the Si–O–Si and Ge–O–Ge groups.

Bridge angle vs bridge frequencies

Lazarev [15] has proposed for pyrosilicates a relationship between the bridge angle and the parameter

$$\Delta = \frac{\nu_{as} - \nu_{sym}}{\nu_{as} + \nu_{sym}} \cdot 100.$$

The values of Δ have been calculated for a series of akermanites by taking, for ν_{as} , the average frequency between the 2 highest-frequency i.r. bands, and for ν_{sym} , the average between the i.r. and Raman frequen-

*The restriction comes from the fact that there is already a peak of the pyrosilicate at 596 cm⁻¹. The occurrence of a new band is deduced from the intensity changes in relation with x values.

Table 8. Calculation of the parameter $\Delta = \frac{\nu_{as} - \nu_{sym}}{\nu_{as} + \nu_{sym}} \cdot 100$ in some pyrosilicates having the akermanite structure

Compound	$\nu_{as}(\text{SiOSi})$	$\nu_{sym}(\text{SiOSi})$	Δ
Ca ₂ MgSi ₂ O ₇	1020	675	20,5
Ca ₂ ZnSi ₂ O ₇	1021	674	20,5
Sr ₂ MgSi ₂ O ₇	1010	662	20,8
Sr ₂ ZnSi ₂ O ₇	1011	659	21,1
Sr ₂ MnSi ₂ O ₇	1010	657	21,2
Ba ₂ MnSi ₂ O ₇	993	642	21,5

cies. Plotting these Δ values on the graph given by Lazarev gives the angles of the bridge. The value obtained for Ca₂MgSi₂O₇ and Ca₂ZnSi₂O₇ (137°) compares favourably with published X-ray diffraction data (137°7 for Ca₂MgSi₂O₇ [10], 138°5 for Ca₂ZnSi₂O₇ [11]). It may be also noticed that the Δ , and hence the angle values increase with increasing size of the cations. A similar behaviour has already been observed in pyrosilicates with either the kentrolite [14], or the barysilite [19] structure.

REFERENCES

- [1] P. TARTE, Thèse d'Agrégation de l'Enseignement Supérieur, Liège (1965).
- [2] V. KOLESOVA, A. ISMATOV and N. TOROPOV, *Izv. Akad. SSSR, Neorg. Mater.* **5**, 1594 (1969).
- [3] C. GORIA, *Atti. Acad. Sci. Torino* **88**, 3 (1954).
- [4] H. A. KLASSENS, A. H. HOEKSTRA and P. COX, *J. Electr. Soc.* **104**, 93 (1957).
- [5] C. BRISI and F. ABBATTISTA, *Ann. Chimica* **50**, 1435 (1960).
- [6] C. BRISI and F. ABBATTISTA, *Ann. Chimica* **50**, 1786 (1960).
- [7] C. BRISI and F. ABBATTISTA, *Atti. Acad. Sci. Torino* **95**, 1 (1961).
- [8] C. BRISI, *Ann. Chimica* **54**, 673 (1964).
- [9] H. KOELMANS and C. VERHAGEN, *J. Electr. Soc.* **106**, 677 (1959).
- [10] J. V. SMITH, *Am. Mineral.* **38**, 643 (1953).
- [11] S. J. LOUISNATHAN, *Z. Krist.* **130**, 427 (1969).
- [12] B. DE ANGELIS, R. E. NEWNHAM and W. P. WHITE, *Am. Mineral* **57**, 255 (1972).
- [13] W. G. FATELEY, N. T. DEVITT and F. F. BENTLEY, *Appl. Spectry* **25**, 155 (1971).
- [14] M. GABELICA-ROBERT and P. TARTE, *J. Solid State Chem.* (in press).
- [15] A. N. LAZAREV, *Vibrational Spectra and Structure of Silicates*. Consultants Bureau, N.Y. (1972).
- [16] P. TARTE, M. J. POTTIER and A. M. PROCES, *Spectrochim. Acta* **29A**, 1017 (1973).
- [17] A. N. LAZAREV and A. P. MIRGORODSKII, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **7**, 1224 (1971).
- [18] J. CHOISNET, N. NGUYEN, B. RAVEAU, M. GABELICA-ROBERT and P. TARTE, *J. Solid State Chim.* **26**, 83 (1978).
- [19] J. LAJZEROWICZ, *Acta Cryst.* **20**, 357 (1965).
- [20] O. H. J. CHRISTIE, *A Contribution to the Mineralogy of the Melilite Group*, Oslo (1964).