Synthesis, X-Ray Diffraction and Vibrational Study of Silicates and Germanates Isostructural with Kentrolite Pb₂Mn₂Si₂O₉

M. GABELICA-ROBERT AND P. TARTE

University of Liège, Institute of Chemistry, B-4000 Sart Tilman par Liege 1, Belgium

New germanates $Pb_2M_2^{III}Ge_2O_9$ (M^{III} = Fe, Mn, Sc, In) and silicates $Pb_2M^{II}M^{IV}Si_2O_9$ (M^{II} = Mg, Ni, Co, Cu for M^{IV} = Sn; M^{II} = Co, Ni for M^{IV} = Ti) have been synthesized by solid state reaction. Their X-ray powder diagrams may be indexed in the orthorhombic system and show that these compounds are isostructural with kentrolite $Pb_2Mn_2Si_2O_9$. Doubts are expressed about the published structure of kentrolite and it is shown that some aspects of the structure should be re-examined.

The *I.R.* and Raman spectra of these compounds are fairly complicated, and their discussion is restricted to the region of Si–O or Ge–O stretching frequencies. These spectra show the existence of a *pyro*-silicate or -germanate group. The symmetric and antisymmetric frequencies of the Si–O–Si bridge have been identified with the help of ^{28}Si–^{30}Si isotopic shifts. Their difference ν_{as}–ν_{sym} depends on the ionic radius of the cations, and points to a non-linear bridge of the pyrosilicate group.

Introduction

According to Gabrielson (*1*), the structure of kentrolite Pb_2 (Mn, Fe)$_2Si_2O_9$ is characterized by the presence of pyrosilicate groups Si_2O_7, a structural unit which is not evident from the chemical formula. Although natural occurrences are essentially restricted to Mn and Fe compounds, synthesis experiments have led to new kentrolite-type phases $Pb_2M_2^{III}Si_2O_9$ with M^{III} = Cr, Ga, Sc and In (*2, 3, 4, 5*). This prompted us to investigate the infrared and Raman spectra of these compounds in connection with a systematic study of the vibrational behavior of pyro $(X_2O_7)^{n-}$ groups. This study was also extended to chemical aspects of this problem and eventually led to the synthesis of new silicates and germanates having the kentrolite structure.

Synthesis of Compounds and X-ray Diffraction Data

Ito and Frondel[2,3,4] have synthesized the silicates $Pb_2M_2^{III}Si_2O_9$ (M^{III} = Fe, Mn, Cr, Ga, Sc, In) by dry or hydrothermal crystallization of gels having the appropriate composition. We have prepared the same phases (except for the Ga compound) in a pure and well crystallized state by conventional solid state reaction techniques, starting from the stoichiometric mixtures of the appropriate oxides, carbonates or oxalates, and progressively heating up to 850–900°C.

The same procedure was applied to the following new compounds:

New germanates $Pb_2M_2^{III}Ge_2O_9$. By working at slightly lower temperatures (820–850°C), we obtained four germanates (M^{III} =

Fe, Mn, Sc, In) whose X-ray powder diagram is similar to that of kentrolite. The corresponding Cr and Ga analogues were not obtained, possibly because these cations are too small to give stable germanium compounds.

New silicates $Pb_2M^{II}M^{IV}Si_2O_9$. New compounds may be derived from the known silicates by the double substitution 2 $M^{III} \rightarrow M^{II} + M^{IV}$. Six of the investigated $M^{II}M^{IV}$ compositions lead to a kentrolite-like phase, namely MgSn, NiSn, CoSn, CuSn, CoTi and NiTi. Attempts to synthesize the corresponding germanates lead to mixtures possibly containing a kentrolite phase. This point should be reinvestigated. The X-ray powder diagrams were obtained with monochromatized Co $K\alpha$ radiation; no internal standard was used. The unit cell

dimensions and their standard deviations were deduced and refined from d values through a conventional least-square procedure.

Synthesis temperatures and unit cell dimensions for all the known synthetic compounds are collected in Table I. The X-ray powder diagrams of $Pb_2Mn_2Ge_2O_9$ and $Pb_2CoSnSi_2O_9$ are given in Table II. Indexed powder diagrams of the other phases are available on request to the authors.

Relation between the Unit Cell Dimensions and the size of M

The unit cell parameters increase with the size of the M cation, but the relationship is not linear, and the variation of a is small (Fig. 1 for the silicates $Pb_2M_2^{III}Si_2O_9$).

TABLE I

Synthesis Temperatures and Unit Cell Dimensions of Compounds having the Kentrolite Structure

	Synthesis temperatures (°C)	a(Å)	b(Å)	c(Å)	Ref.
$Pb_2Fe_2Si_2O_9$		6.93(1)	10.98(2)	10.06(2)	(2)
	875	6.972(3)	10.990(4)	10.043(5)	[a]
$Pb_2Mn_2Si_2O_9$		6.98(1)	11.04(2)	9.96(2)	(2)
	900	6.986(6)	11.027(9)	9.995(9)	[a]
$Pb_2Cr_2Si_2O_9$		6.88(1)	10.84(2)	10.01(2)	(3)
	875	6.882(2)	10.827(3)	9.994(2)	[a]
$Pb_2Sc_2Si_2O_9$		7.00(1)	11.30(2)	10.44(2)	(3)
	900	7.000(4)	11.278(5)	10.414(4)	[a]
$Pb_2In_2Si_2O_9$		7.02(1)	11.39(2)	10.54(2)	(4)
	900	7.006(2)	11.365(3)	10.541(3)	[a]
$Pb_2Ga_2Si_2O_9$		6.95(1)	10.90(2)	9.91(2)	(3)
$Pb_2Fe_2Ge_2O_9$	820	7.172(2)	11.183(2)	10.170(3)	[a]
$Pb_2Mn_2Ge_2O_9$	850	7.162(2)	11.279(5)	10.063(2)	[a]
$Pb_2Sc_2Ge_2O_9$	850	7.242(2)	11.501(6)	10.491(4)	[a]
$Pb_2In_2Ge_2O_9$	850	7.292(3)	11.595(2)	10.615(2)	[a]
$Pb_2MgSnSi_2O_9$	775–800	6.970(2)	11.179(3)	10.217(2)	[a]
$Pb_2CoSnSi_2O_9$	800–900	6.964(1)	11.178(2)	10.261(2)	[a]
$Pb_2NiSnSi_2O_9$	925	6.970(2)	11.125(3)	10.197(2)	[a]
$Pb_2CuSnSi_2O_9$	750	6.975(2)	11.228(3)	10.129(2)	[a]
$Pb_2CoTiSi_2O_9$	800	6.897(3)	11.025(3)	10.102(2)	[a]
$Pb_2NiTiSi_2O_9$	775	6.915(3)	10.983(3)	10.048(3)	[a]

[a] This work.

TABLE II

X-RAY POWDER DIAGRAMS OF $Pb_2Mn_2Ge_2O_9$ AND $Pb_2CoSnSi_2O_9$

\multicolumn{3}{c}{$Pb_2Mn_2Ge_2O_9$}	\multicolumn{3}{c}{$Pb_2CoSnSi_2O_9$}
d	I	hkl	d	I	hkl
5.641	15	020	5.580	8	020
5.021	9	002	5.114	24	002
3.755	40	022	3.779	8	022
3.580	25	200	3.481	30	200
3.329	45	130	3.285	52	130
3.234	15	211	3.161	15	211
3.163	12	131			
3.024	27	220			
2.933	100	113	2.960	70	113
			2.915	15	023
2.920	80	202	2.880	40	20$\bar{2}$
2.894	65	221	2.839	20	221
2.776	85	132	2.766	100	132
2.715	25	041	2.695	15	041
2.592	12	222	2.563	14	222
2.517	20	004			
2.459	15	042	2.454	4	042
2.374	10	104	2.369	4	133
2.326	6	142	2.280	5	232
2.275	10	311	2.236	4	223–050
2.215	8	240	2.164	10	043
2.150	30	{150 321	2.129	10	150
			2.098	10	321
1.978	22	015	2.082	10	312
1.910	30	115–250	2.065	6	204
1.896	7	025	2.006	6	242
1.871	30	332	1.968	15	105
1.849	25	243–061	1.939	15	115
1.790	12	400	1.926	10	025
1.761	10	062–401	1.893	12	313
1.723	18	135	1.863	8	060
1.676	25	225	1.839	35	332
1.664	12	244	1.805	4	234
1.639	30	045	1.760	10	341
1.572	15	334–170	1.751	10	062
1.526	8	315	1.741	12	400–135
1.501	8	172–055	1.697	10	411
1.490	13	245	1.685	12	054
			1.655	15	045
			1.643	15	260

It is worth while to mention the peculiar behavior of the Mn^{III} compounds: b is larger and c is smaller than for the corresponding Fe^{III} compounds, despite the fact that the ionic radii of Mn^{III} and Fe^{III} are the same;
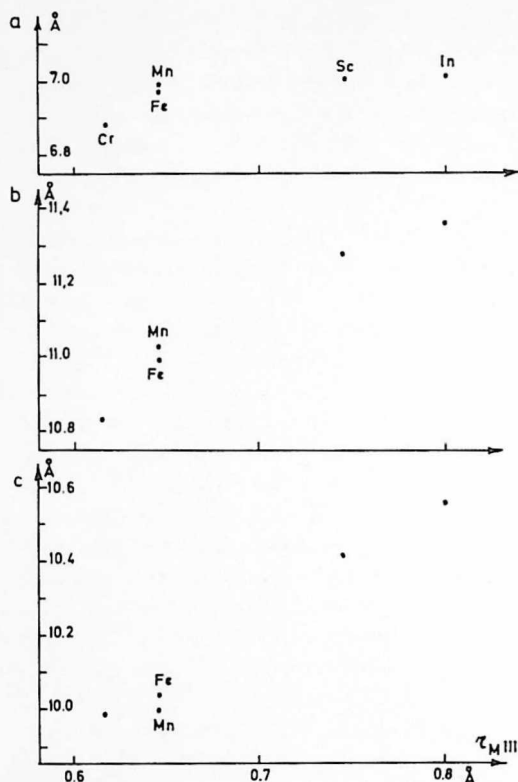

FIG. 1. Relationship between the unit cell dimensions and the ionic radius of M^{III} in the $Pb_2M_2^{III}Si_2O_9$ compounds.

moreover, the c/b ratio is smaller than for any other compound. This is possibly related to a Jahn–Teller effect of Mn^{III}. A similar behavior, with the same origin, is observed for the Cu^{II} compound $Pb_2CuSnSi_2O_9$.

Some Structural Considerations

The essential features of the kentrolite structure proposed by Gabrielson[1] are as follows: orthorhombic, space group $C222_1$ (D_2^5), $Z = 4$. The space group is based on the systematic absence of the reflections $00l$ for $l = 2n + 1$, and hkl for $h + k = 2n + 1$, as observed in Weissenberg diagrams. The silicon atoms are in the form of pyrosilicate Si_2O_7 groups. Pb atoms are bonded to 8 oxygens in an irregular configuration, and

there are 2 structurally different M^{III} cation sites: one of them is tetrahedrally coordinated; the other is bonded to 6 oxygens atoms forming a trigonal prism.

However, other data on kentrolite-type compounds show that the proposed structure is open to criticism on at least two points.

The powder diagrams published by Glasser for natural kentrolite[5] and by Ito and Frondel for the synthetic phases $Pb_2Fe_2Si_2O_9$ and $Pb_2Mn_2Si_2O_9$, exhibit diffraction peaks (such as 211, 213, 141, 052, 015, 411, 016, 254, 145, ...) which are forbidden in the proposed space group. This is also true for some of the peaks observed in the powder diagrams of our own synthetic samples (Table II). This suggests either that compounds with kentrolite-type structures could exist in more than one space group or, and perhaps more likely, that the space group proposed by Gabrielson is incorrect.

Another point of concern is the proposed tetrahedral coordination for half of the trivalent cations. The existence of pure kentrolite phases such as $Pb_2Cr_2Si_2O_9$ and $Pb_2Sc_2Si_2O_9$ is by itself in contradiction with such a coordination (all attempts to synthesize other oxygen compounds with Cr^{3+} or Sc^{3+} as tetrahedral cations have failed so far), and strongly suggests an octahedral coordination for the trivalent cation. Such an octahedral coordination is also supported by the easy synthesis of the compounds $Pb_2NiTiSi_2O_9$ and $Pb_2NiSnSi_2O_9$. It is clear that the structure proposed by Gabrielson needs reinvestigation. However, one aspect of the structure, namely the existence of pyrosilicate groups, will be confirmed by vibrational spectroscopy.

Vibrational Spectra

Experimental

The vibrational spectra were registered according to standard procedures. Infrared: KBr discs, Beckman IR 12 spectrometer; Raman: CODERG PHO double monochromator and Spectra-Physics He–Ne laser.

General Considerations on the Vibrational Behavior of a Linear Pyrosilicate Group

According to Gabrielson, the bridging oxygen of the pyrosilicate group is colinear with the 2 Si atoms, thus leading to a so-called linear bridge. Thus, we shall first discuss the vibrational behavior of such a group from 2 points of view: the IR or Raman activity, and the frequency values of the bridge vibrations. As a rough approximation, the stretching vibrations of a *pyro* X_2O_7 group (=O_3X–O–XO_3) may be divided into vibrations of the pyramidal, terminal XO_3 groups, and the 2 vibrations (symmetric and antisymmetric) of the X–O–X bridge. The "bridge vibrations" are the most characteristic ones of a X_2O_7 group, and we have deduced their symmetry class and activity for different possible symmetries of a linear X_2O_7 group:

	D_{3d}	D_{3h}	C_{3h}
ν_{sym}XOX) ν_{as}(XOX)	$A_{1g}(R)$ $A_{2u}(IR)$	$A_1'(R)$ $A_2''(IR)$	$A'(R)$ $A''(IR)$
	C_{2h}	D_3	C_{3v}	C_3
---	---	---	---	---
$A_g(R)$ $B_u(IR)$	$A_1(R)$ $A_2(IR)$	$A_1(IR, R)$ $A_1(IR, R)$	$A(IR, R)$ $A(IR, R)$

D_{3d} and D_{3h} are the highest possible symmetries of a X_2O_7 group with either a staggered, or an eclipsed, configuration, respectively.

It will be noticed that, in most cases, the symmetric stretch is Raman active and IR inactive, the reverse being true for the antisymmetric mode.

This has indeed been observed for linear Si_2O_7 groups in different types of structure such as $K_2Pb_2Si_2O_7$ with D_{3d} symmetry (6), thortveitite $Sc_2Si_2O_7$ with C_{2h} symmetry (7) and in more complex compounds such as $Ba_3Nb_6Si_4O_{26}$ with C_{3h} symmetry (8).

On the other hand, the activity in both IR and Raman spectra predicted for C_{3v} or C_3 symmetries does not imply that the corresponding bands are necessarily observed. We failed to observe the band corresponding to the bridge symmetric stretch in the *IR* spectrum of $Tl_6X_2O_7$ (X = Si, Ge) (*9*), despite the fact that this mode is *IR*-allowed by the C_3 symmetry of this group (*10, 11*). Thus, the intensity of this band is too weak to be observed, probably because this vibration remains essentially localized on the X–O–X group, which thus behaves as a triatomic linear "molecule" for which this mode is *IR*-forbidden. As far as the frequency values of these vibrations are concerned, it is well known that the frequency difference between the antisymmetric and the symmetric modes strongly depends on the bridge angle, this difference being maximum for a linear bridge (see Ref. *12* for a general discussion of this point, and Ref. *13* and *14* for specific cases).

Experimental Results and Discussion

Silicates $Pb_2M_2^{III}Si_2O_9$

The observed frequencies, including Raman data (for the colourless compounds) and ^{28}Si–^{30}Si isotopic frequencies, are collected in Table III. Figure 2 shows the *IR* spectra of the isotopic species of $Pb_2In_2Si_2O_9$. The Raman spectrum of $Pb_2Sc_2Si_2O_9$ is reproduced in Fig. 3.

For the purpose of discussion, the spectrum may be divided more or less arbitrarily into 2 parts:

(i) A low frequency region (between 650 and 300 cm^{-1}), where the spectrum strongly depends on the nature of the trivalent cation M^{III}. Since the ^{28}Si–^{30}Si isotopic shifts are small to negligible, it may be deduced that
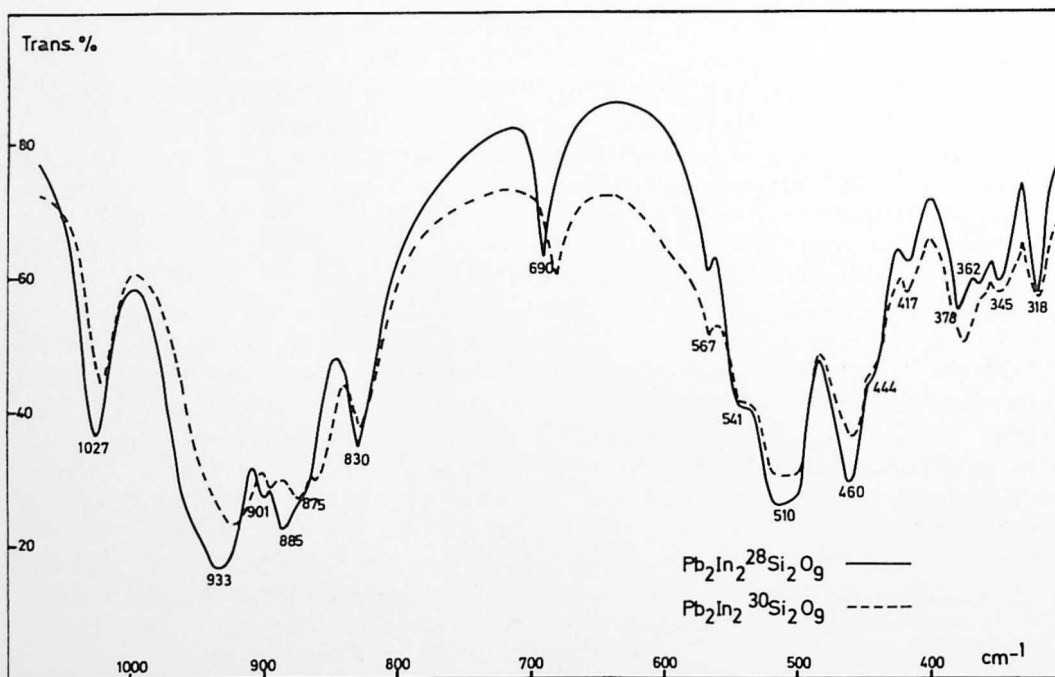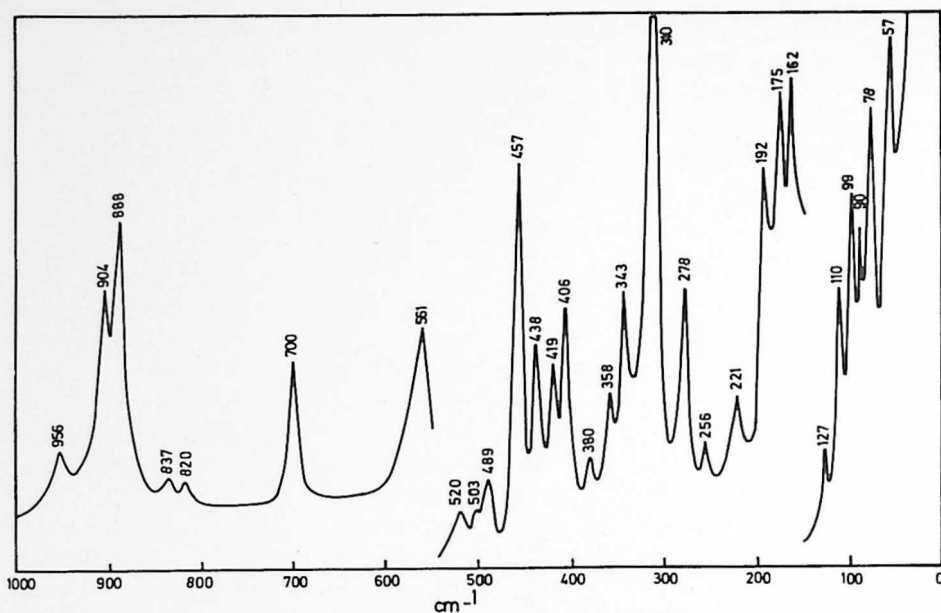

FIG. 2. Infrared spectrum of $Pb_2In_2Si_2O_9$ showing the ^{28}Si–^{30}Si isotopic shifts. The frequency values are related to the ^{28}Si compound.

FIG. 3. Raman spectrum of $Pb_2Sc_2Si_2O_9$.

this part of the spectrum is of complex origin, with contributions from both Si_2O_7 bending vibrations, and lattice vibrations.

(ii) A higher frequency region (650–1050 cm^{-1}), in which the various compounds exhibit a similar pattern with large (up to 13 cm^{-1}) ^{28}Si–^{30}Si isotopic shifts for some bands at least. These bands are clearly related to stretching vibrations of Si–O bonds, and in addition, the general pattern is fairly characteristic of a pyrosilicate group.

The next problem is to attempt to discriminate between the respective vibrations of the Si–O–Si bridge, and the —SiO$_3$ pyramidal groups, and to search for a correlation between the observed spectra and the geometry of the pyrosilicate group. This problem may be introduced by considering the stretching modes of a *pyro* X_2O_7 group and their activities for 2 characteristic cases; namely, a linear group with $\dot{D}_{3h}$ symmetry, or a bent group with C_{2v} symmetry. Both cases are easily distinguished by the number of *IR*-Raman coincidences (Table IV).

Identification of the Stretching Vibrations of the Si–O–Si Bridge

Owing to the large quantity of published spectroscopic data on pyrosilicates, the frequency range related to the bridge symmetric stretch is well known (630–730 cm^{-1}), and the band observed near 700 cm^{-1} (Table III) may be assigned with confidence to this vibrational mode. This assignment is fully substantiated by the large ^{28}Si–^{30}Si isotopic shift, resulting from the large displacement of Si atoms associated with this type of motion. A similar isotopic shift has been observed in the Raman spectrum of $K_2Pb_2Si_2O_7$ (6).

It should be noticed that this mode appears here in both *IR* and Raman spectra with a medium to high intensity, thus suggesting that the bridge is bent. Accordingly, the remainder of the spectrum will be discussed on the basis of a C_{2v} symmetry.

The assignment of the antisymmetric stretch is not straightforward. For a linear bridge, its frequency is significantly higher

TABLE III

IR AND RAMAN FREQUENCIES OF THE SILICATES Pb$_2$M$_2^{III}$Si$_2$O$_9$

Kentrolite[a] IR	Pb$_2$Cr$_2$Si$_2$O$_9$ IR	Pb$_2$Fe$_2$Si$_2$O$_9$ IR	Pb$_2$Mn$_2$Si$_2$O$_9$ IR	Pb$_2$Sc$_2$Si$_2$O$_9$ IR	Pb$_2$Sc$_2$Si$_2$O$_9$ R	Pb$_2$In$_2$Si$_2$O$_9$ IR	Pb$_2$In$_2$Si$_2$O$_9$ R	$\Delta\nu$(Si)[b] IR	$\Delta\nu$(Si)[b] R	Assignments
992 s	996 s	992 s	988 s	1008 s	956 w	1027 s		5	12 }	ν_{as} (SiOSi)
926 s	930 s	935 s	922 s	929 s	904 m	933 s	942 vw	11		ν_{as} (SiO$_3$)
		900 sh		910 sh		901 sh		6	10 }	
887 s	897 s	885 s	892 s	888 s	888 s	885 s	887 s	10		
						875 sh, b		~13	?	
835 s	848 s	835 s	835 s	837 s	837 vw	830 s	820 vw	2		ν_{sym} (SiO$_3$)
					820 vw					
699 m	704 m	696 m	{ 701 sh / 694 m }	702 m	700 m	690 m	689 m	9	13	ν_{sym} (SiOSi)
610 m, b	608 m	572 m	615 m	587 sh		567 m	569 w	2	3 }	complex modes, including bending vibrations of the Si$_2$O$_7$ groups and lattice vibrations.
580 sh	558 sh		572 m	560 sh	561 m	541 sh, b	542 vw	?	?	
560 sh	542 sh						532 vw		?	
527 m, b	526 m	499 m	534 m, b	531 sh, b	520 w	510 m, b		?		
502 m, b	496 m		502 m, b	509 m	503 w					
					489 w					
450 m	465 m	467 m, b	450 m, b	462 s, b	457 s	460 m	444 m	2	0	
420 m	439 m	451 m, b	415 m, b	437 m	438 m	444 sh		0		
	430 sh			413 m, b	419 m	417 w		0		
398 sh	405 w	395 m			406 m		397 w	3	1	
367 w	375 w		373 w, b	375 m, b	380 w	378 m		3		
	365 w, b				358 w	362 w, b		?		
	350 w, b	350 w				345 w, b	342 m	0	0	
	332 w, b	334 sh, b	330 w, b		343 m	318 w	322 m	0	0	
	312 w, b	320 sh, b		309 w, b	310 vs		304 vs	0	0	

[a] Natural kentrolite.

[b] $\Delta\nu$(Si) = ν(Pb$_2$In$_2^{28}$Si$_2$O$_9$) − ν(Pb$_2$In$_2^{30}$Si$_2$O$_9$).

?: Isotopic shift not measurable because of the broadness of the band.

s, strong; m, middle; w, weak; sh, shoulder; v, very; b, broad.

TABLE IV

STRETCHING VIBRATIONS OF A LINEAR OR BENT X_2O_7 GROUP

Description of the vibrations	D_{3h} (linear)	C_{2v} (bent)
$\nu_{sym}(XOX)$	$A_1'(R)$	$A_1\ (IR, R)$
$\nu_{sym}(XO_3)$	$A_1'(R)$	$A_1\ (IR, R)$
$\nu_{sym}'(XO_3)$	$A_2''(IR)$	$B_1\ (IR, R)$
$\nu_{as}(XOX)$	$A_2''(IR)$	$B_1\ (IR, R)$
$\nu_{as}(XO_3)$	$E'\ (IR, R)$	$\begin{cases} A_1\ (IR, R) \\ B_1\ (IR, R) \end{cases}$
$\nu_{as}'(XO_3)$	$E''(R)$	$\begin{cases} A_2\ (R) \\ B_1\ (IR, R) \end{cases}$

than those of the SiO_3 modes, and it is easily identified (6, 7, 8). For a bent bridge however, its frequency is lowered and may well be near or even within the range of the SiO_3 frequencies. Here again, the knowledge of $^{28}Si-^{30}Si$ isotopic frequencies is of great help, since this vibration is essentially characterized by a significant displacement of the bridge oxygen, and a small $^{28}Si-^{30}Si$ isotopic shift (6, 8).

In accordance with these considerations, we assign to the bridge antisymmetric stretch the IR band located near 1000 cm^{-1}, which is characterized by the highest observed frequency combined with a small $^{28}Si-^{30}Si$ isotopic shift. There is no equivalent peak in the Raman spectrum, but this is not a definite argument against a bent bridge, since this band is possibly too weak to be observed in powder Raman spectra.

Vibrations of the Terminal SiO₃ Groups

These vibrations may be roughly classified as symmetric (ν_{sym}) or antisymmetric (ν_{as}) with respect to the local ternary axis of the SiO_3 group. For each type of vibrations, there are 2 further possibilities, depending on the fact that the 2 SiO_3 groups are vibrating in phase (ν) or out of phase (ν').

The 830–850 cm^{-1} band is characterized by a very small $^{28}Si-^{30}Si$ isotopic shift. A similar band, in the same frequency region

and with the same isotopic behavior, is observed in different pyrosilicates, either with a linear bridge ($Ba_3Nb_6Si_4O_{26}$) (8), or with a bent bridge: barysilite $MnPb_8(Si_2O_7)_3$ and akermanite $Ca_2MgSi_2O_7$ (9). Because of its moderately low frequency, and since this band is weak or missing in the Raman spectrum, it is assigned to the symmetrical, out of phase vibration ν_{sym}' of B_1 class (for a pyro group with C_{2v} symmetry). The corresponding in-phase vibration ν_{sym} is assigned to the 885–900 cm^{-1} band, which appears fairly strongly in both IR and Raman spectra.

The higher frequency bands (between 900 and 960 cm^{-1}) are assigned to the antisymmetric stretching motions ν_{as} as a whole, without the possibility of a discrimination between in-phase and out-of-phase vibrations.

These results do not allow a discussion of the true symmetry (C_{2v} or lower) of the pyrosilicate group, since nearly all the modes are already IR and Raman active for the C_{2v} symmetry. One mode only (the A_2 component of ν_{as}' (XO_3)) is only Raman active in the C_{2v} configuration (Table IV), and would become also IR active by a lowering of symmetry. It should also be borne in mind that the total number of observed bands is not definitely significant, since there are several Si_2O_7 groups in the unit cell.

Two comments can be made in connection with the proposed presence of pyrosilicate groups:

(i) Some of the frequencies (i.e. near 1000 and 830 cm^{-1}) and of the associated isotopic shifts are very similar to those observed in akermanite and akermanite-like compounds (9), which are well-known representatives of the pyrosilicate family. Such analogies add further support to our interpretation.

(ii) There are two excess oxygens per formula unit, and this implies that these oxygens are bond only to the cations (Pb and/or M^{III}), and not to silicon. Although not very frequent in silicates, this situation is by no means exceptional, but a precise

description of the bonding is impossible without a detailed knowledge of the structure.

Relationship between the Bridge Frequencies and the Ionic Radius of the Trivalent Cation

For pyrosilicates $M^{II}Pb_8(Si_2O_7)_3$ with the barysilite structure, Lajzerowicz has shown a linear relationship between the ionic radius of the bivalent cation M^{II}, and the bridge symmetric stretch $\nu_{sym}(SiOSi)$ (*13*). We have searched for a similar relationship between the ionic radius of the trivalent cation M^{III} (as given by Shannon and Prewitt (*15, 16*), and the bridge stretching frequencies. We found that no such relationship exists for the kentrolite-type compounds, probably because the influence of the trivalent cation on the bridge frequencies depends, not only on the ionic radius of M^{III}, but also on the M^{III}–O bonding force. Better results are obtained by investigating the relationship between the ionic radius of M^{III} and, either the frequency difference $\nu_{as} - \nu_{sym}$ (Fig. 4a), or better the ratio

$$\frac{\nu_{as} - \nu_{sym}}{\nu_{as} + \nu_{sym}};$$

in this latter case, the relationship is practically linear (Fig. 4b). The increase of the difference $\nu_{as} - \nu_{sym}$ with the ionic radius of the trivalent cation is probably related to an increase of the bridge angle when the size of the trivalent cation increases. The value of

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

varies between 17.2 (Cr compound) and 19.6 (In compound). By comparison with the relationship between Δ and the bridge angle, proposed by Lazarev (*12*) for pyrosilicates, this leads to an angle of about 125–130° for the kentrolite compounds.

Silicates $Pb_2M^{II}M^{IV}Si_2O_9$

The *IR* spectra of these compounds are very similar to those of the $Pb_2M_2^{III}Si_2O_9$

compounds, at least in the 1050–650 cm^{-1} region, and their interpretation is the same (Table V). There is, however, no relationship between the average ionic radius of the cations

$$\frac{r_{M^{II}} + r_{M^{IV}}}{2},$$

and, either the difference $\nu_{as} - \nu_{sym}$, or the ratio

$$\frac{\nu_{as} - \nu_{sym}}{\nu_{as} + \nu_{sym}}.$$

The scattering of the points is probably related to the presence of 2 different cations M^{II} and M^{IV}, leading to a more complex influence of these cations. Nevertheless, it is qualitatively verified that the value of the difference $\nu_{as} - \nu_{sym}$ increases with the ionic radius of either cation ($r_{Ni} < r_{Mg} < r_{Cu} < r_{Co}$, and $r_{Ti} < r_{Sn}$), except for the copper compound, which gives an abnormally high value of $\nu_{as} - \nu_{sym}$ (Table V), probably in connection with distortion effects which are well known in various copper compounds.

Germanates $Pb_2M_2^{III}Ge_2O_9$

Here again, the spectrum (Fig. 5) may be divided into 2 parts, one corresponding to the stretching modes of the pyrogermanate group, the other to bending modes of the same group and/or lattice modes. The discussion will be restricted to the first part of the spectrum (900–550 cm^{-1} region: Table VI).

Bridge frequencies.—The moderately strong, sharp band systematically present in the 570–550 cm^{-1} region in both *IR* and Raman spectra is assigned to the symmetric stretch ν_{sym} (GeOGe). This is in agreement with the values already observed in other pyrogermanates such as $M^{II}Pb_8(Ge_2O_7)_3$ (590–560 cm^{-1}) (*13*), or akermanites $A_2^{II}B^{II}Ge_2O_7$ (~530 cm^{-1}) (*9*).

By analogy with the silicates, the highest frequency band (870–860 cm^{-1}) is assigned to the bridge antisymmetric stretch. The
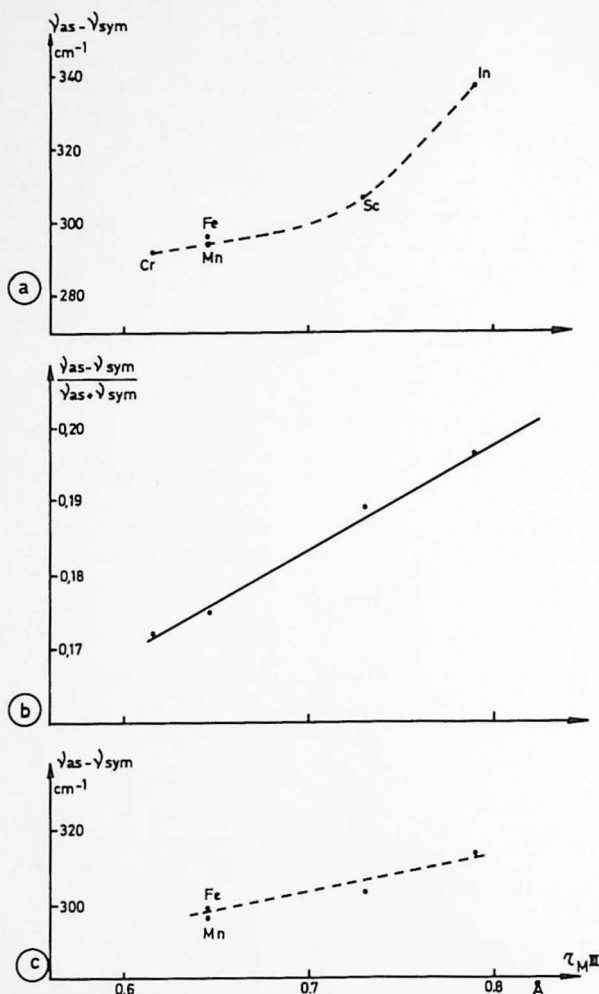
FIG. 4. Relationship between the ionic radius of M^{III} and (a) the difference $\nu_{as} - \nu_{sym}$, (b) the ratio $\nu_{as} - \nu_{sym}/\nu_{as} + \nu_{sym}$ for the silicates $Pb_2M_2^{III}Si_2O_9$, and (c) the difference $\nu_{as} - \nu_{sym}$ for the germanates.

frequency difference $\nu_{as} - \nu_{sym}$ increases nearly linearly with the ionic radius of the trivalent cation, but the variation is small (Fig. 4c).

Vibrations of the external GeO_3 groups.— The corresponding bands are observed in the $840-720 \text{ cm}^{-1}$ region, but the existing data do not allow discrimination between the vibrations of the symmetric or antisymmetric type.

General Conclusions

New compounds with the kentrolite structure have been synthesized and investigated by X-ray diffractometry and vibrational spectroscopy. The chemical nature of the cations which are able to enter the kentrolite structure, and some of the hkl indices observed in the X-ray powder diagram, strongly suggest that some aspects of the

TABLE V

STRETCHING MODES OF THE Si$_2$O$_7$ GROUPS IN Pb$_2$M^{II}M^{IV}Si$_2$O$_9$

Pb$_2$MgSnSi$_2$O$_9$	Pb$_2$NiSnSi$_2$O$_9$	Pb$_2$CoSnSi$_2$O$_9$	Pb$_2$CuSnSi$_2$O$_9$	Pb$_2$NiTiSi$_2$O$_9$	Pb$_2$CoTiSi$_2$O$_9$	Assignments
1025 sh	1031 m	1041 m	1052 m	1007 m	1018 m	ν_{as} (SiOSi)
1008 sh, b	1005 m					
962 s	955 s	947 s	960 s, b	937 s, b	932 s, b $\Big\}$	ν_{as} (SiO$_3$)
~925 sh		924 s, b	931 s, b			
902 s, b	907 s, b	900 s	905 s, b	888 s, b	890 sh, b$\Big\}$	ν_{sym} (SiO$_3$)
842 s, b	845 s	845 s	853 s	843 s	841 s	
700 m	700 m	687 m	674 m	703 m	694 m	ν_{sym} (SiOSi)
325	331	354	378	304	324	$\nu_{as} - \nu_{sym}$

s, strong; m, middle; w, weak; sh, shoulder; v, very; b, broad.

structure proposed by Gabrielson (1) are erroneous. The vibrational spectrum shows the presence of bent pyrosilicate (or pyrogermanate) groups, the existence of which could not be deduced from the chemical formula.
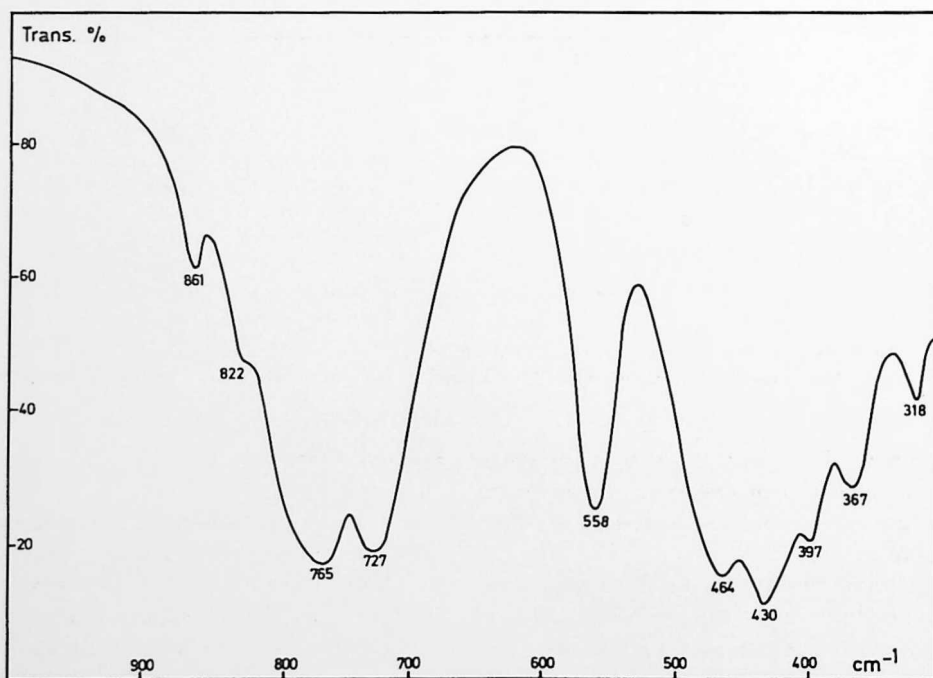
Acknowledgements

FIG. 5. Infrared spectrum of Pb$_2$Sc$_2$Ge$_2$O$_9$.

TABLE VI

IR AND RAMAN FREQUENCIES OF THE GERMANATES $Pb_2M_2^{III}Ge_2O_9$

$Pb_2Fe_2Ge_2O_9$ IR	$Pb_2Mn_2Ge_2O_9$ IR	$Pb_2Sc_2Ge_2O_9$		$Pb_2In_2Ge_2O_9$		Assignments
		IR	R	IR	R	
861 m	865 m	861 m		869 m		ν_{as} (GeOGe)
			840 m		827 m	
827 sh	832 sh	822 sh		819 sh		
			800 m			
770 s	774 s	765 s		769 s, b		ν (GeO$_3$)
			747 s		740 s	
738 s	743 sh	727 s, b		731 s, b		
	720 sh			715 sh		
620 w						?
562 m	567 w	558 m	555 s	551 m	544 s	ν_{sym} (GeOGe)
	545 w, b					
535 m	525 w, b			522 sh		
	485 w, b			508 m		
452 m, b		464 m		457 sh		complex vibrations
408 s	410 w, b	430 s		438 s		
368 sh		397 m				
347 m, b	360 w, b	367 m		357 m		
	324 w, b	318 w		324 sh		
275 m	300 w, b	242 w		296 w		

s, strong; m, middle; w, weak; sh, shoulder; v, very; b, broad.

References

1. O. GABRIELSON, *Arkiv. Mineral. Geol.* **3**, 141 (1963).
2. J. ITO AND C. FRONDEL, *Arkiv Mineral. Geol.* **4**, 387 (1966).
3. J. ITO AND C. FRONDEL, *Am. Mineral.* **53**, 1276 (1968).
4. J. ITO, *Am. Mineral.* **53**, 1663 (1968).
5. F. P. GLASSER, *Am. Mineral.* **52**, 1085 (1967).
6. P. TARTE, M. J. POTTIER, AND A. M. PROCES, *Spectrochim. Acta*, **29A**, 1017 (1973).
7. A. N. LAZAREV AND A. P. MIRGORODSKII, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **7**, 1224 (1971).
8. J. CHOISNET, N. NGUYEN, B. RAVEAU, M. GABELICA-ROBERT AND P. TARTE, *J. Solid State Chem.*, accepted for publication.
9. M. GABELICA-ROBERT, to be published.
10. Y. PIFFARD, R. MARCHAND AND M. TOURNOUX, *Rev. Chim. Min.* **12**, 210 (1975).
11. M. TOUBOUL, Y. FEUTELAIS AND M. A. HEBRARD, *C. R. Acad. Sc. Paris, Ser. C* **283**, 347 (1976).
12. A. N. LAZAREV, Vibrational Spectra and Structure of Silicates, Consultants Bureau N.Y., (1972).
13. J. LAJZEROWICZ, *Acta Crystallogr.* **20**, 357 (1965).
14. R. PASCARD, M. CHAUNAC AND E. GRISON, *Bull. Soc. Chim. Fr.* **2**, 429 (1971).
15. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. B* **25**, 925 (1969).
16. R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).