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Solid Solutions $Ca_3Sn_{2+x}Si(Ge)_{1-x}Ga_2O_{12}$ ($0 \leq x \leq 0.95$) and Tetrahedral Coordination of Sn^{4+} in the Garnet Structure

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Pure solid solutions $Ca_3Sn_{2+x}Si(Ge)_{1-x}Ga_2O_{12}$ with the garnet structure have been evidenced in the composition range $0 \leq x \leq 0.95$. This implies that a part of the Sn^{4+} cations (equal to x) is located on the tetrahedral sites, a quite unusual coordination for this cation in oxygen compounds. This has been definitely confirmed by X-ray powder diffraction structure calculations. Information about the cation–oxygen distances and the distortion of the different coordinated groups is presented. No band characteristic of the SnO_4 tetrahedra is observed in the IR spectrum, probably because of a strong mixing between SnO_4 and GaO_4 vibrations. In contrast, the totally symmetric stretching mode ν_1 of the SnO_4 tetrahedra is easily observed near 775 cm^{-1} in the Raman spectrum, where it is well separated from the corresponding mode of the GaO_4 tetrahedra. The different vibrational behavior observed in IR and Raman spectra is discussed on the basis of the symmetry properties of the vibrations.

Introduction

Tetrahedral coordination of tin(IV) in its oxygen compounds may be considered as exceptional. It has been evidenced in the stannates $M^I_4SnO_4$ (M^I = Na, K) (*1*) and, quite recently, in solid solutions with the garnet structure in the pseudoquaternary system $CaO–Fe_2O_3–TiO_2–SnO_2$ (*2*). It should also be present in a garnet "$Ca_3Sn_3Ga_2O_{12}$" discovered by Mill' (*3*), but whose true composition is possibly slightly different from the proposed ideal formula (*4*).

Because of this uncertainty, and also because of the interest of such a composition for a study of the vibrational behavior of the (SnO_4) group, we have investigated the formation of pure garnet phases in the systems $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ and $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ whose first end-members (x = 0) are pure garnets, the second end-member (x = 1) being the compound under discussion.

Experimental

Synthesis of the compounds. All compounds and solid solutions were prepared by conventional solid state reaction techniques, starting from the stoichiometric quantities of $CaCO_3$, SnO_2, SiO_2 (aerosil) or GeO_2, and Ga_2O_3.

The mixture is heated in covered Pt crucibles, first to 900°C, and then by steps of 100°C with intervening mixing and grinding up to 1300°C; this temperature is maintained for one or several days with repeated grind-

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ings, until no change is observed in the X-ray diffraction pattern. The full synthesis procedure was repeated two or three times for some compositions containing a small amount of impurity.

X-ray powder diffraction. For the phase analysis and cell parameter determination, powder diagrams were recorded with a CGR diffractometer, Co$K\alpha$ radiation. Unit cell parameters (accurate to 0.001 Å) were deduced from high-angle diffraction peaks (up to 75° θ) corresponding to the (10.4.0), (10.4.2), (8.8.0), (12.0.0), (12.2.2), (12.6.0), and (12.6.2) reflections. As regards structure calculations, diffractograms were recorded up to 100° 2θ on a Siemens D 500 diffractometer, Cu$K\alpha$ radiation.

Vibrational spectroscopy. The infrared spectra were recorded with a Beckman 4250 infrared spectrometer (1400–300 cm^{-1}, KBr discs) and a Polytec FIR 30 interferometer (350–30 cm^{-1} polyethylene discs). The Raman spectra were recorded with a Coderg PHO double monochromator equipped with an Ar^+ laser; most spectra were recorded with a slit width of about 3 cm^{-1}, with a laser power of 200 mW on the 514.5-nm green line.

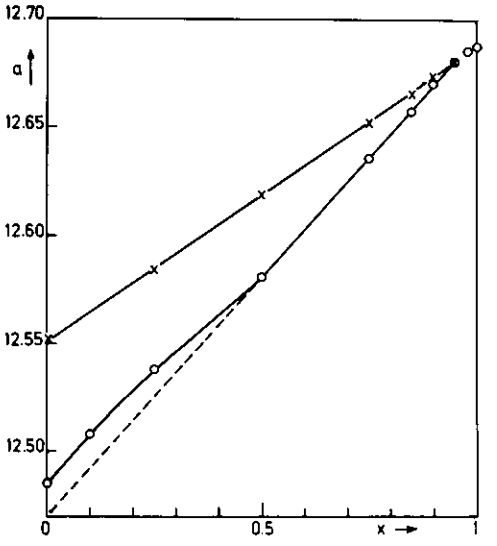

FIG. 1. Variation of the unit cell parameter of the garnet phase as a function of the Si–Sn (circles) or Ge–Sn (crosses) replacement in the solid solutions $Ca_3Sn_{2+x}Si(Ge)_{1-x}Ga_2O_{12}$.

Results

Reproducibility of the Syntheses

Some difficulties were experienced in obtaining pure phases with the SnO_2-rich compositions, the main impurity being a small quantity of $CaSnO_3$, easily evidenced by X-ray diffraction (and also appearing in the Raman spectrum). In these cases, the full synthesis process (starting again from the initial mixture of oxides and carbonates) was repeated two or three times, and it was generally possible to obtain $CaSnO_3$-free solid solutions. We suspect this problem of nonreproducibility to be of kinetic origin: once formed, $CaSnO_3$ (which is a very stable perovskite) reacts very slowly with the remaining reactants or intermediate products, and it is very difficult to get rid of the last parts of this impurity. Despite repeated experiments, we were unable to obtain $CaSnO_3$-free phases for the SnO_2-richest compositions, corresponding to $x = 0.98$ and $x = 1$. Thus, the existence of a pure garnet $Ca_3Sn_3Ga_2O_{12}$ is doubtful, in agreement with Geller's results (*4*).

X-Ray Diffraction

Cell parameters. The values of the a_0 parameter for all investigated compositions are plotted in Fig. 1.

$Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$: A linear relationship between a_0 and x is observed in the composition range $0.5 \leq x \leq 0.95$, namely the Sn-rich solid solutions; but for increasing amounts of Si ($0.5 \geq x \geq 0$), the relationship exhibits a positive deviation, the unit cell parameter being greater than expected from the extrapolated initial straight line.

As a consequence of the large difference between the ionic radii of Si^{4+} (0.26 Å) and Ga^{3+} (0.47 Å) or Sn^{4+} (0.55 Å) (*5*), one can assume some nonstatistical trend in the cationic distribution, in terms of a segregation of Si^{4+}-rich microdomains.

TABLE I

ATOMIC PARAMETERS FOR THE GARNET TYPE STRUCTURE OF THE SOLID SOLUTIONS $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ (x = 0.0, 0.05, 0.95)

Composition (x value)	Oxygen sites (96 h)			
	x	y	z	B(Å)^2
0.0	0.962(1)	0.050(1)	0.157(1)	1.8(3)
0.05	0.963(2)	0.049(1)	0.155(1)	2.1(2)
0.95	0.966(2)	0.048(1)	0.153(1)	1.0(2)

Composition (x value)	Isotropic thermal factors of cations		
	CN VIII site Ca^{2+} B(Å)^2	CN VI site Sn^{4+} B(Å)^2	CN IV site Ga^{3+}, Si^{4+}, Sn^{4+} B(Å)^2
0.0	0.9(1)	0.2(1)	0.6(2)
0.05	0.8(1)	0.2(1)	0.5(2)
0.95	0.6(1)	0.5(1)	0.5(1)

$$RI = \frac{\Sigma|I_o - I_c|}{\Sigma I_o}$$

	(1)	(2)
x = 0.0	0.040	0.061
x = 0.05	0.038	0.064
x = 0.95	0.042	0.078

(1) calculated from the observed reflections
(2) calculated from the whole possible reflections (see text)

For x = 0.98 and 1, there is a weak, downward curvature suggesting that the increase of the a_0 parameter with x is smaller than expected from the main curve. This is probably correlated with the fact that it was impossible to obtain these two compositions completely free from $CaSnO_3$, thus suggesting that, for these last garnets, the true composition is slightly different from the nominal one. Geller (*4*) had already noticed the existence of very weak extra lines in the X-ray powder diagram of $Ca_3Sn_3Ga_2O_{12}$. For this composition, we find a_0 = 12.687 Å, in good agreement with the values proposed either by Mill' (*3*) (12.69 Å) or by Geller (*4*) (12.685 Å).

$Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$. The experimental results suggest a practically linear relationship between the unit cell parameter a_0 and the substitution rate x, since the very small observed deviations have no systematic character. This behavior is rather different from that observed with the Si-bearing solid solutions, but this is not unexpected in view of the larger difference between the ionic radii of the tetracoordinated Si^{4+} (0.26 Å) and Sn^{4+} (0.55 Å) cations (to be compared with the ionic radius of 0.39 Å for Ge^{4+}). In any case, the most important point of these results is the conclusion that, for x values up to 0.95 (namely the range of pure garnet solid solutions), a part of Sn^{4+}, equal to x, is necessarily located on the tetrahedral sites.

Structure calculations. In order to check some structural characteristics related to the simultaneous presence of Sn^{4+} in octahedral and tetrahedral coordination, calculations from integrated intensities of X-ray diffractograms were undertaken.

Two kinds of calculations (*6*) were systematically performed:

(i) by using 22 observed reflections, with or without superpositions, i.e., 27 *hkl* up to 100 2θ;

(ii) by including the nonobserved reflections which are possible in the space group

TABLE II

(M–O) AND (O–O) DISTANCES (Å) FOR THE POLYHEDRA OF THE GARNET TYPE STRUCTURE OF THE SOLID SOLUTIONS $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ (x = 0.0, 0.05, 0.95).

		x = 0.0	x = 0.05	x = 0.95
		(M–O_4) tetrahedra, M = Ga^{3+}, Si^{4+}, Sn^{4+}		
(M–O)	4×	1.70(1)	1.73(1)	1.79(1)
(O–O)I	2×	2.63(2)	2.66(3)	2.74(3)
(O–O)I′	4×	2.85(2)	2.89(3)	3.01(3)
		(M–O_6) octahedra, M = Sn^{4+}		
(M–O)	6×	2.11(1)	2.09(1)	2.08(1)
(O–O)II	6×	2.99(2)	2.95(3)	2.91(3)
(O–O)II′	6×	2.98(2)	2.95(3)	2.97(3)
		(M–O_8) dodecahedra, M = Ca^{2+}		
(M–O)	4×	2.43(2)	2.42(3)	2.44(3)
(M–O)	4×	2.57(2) ~2.50	2.58(3) ~2.50	2.62(3) ~2.53
(O–O)I	2×	2.63(2)	2.66(3)	2.74(3)
(O–O)II	4×	2.99(2)	2.95(3)	2.91(3)
(O–O)III	2×	2.96(2)	2.99(3)	3.09(3)
(O–O)IV	4×	2.98(2)	3.00(3)	3.05(3)

Note. (O–O) (I) and (II): shared between tetrahedra (octahedra) and dodecahedra. (O–O) (IV): shared between two dodecahedra. (O–O)I′, (O–O) II′, (O–O) III: unshared.

and giving them an intensity equal to 1% of the highest observed intensity: the total number of reflections is 46, i.e., 68 *hkl*.

Owing to the greater difference between the scattering factors of Si and Sn, the Si-bearing solid solutions $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ (compositions x = 0, 0.05 and 0.95) were preferred. The usual model of the garnet type structure was used, namely space group $Ia3d$;

Ca^{2+}, coordination VIII, site 24(c): $\frac{1}{8}$, 0, $\frac{1}{4}$

Sn^{4+}, coordination VI, site 16(a): 0, 0, 0

(Ga^{3+}, Si^{4+}, Sn^{4+}), coordination IV, site 24(d): $\frac{3}{8}$, 0, $\frac{1}{4}$

O^{2-}, coordination IV, site 96(h): x = 0.96, y = 0.05, z = 0.15.

Table I reports the values of oxygen atomic parameters and isotropic thermal factors of both cations and oxygen, obtained after a least-squares refinement procedure. In any case, satisfactory results are observed: RI confidence factors close to 0.04; RI confidence factors calculated for the whole set of possible reflections up to 100° 2θ in the range 0.06–0.08; values of oxygen atomic parameters slightly varying; isotropic thermal factors at the octahedral and tetrahedral sites of the right order of magnitude—$0.2 \leq B \leq 0.5$ Å^2—though the small differences between individual cations are not significant.

The M–O and O–O distances at the three cationic sites are listed in Table II. The main feature to be emphasized is the rather strong increase of the $(M\text{–O})^{IV}$ distance in the tetrahedral sites, as a result of the Si → Sn replacement: the difference $\Delta\,(M\text{–O})^{IV}$ x: 0 → 0.95 is close to 0.09 Å, this being fully consistent with the prediction from ionic radii: $\frac{1}{3}\,(r(Sn^{4+})^{IV} - r(Si^{4+})^{IV}) \simeq 0.10$ Å. Otherwise, the $(Sn^{4+}\text{–O})^{VI}$ distances in the octahedral sites, as well as the $(Ca^{2+}\text{–O})^{VIII}$ distances, are only slightly modified when Sn^{4+} enters the tetrahedral sites.

Because of the lack of data for tetrahedrally coordinated Sn^{4+} in oxides (such data did not exist up to now for the garnet type structure), any precise discussion in this respect is precluded. Nevertheless, we propose in the following a discussion of crystal

chemical trends, in terms of the regularity or possible distortions of polyhedra, a matter of significant interest with numerous data reported up to now (*4*, *7*, *8*). We deal with two points successively: the cooperative distortions of octahedra and tetrahedra, and then the cooperative distortions of tetrahedra and eight-coordinated sites.

(i) Cooperative distortions of octahedra and tetrahedra: From the data of Table II, it can be stated that (SnO_6) octahedra are nearly regular, as their trigonal distortion is very low: the difference between the two sets of six (O–O) values $\Delta\ (O\text{–}O)_{6,6}$ does not exceed 0.06 Å. Conversely, the (MO_4) tetrahedra, including or not including Sn^{4+} ions, exhibit a rather strong axial distortion resulting in a large value of $\Delta\ (O\text{–}O)_{2,4}$: $0.22\ \text{Å} \leq \Delta\ (O\text{–}O)_{2,4} \leq 0.27\ \text{Å}$. This result is in full agreement with the usual trend of the garnet type structure, in terms of the likely impossibility of getting simultaneously a high regularity of both tetrahedra and octahedra (*7*). Such a situation has been proved to result in an excessive lowering of the two unshared $(O\text{–}O)_{III}$ edges of the eight-coordinated site (*8*). As a consequence, it can be stated that cooperative distortions of octahedra and tetrahedra do not occur directly, but by means of eight-coordinated sites which share edges either with octahedra or with tetrahedra (see Fig. 2).

(ii) Cooperative distortions of tetrahedra and eight-coordinated sites: The $(M\text{–}O)^{IV}$ distances observed for the Si-bearing solid solutions are systematically smaller than predicted from ionic radii: $1.70 \rightarrow 1.79$ Å against $1.80 \rightarrow 1.89$ Å. At the same time, the $(Ca\text{–}O)^{VIII}$ distances nearly fit the theoretical value 2.52 Å. The simultaneous existence of these two data seems to be unusual: generally speaking, the $(M\text{–}O)^{IV}$ distances are very close to the theoretical values, as observed, for example, in numerous Ca^{2+} garnet type silicates, but simultaneously, a significant negative deviation, often close to 0.10 Å, exists for the $(Ca\text{–}O)^{VIII}$ distance (*7*, *8*). From this, one can consider our own data to be another example of a cooperative

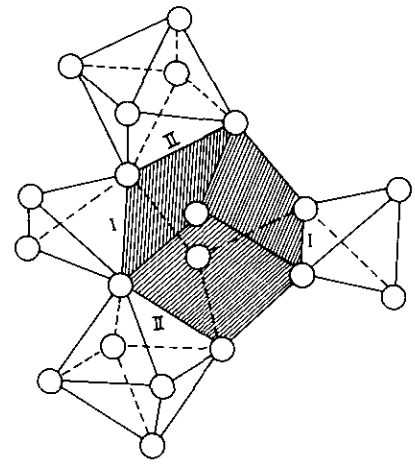

FIG. 2. The distorted dodecahedron (hatched) of the garnet structure, showing edge sharing with two tetrahedra (I) and two octahedra (II). The cationic sites have been omitted.

trend between the distortions of tetrahedra and eight-coordinated sites, ascribed to the $(O\text{–}O)_I$ edge sharing of two tetrahedra with an eightcoordinated site (Fig. 2). Even if no detailed explanation of the behavior of these Si-bearing garnet phases can be proposed, the simultaneous presence of such different cations, at least in terms of geometrical characteristics, can be assumed to play a main role, as above evidenced for the variation of cell parameters.

Infrared Spectra

$Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$. According to the origin of the bands, these IR spectra (Fig. 3) may be more or less arbitrarily divided into four regions: 950–800, 750–600, 500–300, and 300–30 cm^{-1}.

950–800 cm^{-1} region: The intensity of these bands decreases with increasing x values, and they disappear completely for $x = 1$: their assignment to the antisymmetric stretch (ν_3) of the SiO_4 tetrahedron is straightforward. They may be considered as internal vibrations of the SiO_4 tetrahedron, since the other coordinated groups (GaO_4, SnO_4, SnO_6) give significantly lower frequencies and thus are not able to induce

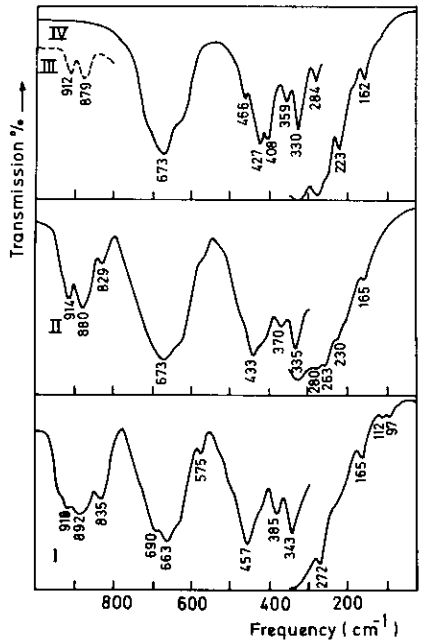

FIG. 3. IR spectra of selected compositions of $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ phases: (I) $Ca_3Sn_2SiGa_2O_{12}$; (II) $Ca_3Sn_{2.5}Si_{0.5}Ga_2O_{12}$; (III) $Ca_3Sn_{2.95}Si_{0.05}Ga_2O_{12}$ (high frequency region only); (IV) "$Ca_3Sn_3Ga_2O_{12}$." The break at 350–300 cm^{-1} is of instrumental origin (grating spectrometer; 2 mgr in KBr discs above; interferometer; 6 mgr in polyethylene discs below 350–300 cm^{-1}).

important vibrational interactions. The overall pattern of these bands is progressively modified with increasing x values, but this is easily explained by the fact that the (SiO_4) groups are progressively "diluted" in the structure when x increases. For x = 0, vibrational interactions between near-neighbor SiO_4 groups are possible and, from this point of view, the situation is more or less similar to that of a pure silicate garnet: the spectrum is approximately that predicted by the factor group splitting (three T_{1u}, IR-active modes); for increasing values of x, the average distance between SiO_4 groups increases, the SiO_4–SiO_4 vibrational interactions are progressively suppressed and, eventually, the number of bands is given by the site group (S_4) splitting alone (two modes only). This is illustrated by the spectrum of the composition $Ca_3Sn_{2.95}Si_{0.05}Ga_2O_{12}$ (Fig. 3III), whereas the $Ca_3Sn_{2.5}Si_{0.5}Ga_2O_{12}$ composition is an example of an intermediate situation. The SiO_4 bands remain fairly broad in the whole series of solid solutions. The origin of the relative broadness or sharpness of some spectra will be discussed later on.

750–600 cm^{-1} region. The antisymmetric stretching vibrations of GaO_4 tetrahedra are known to occur in this spectral region (*9, 10*). According to the factor group analysis, we expect a triplet in this region (this triplet is effectively observed in the IR spectrum of the garnets $Ln_3Ga_5O_{12}$ (*9*)), but we observe only one strong band with one or two shoulders (depending on the x value): this is to be ascribed to the disordered distribution of several cations (Ga, Si and/or Sn) over the tetrahedral sites. Owing to the scarcity of compounds containing SnO_4 tetrahedra, we have no reference data about the vibrational frequencies of these groups, but they may be roughly estimated by comparison with the vibrational behavior of TiO_4 and GeO_4 tetrahedra: in the IR spectrum of Ba_2TiO_4 and Ba_2GeO_4, the antisymmetric vibrations of TiO_4 and GeO_4 groups are observed in the 750–700 cm^{-1} (stretching) and 400–300 cm^{-1} (bending) regions (*10*). The corresponding vibrations of SnO_4 tetrahedra are thus expected to lie at slightly lower frequencies. In the IR spectrum of the actual solid solutions, we do not observe specific bands of the SnO_4 tetrahedra: their frequencies are probably very similar to those of the GaO_4 tetrahedra, with, as a consequence, a practically complete mixing of both GaO_4 and SnO_4 antisymmetric stretching vibrations.

500–300 cm^{-1} region: In this region, definite assignments are very difficult, if not impossible, for the following reasons. If we consider the oversimplified scheme of internal vibrations, we may expect at least four types of vibrations in this region: some of the bending vibrations of the SiO_4 tetrahedra, the bending vibrations of GaO_4 and SnO_4 tetrahedra, and the stretching motions of the SnO_6 octahedra. Since in addition all the IR-active modes belong to the same T_{1u} representation, all these vibrations may in-

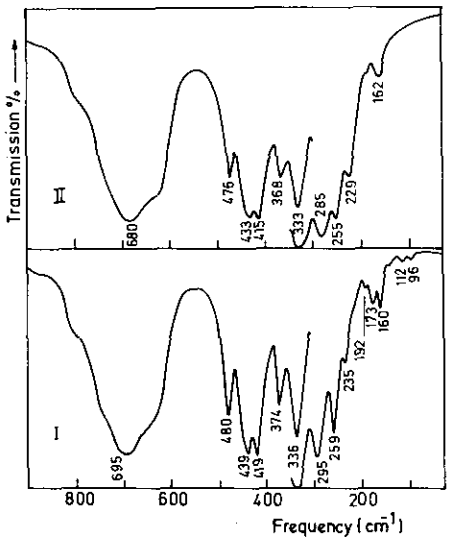

FIG. 4. IR spectra of $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ phases: (I) $x = 0$; (II) $x = 0.50$.

teract, thus leading to complex, nonlocalized motions. An additional difficulty comes from the occurrence of several different cations statistically distributed over the tetrahedral sites. This contributes to the complexity of the vibrations, and to the broadness of the bands.

Low frequency region (below 300 cm^{-1}): Little can be said about this spectral region. The systematic occurrence of bands (or at least shoulders) near 280, 230 and 165 cm^{-1} suggests their assignment to translations of the Ca^{2+} cation.

$Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$. 800–600 cm^{-1} region: Contrary to the vibrational behavior of Si-bearing garnets, no specific band of the GeO_4 stretching vibrations can be seen in the IR spectra of these solid solutions (Fig. 4). We observe only a broad absorption (with ill-defined shoulders), whose main maximum is slightly displaced towards lower frequencies when Ge is progressively replaced by Sn. This is easily explained by the fact that the GeO_4, SnO_4, and GaO_4 antisymmetric stretching frequencies are not very different and are thus strongly coupled.

500–30 cm^{-1} region: As previously stated, no definite assignment can be proposed for this region, but an interesting feature is the sharpness of the spectra, which is much greater than that of the Si-bearing solid solutions. This point will be considered under the heading "Discussion."

Raman Spectra

$Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$. One of the most evident features of these spectra (Fig. 5) is their great similarity in the 600–100 cm^{-1} region: there are just two strong bands (plus a few very weak ones), whose frequency is shifted toward lower frequencies with increasing values of x. No definite assignments can be proposed for these bands.

In contrast, important modifications (better illustrated in Fig. 6) are observed in the 1000–600 cm^{-1} region:

(i) The weak bands of the 1000–800 cm^{-1} region disappear progressively when Si is replaced by Sn: their assignment to stretching vibrations of the SiO_4 tetrahedra is straightforward.

(ii) The broad band near 753 cm^{-1} in the

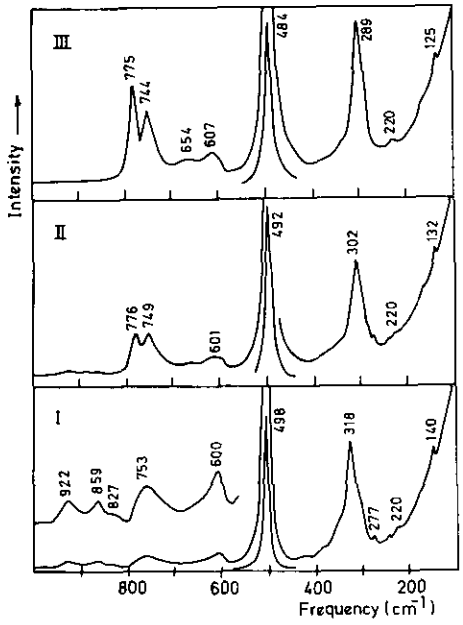

FIG. 5. Raman spectra of $Ca_3Sn_2SiGa_2O_{12}$: (I), $Ca_3Sn_{2.5}Si_{0.5}Ga_2O_{12}$ (II), and $Ca_3Sn_{2.95}Si_{0.05}Ga_2O_{12}$ (III).

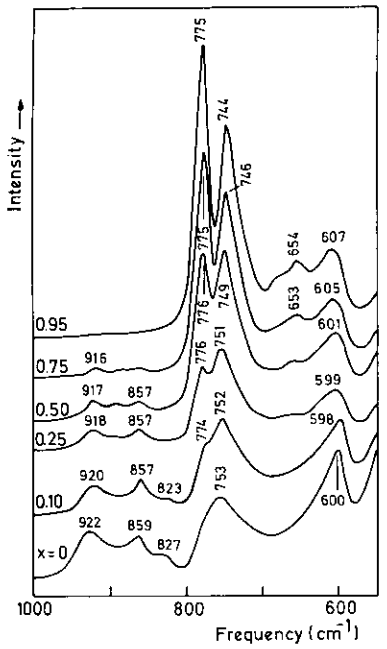

FIG. 6. Raman spectra of $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ solid solutions in the 1000–600 cm^{-1} region.

spectrum of the Si end-member ($x = 0$) is assigned to a stretching vibration of the GaO_4 tetrahedra, possibly the ν_1 totally symmetric mode (A_{1g} representation): this vibration has been observed at 770, 767, and 753 cm^{-1} in the Raman spectrum of Yb_3, Lu_3, and $Gd_3Ga_5O_{12}$ garnets, respectively (*11*, *12*). But the most interesting feature of these spectra is the early appearance (for $x = 0.10$; in fact, already visible for $x = 0.05$), followed by the rapid growing, of a new band at 775 cm^{-1}. This behavior strongly suggests its assignment to the ν_1 mode of SnO_4 tetrahedra.

(iii) The remaining broad bands in the 700–600 cm^{-1} region are assigned to antisymmetric stretching motions of GaO_4 tetrahedra (band near 600 cm^{-1}, with an approximately constant intensity) and SnO_4 tetrahedra (near 650 cm^{-1}, missing for $x = 0$; intensity increasing with the x values).

$Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$. The medium and low frequency spectra (Fig. 7) are rather similar to those of the Si-bearing solid solutions, with the two very strong peaks near 500 and 300 cm^{-1}. A significant difference is the occurrence, in the Ge end-member, of several weak, more or less sharp bands, which are apparently missing in the Si end-member (in fact, they are probably too weak and too broad to be observed: see "Discussion"). The high frequency part of the spectra exhibit a peculiar behavior (Fig. 8).

Two relatively sharp peaks (808 and 757 cm^{-1}) are observed in the spectrum of the Ge end-member. They are assigned to the symmetric stretch ν_1 of the GeO_4 and GaO_4 tetrahedra, respectively. When Ge is progressively replaced by Sn, the following changes are observed:

$x = 0.25$: the existing bands are slightly broadened and shifted towards lower frequencies, and a small hump is observed near 780 cm^{-1}

$x = 0.50$: the preceding hump has grown to a weak band at 777 cm^{-1}, which corresponds to the frequency of the band assigned to the SnO_4 ν_1 mode in the Si-bearing solid solutions

$x = 0.75$: the new band, at 775 cm^{-1}, is now largely predominant, whereas the band assigned to GeO_4 is reduced to a weak shoulder

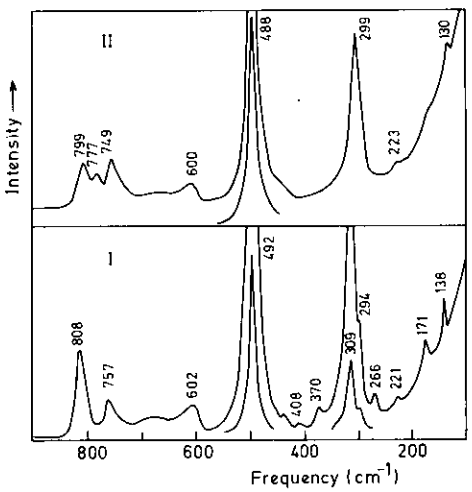

FIG. 7. Raman spectra of $Ca_3Sn_2GeGa_2O_{12}$ (I) and $Ca_3Sn_{2.5}Ge_{0.5}Ga_2O_{12}$(II).

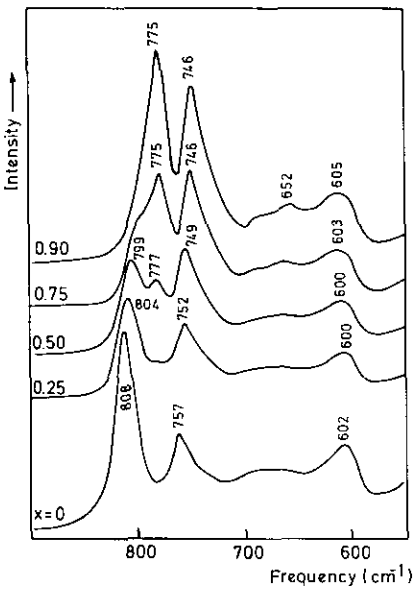

FIG. 8. Raman spectra of $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ solid solutions in the 900–600 cm^{-1} region.

$x = 0.90$: the relative intensity of the 775 cm^{-1} band is still greater; the band assigned to GeO_4 has disappeared.

This latter spectrum is very similar to that of the $Ca_3Sn_{2.95}Si_{0.05}Ga_2O_{12}$ garnet, and it is clear that the 775 cm^{-1} band must be assigned to the ν_1 mode of SnO_4 tetrahedra.

This series of spectra, with a late appearance of the SnO_4 band and a premature disappearance of the GeO_4 band, is a typical example of mixed vibrational behavior, with either one-mode or two-modes vibrational behavior as a function of composition. This is to be correlated with the similarity of the GeO_4 and SnO_4 frequencies, whereas the large difference between the SiO_4 and SnO_4 frequencies leads to systematic two-modes behavior in the whole series of garnets $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$.

The high-frequency assignments are summarized in Table III.

Discussion

Tetrahedral Coordination of Sn^{4+}

As stated in the introduction, the tetrahedral coordination of Sn^{4+} in its oxygen compounds may be considered as exceptional, with only two types of known occurrences: the isotypic compounds K_4SnO_4 and Na_4SnO_4 (*1*), and the impure garnets "$Ca_3Sn_3Fe_2O_{12}$" and "$Ca_3Sn_3Ga_2O_{12}$" (*3, 4*) recently reinvestigated as a part of our work on the system $CaO–SnO_2–TiO_2–Fe_2O_3$ (*2*) or of the system $Ca_3Sn_{2+x}Si(Ge)_{1-x}Ga_2O_{12}$ (this paper). It is thus interesting to discuss the reasons (or at least some of the reasons) of this peculiar behavior.

First of all, the preference of Sn^{4+} for octahedral sites is not the result of a peculiar electronic configuration (as is the case for some transition elements): it is a consequence of the relatively large value (0.55) of the ratio $r_{ion\,Sn^{4+}}/r_{ion\,O^{2-}}$ (to be compared with the 0.26 figure of the $r_{ion\,Si^{4+}}/r_{ion\,O^{2-}}$ ratio). This is supported by the fact that the tetrahedral coordination of Sn^{4+} is more frequent in its sulfur compounds (*13*). It may be inferred, at least as a working hypothesis, that in solid solutions of oxygen compounds, the introduction of tetrahedrally coordinated Sn^{4+} will be possible only if the tetrahedral sites of the host compounds are large enough to accommodate the Sn^{4+} ions without too large a distortion of the structure.

This seems to be supported by the actual data on the garnet structure. To the best of our knowledge, there is no reported

TABLE III
SUMMARY OF THE HIGH FREQUENCY ASSIGNMENTS

Infrared spectra
918–912, 892–879, 835–829 cm^{-1}: ν_3 SiO_4
690–663 cm^{-1}: mixed ν_3 GeO_4 + GaO_4 + SnO_4 vibrations
Raman spectra
922–916, 859–857, 827–823 cm^{-1}: ν_1 + ν_3 SiO_4
808–799 cm^{-1}: ν_1 GeO_4 (A_{1g}) in $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ solid solutions
777–774 cm^{-1}: ν_1 SnO_4 (A_{1g}) in all solid solutions with $x \neq 0$
757–744 cm^{-1}: ν_1 GaO_4 (A_{1g}) in all solid solutions
654–652 cm^{-1}: ν_3 SnO_4 in Sn-rich solid solutions only
607–598 cm^{-1}: ν_3 GaO_4 in all solid solutions

case of tetrahedrally coordinated Sn^{4+} in silicate garnets ($r_{Si^{4+}}$: 0.26 Å). We are actually investigating the possibility of tetrahedral Ge–Sn replacement in suitable garnet germanates ($r_{Ge^{4+}}$: 0.39 Å). So far, only two pairs of compositions have been investigated by X-ray diffraction, namely $Sr_3Y_2Ge_{3-x}Sn_xO_{12}$ (x = 0 and 0.5) and $Na_2CaSn_{2+x}Ge_{3-x}O_{12}$ (x = 0 and 0.5). With respect to the pure garnet phase (x = 0), both Ge–Sn substituted compositions exhibit a small increase of the unit cell parameter, indicating the occurrence of some Ge–Sn replacement; but they exhibit also a number of additional diffraction peaks, showing that they are well outside the region of homogeneous solid solutions. The precise limit is still to be determined, but we may roughly estimate, from the variation of the unit cell parameter, a maximum value of x of 0.2 for $Na_2CaSn_{2+x}Ge_{3-x}O_{12}$, and of 0.05 only for $Sr_3Y_2Ge_{3-x}Sn_xO_{12}$ solid solutions. These low limits are to be compared with the x = 0.95 value observed when most of the tetrahedral sites are occupied by the Ga^{3+} ion (r_{ion}: 0.47 Å).

It is clear that additional experiments are needed to check this trend.

Another point (raised by a reviewer) is the exclusive localization of the Ga^{3+} cations on the tetrahedral sites, instead of a distribution $(Ga, Sn)_{tetra} \leftrightarrow (Ga, Sn)_{octa}$. The possibility of such a distribution cannot be neglected if we consider that the tetrahedral ionic radii are not very different for Ga^{3+} (0.47 Å) and Sn^{4+} (0.55 Å). However, we know a large number of oxygen compounds with tetrahedrally coordinated Ga^{3+} ($LiGaO_2$, $CaGa_2O_4$, $LiGaGeO_4$, $GaPO_4$, etc., see, e.g., Ref. (*13*)), whereas (as stated in the introduction) the tetrahedral coordination of Sn^{4+} is really exceptional.

From this experimental basis, we may conclude that the relative preferences of Sn^{4+} and Ga^{3+} for tetrahedral sites are drastically different, and cannot be deduced merely from a comparison of the ionic radii: the electronic structure must play an important role in this matter.

Vibrational Spectra

Compared vibrational behavior in the high frequency parts of the Raman and infrared spectra. We have already noticed that, if SiO_4 stretching vibrations can be observed in both IR and Raman spectra, discrete bands which can be assigned to stretching vibrations of SnO_4 tetrahedra are never observed in the IR spectrum, whereas such bands are easily evidenced in the Raman spectrum of $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ solid solutions. The situation is still more complicated for the $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ solid solutions: in the IR spectrum, the contributions of the three types of tetrahedral groups (SnO_4, GeO_4, and GaO_4) are mixed in a single broad, asymmetric absorption, whereas discrete bands are observed, at least for some compositions in the Raman spectrum.

This can be explained by the different symmetry properties of these vibrations.

Let us consider (as an approximation) the existence of internal stretching modes of the SiO_4, GeO_4, GaO_4 and SnO_4 tetrahedra.

In the IR spectrum, and according to the factor group analysis (*14*), the stretching vibrations of each type of tetrahedral group lead to 3 T_{1u} modes.

For the higher SiO_4 frequencies, the interactions with the lower SnO_4 or GaO_4 frequencies are small, and discrete SiO_4 bands are observed in the spectra.

But for the GeO_4, SnO_4, and GaO_4 tetrahedra, whose stretching frequencies are of the same order of magnitude, we should have in the same spectral range either six (SnO_4 + GaO_4) or nine (GeO_4 + SnO_4 + GaO_4) vibrational frequencies which all belong to the same representation T_{1u}.

This leads to strong vibrational interactions, and the individual frequencies coalesce into a broad, asymmetric absorption.

The situation is different in the Raman spectrum: for a pure compound, the tetrahedral groups should give six Raman-active stretching vibrations, but they are distributed over three different representations (1

$A_{1g} + 2\,E_g + 3\,T_{2g}$). Among these, the most important one is the totally symmetric mode A_{1g} which, in the approximation of tetrahedral internal modes, is issued from the symmetric stretching mode ν_1 of the tetrahedron. It is interesting for the following reasons:

(i) The corresponding motion is limited to a simple symmetric displacement of the oxygen atoms only (all cations are necessarily at rest during this type of vibration).

(ii) For a given tetrahedral group, it is the only stretching vibration of this class

(iii) It is expected to give a reasonably strong Raman peak. For these reasons, the probability of vibrational interactions between different tetrahedral groups is much smaller than for the IR-active vibrations, and it should be possible to observe a specific band for each tetrahedral group, provided the individual frequencies of these groups are not too similar.

This is well illustrated by the Raman spectra of the solid solutions $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$, with individual SiO_4, SnO_4, and GaO_4 ν_1 frequencies in the whole series of solid solutions, and on the other hand the solid solutions $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$, for which individual GeO_4 and SnO_4 ν_1 vibrations are observed only for a limited range of compositions, probably because of the similarity of their individual frequencies.

Origin of the two strong Raman peaks near 500 and 300 cm^{-1}. For a pure compound, the factor group analysis predicts the existence of three totally symmetric A_{1g} vibrations. One of these, located in the high frequency part of the spectrum, is generally assigned to the ν_1 mode of the tetrahedral group (as far as this vibration can be considered as an internal mode). The two Raman peaks near 500 and 300 cm^{-1} may be tentatively assigned to the two remaining A_{1g} modes, on the basis of their great intensity (though this is not a definitive argument). Since the cations are at rest during these vibrations, their frequency is essentially determined by the different cation–oxygen bonding forces, the sum of which gives the overall restoring force determining the vibrational frequency.

If one of these bonds is much stronger than the others, its contribution to the overall restoring force is predominant, and the vibration may be considered (at least as a first approximation) as an internal mode: this is the case of the ν_1 mode of the tetrahedral group discussed previously. But for the 500 and 300 cm^{-1} bands under discussion, there is no prevailing "local" restoring force: this would explain why no specific cationic influence can be observed on these frequencies.

Broadness of some spectra. We have already noticed the following features:

(i) The bands assigned to the stretching vibrations of the SiO_4 tetrahedra are broad in both IR (Fig. 3) and Raman spectra (Fig. 6) of the solid solutions $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$.

(ii) For the end-member compositions, the diffuseness of the spectra decreases in the sequence $Ca_3Sn_2SiGa_2O_{12}$, "$Ca_3Sn_2SnGa_2O_{12}$," and $Ca_3Sn_2GeGa_2O_{12}$, this latter composition giving sharp bands, at least below 600 cm^{-1}. This appears clearly by comparison of Figs. 3I, 3IV, and 4I for the IR spectra, 5I and 7I for the Raman spectra.

These results can be explained by considering the following points:

(i) The occurrence of two (or several) different cations statistically distributed over the tetrahedral sites (as is the case for all compositions investigated in this paper) must induce some broadening of the vibrational spectrum. This is a classical consequence of disorder phenomena.

(ii) Our results show that the smallest broadening is observed for the smallest difference between the ionic radii of the tetrahedral cations, namely Ge (0.39 Å) and Ga (0.47 Å) in $Ca_3Sn_2GeGa_2O_{12}$; in contrast, the greatest diffuseness is observed for the greatest difference between the ionic radii, Si (0.26 Å) and Ga in $Ca_3Sn_2SiGa_2O_{12}$. This should induce a greater distortion of the oxygen sublattice and an accordingly broader distribution of the vibrational frequencies.

As expected, the broadness of the bands is still greater for the intermediate solid solution $Ca_3Sn_{2.5}Si_{0.5}Ga_2O_{12}$, with three different cations on the tetrahedral sites (Fig. 3II).

(iii) An additional cause of broadness should be considered in the specific case of (SiO_4) vibrations: the average size of the tetrahedral voids is probably too large for the small Si cation, and this should also contribute to the broadness of the SiO_4 bands, particularly in the range of Si-poor compositions.

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