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Simultaneous Occurrence of Sn^{4+} on the Three Cationic Sites of the Garnet Structure: The Solid Solutions $Ca_xSn_xGa_{8-2x}O_{12}$ ($2.5 < x < 3.0$)

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The first example of the simultaneous occurrence of the same cation, namely Sn^{4+}, on the three cationic sites of the garnet structure is reported; the single phase solid solution $Ca_xSn_xGa_{8-2x}O_{12}$, resulting from the double substitution $2Ga^{3+} \rightarrow Sn^{4+} + Ca^{2+}$ exists within the composition range $2.65 \leq x \leq 2.95$, i.e., between the limiting compositions $Ca_{2.65}Sn_{2.65}Ga_{2.70}O_{12}$ and $Ca_{2.95}Sn_{2.95}Ga_{2.10}O_{12}$. Such compositions imply that the Sn^{4+} cations are distributed over the three cationic sites of the garnet structure, e.g. for $x = 2.65$ $(Ca_{2.65}Sn_{0.35})^{VIII}(Sn_2)^{VI}(Ga_{2.70}Sn_{0.30})^{IV}$. This has been definitely confirmed by X-ray powder diffraction structure calculations. In the Raman spectrum, the totally symmetric (ν_1) stretches of SnO_4 and GaO_4 tetrahedra are observed near 780 and 750 cm^{-1}, respectively, whereas in the infrared spectrum, the corresponding antisymmetric vibrations coalesce in a broad, asymmetric absorption. © 1995 Academic Press, Inc.

INTRODUCTION

We have shown in a previous paper that the composition $Ca_3Sn_3Ga_2O_{12}$ gives a nearly pure garnet phase, determined on the basis of a significant amount of tetrahedrally coordinated Sn^{4+}, in agreement with the theoretical structural formula $(Ca_3)^{VIII}(Sn_2)^{VI}(Ga_2Sn)^{IV}O_{12}$ (1). On the other hand, attempts to synthesize the compound $Ca_{2.5}Sn_{2.5}Ga_3O_{12}$, including some Sn^{4+} in eightfold coordination in place of Zr^{4+} in the similar composition $Ca_{2.5}Zr_{2.5}Ga_3O_{12}$ (2), lead to an impure garnet phase whose unit cell parameter is much smaller than that of the $Ca_3Sn_3Ga_2O_{12}$ composition. This suggested the possible existence of pure garnets of intermediate composition, resulting from the double substitution $2Ga^{3+} \rightarrow Ca^{2+} + Sn^{4+}$. We have accordingly investigated the existence of garnet-type compositions $Ca_xSn_xGa_{8-2x}O_{12}$ ($2.5 < x < 3.0$). These phases have been characterized by X-ray diffraction and vibrational spectroscopy.

EXPERIMENTAL

All experimental techniques (synthesis by solid state reaction, X-ray diffraction, and vibrational spectroscopy) are classical and have been reported previously (1).

RESULTS

X-Ray Diffraction

Cell parameters. The values of the a_0 parameter for all investigated compositions are plotted in Fig. 1. Pure garnet phases are obtained in the composition range $2.65 \leq x \leq 2.95$; these two values are very near the limits (2.63 and 2.96, respectively) deduced by extrapolation of the straight relationship between x and a_0.

The strong increase in a_0 agrees well with that predicted from the variation of ionic radii, resulting from the double substitution $2Ga^{3+} \rightarrow Sn^{4+} + Ca^{2+}$.

Structure calculations. From the relative preferences of Ca^{2+}, Sn^{4+}, and Ga^{3+} cations for the dodecahedral, octahedral, and tetrahedral sites, respectively, the solid solution $Ca_xSn_xGa_{8-2x}O_{12}$ ($2.5 < x < 3.0$) is better understood in terms of the garnet-type structural formula $(Ca_xSn_{3-x})^{VIII}(Sn_2)^{VI}(Ga_{8-2x}Sn_{2x-5})^{IV}O_{12}$; since the number of Sn^{4+} cations is always greater than two, two of these cations are first located on the octahedral sites. The remainder is then distributed over the available dodecahedral and tetrahedral sites, so as to give a total of three cations ($Ca^{2+} + Sn^{4+}$, or $Ga^{3+} + Sn^{4+}$) for each of these sites.

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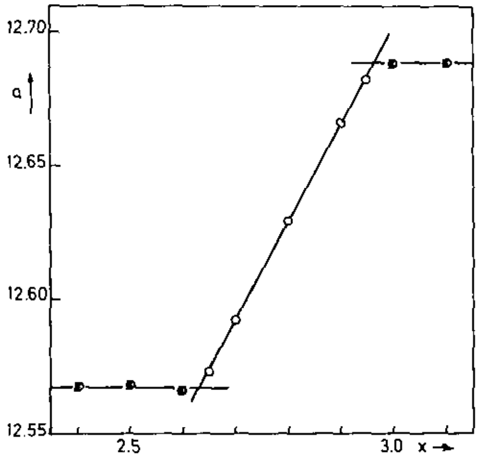

FIG. 1. Variation in the unit cell parameter a_0 of the garnet phase as a function of x in the $Ca_xSn_xGa_{8-2x}O_{12}$ nominal compositions.

For structure calculations, it was decided to check the lower limiting composition, i.e., $x = 2.65$, which is most significant for the cationic substitution in the dodecahedral sites. Calculations were performed from the integrated intensities of X-ray powder diffractograms recorded on a Siemens D 500 apparatus, Cu$K\alpha$ radiation, up to 100° 2θ. Under these conditions, an overall number of 68 reflections, with or without superposition, including the nonobserved reflections arbitrarily assumed to be equal to 1% of the highest observed intensity, were used in a least-squares refinement procedure.

The usual model of the garnet type structure, space group $Ia3d$, is

(VIII) coordination site	24(c)	1/8 0 1/4
(VI) coordination site	16(a)	0 0 0
(IV) coordination site	24(d)	3/8 0 1/4
Oxygen site	96(h)	$x \approx 0.96$; $y \approx 0.05$; $z \approx 0.15$.

Table I reports the values of the variable parameters, i.e., the site occupancy in (VIII) and (IV) coordination, the positional parameters of oxygen and the isotropic thermal factors, as obtained for the best value of the confidence factor $RI = \sum|I_0 - I_c|/\sum I_0 = 0.058$.

As a main result, the mixed occupancy of the dodecahedral and tetrahedral sites by ($Ca^{2+}Sn^{4+}$) and ($Ga^{3+}Sn^{4+}$), respectively, is ensured. Moreover, there is good agreement between the calculated values and the theoretical ones, as deduced from the composition $x = 2.65$, i.e., 0.35 Sn^{4+} in the dodecahedral sites and 0.30 Sn^{4+} in the tetrahedral sites. The values of the isotropic thermal factors at the cationic sites are further proof of the validity of the cationic distribution.

TABLE 1

Atomic Parameters for the Garnet-type Structure of $Ca_{2.65}Sn_{2.65}Ga_{2.70}O_{12}$

	Occupancy	B(Å^2)
Dodecahedral site	$Ca_{2.61(2)}Sn_{0.39(2)}$	0.8(1)
Octahedral site	Sn_2	0.7(1)
Tetrahedral site	$Ga_{2.70(2)}Sn_{0.30(2)}$	0.5(1)
Oxygen site	$x = 0.964(2)$ $y = 0.048(2)$ $z = 0.156(1)$ $B = 0.5(3)$	

$RI = \sum|I_o - I_c|/\sum I_o = 0.058$ for 68 reflections, including allowed, but nonobserved ones (see text)

$RI = 0.034$ for 28 effectively observed reflections

By contrast, the B value for the oxygen atoms is low, but it must be pointed out that, for the oxygen, the confidence factor RI is only slightly sensitive to the B value (e.g., $RI = 0.058$ or 0.059 for $B = 0.5$ or 1, respectively).

The M–O distances are very similar to those already obtained for the garnet $Ca_3Sn_{2.95}Ga_2Si_{0.05}O_{12}$ (1).

Infrared Spectra

These spectra (Fig. 2) are very similar, with practically no change in the 800–600 cm^{-1} region, and only minor modifications in the 600–100 cm^{-1} region: small frequency shifts, some broadening of the medium-frequency bands,

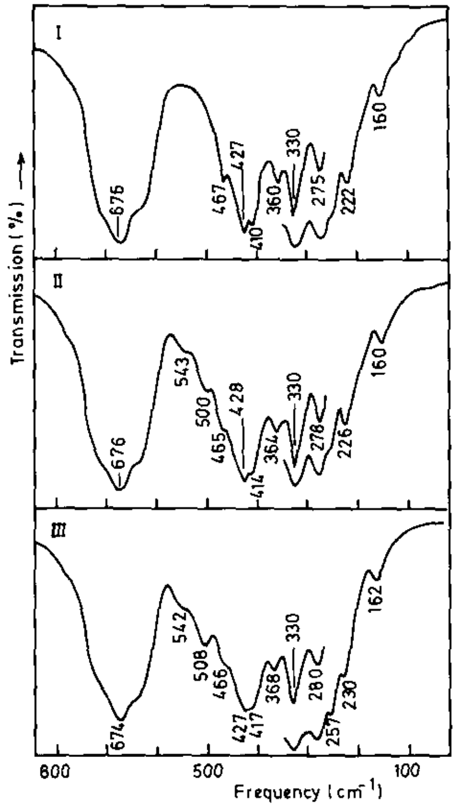

FIG. 2. IR spectra of the garnet phases for $x = 2.95$ (I), 2.80 (II), and 2.65 (III).

and the growth of two additional weak bands near 540 and 500 cm^{-1} for decreasing values of x.

As discussed in a previous paper (1), the reason for such limited modifications is the fact that, for the garnet structure, all the IR-active vibrations belong to the same representation T_{1u}; moreover, the internal mode approximation does not hold here, and most, if not all of the bands cannot be assigned to the displacement of a single definite cation or coordinated group.

We have no definite assignment for the two weak bands near 540 and 500 cm^{-1}; but, according to unpublished results (A. Rulmont and P. Tarte), a similar behavior is observed in the IR spectra of other compounds with the garnet structure, e.g., the solid solutions $(Li_{1-x}Na_x)Ca_2Mg_2As_3O_{12}$, with, a weak band near 490 cm^{-1}, present in the spectrum of the Na compound, missing in the spectrum of the Li compound, and growing in intensity with the x value in the spectrum of the solid solutions.

Likewise, a weak band is observed in the 650–600 cm^{-1} region of the IR spectrum of nearly all silicate garnets, with the notable exception of pyrope $Mg_3Al_2Si_3O_{12}$ (3); this band is missing in the IR spectrum of pyrope, whether natural or synthetic (4), but it appears with an increasing intensity in the spectrum of the solid solutions $(Mg_{3-x}Fe_x)Al_2Si_3O_{12}$ (pyrope-almandin) (5).

It is actually impossible to decide whether such analogies are fortuitous or not.

Notable also is the systematic occurrence of weak bands near 280, 230, and 160 cm^{-1}. Translational motions of eightfold coordinated Ca^{2+} are expected to lie in this frequency range, but additional experiments are needed to check this assignment.

Raman Spectra

All Raman spectra are very similar in the 550–100 cm^{-1} (Fig. 3) region, with two very strong bands near 490 and 300 cm^{-1} exhibiting a small frequency increase when the a_0 parameter decreases (extreme values of 484–493 and 290–300 cm^{-1}, respectively, when a_0 decreases from 12.682 ($x = 2.95$) to 12.573 Å ($x = 2.65$).

In contrast, significant variations of the relative intensities of some bands are noted in the 800–600 cm^{-1} region.

The origin of these bands has already been discussed on the basis of their relative intensities in the Raman spectra of the solid solutions $Ca_3Sn_{2+x}Si_{1-x}Ga_2O_{12}$ (1); their assignment is as follows:

780 cm^{-1}:	SnO_4 ν_1 symmetric stretch (A_{1g})
750 cm^{-1}:	GaO_4 ν_1 symmetric stretch (A_{1g})
near 650 cm^{-1}:	SnO_4 antisymmetric stretch
near 615 cm^{-1}:	GaO_4 antisymmetric stretch.

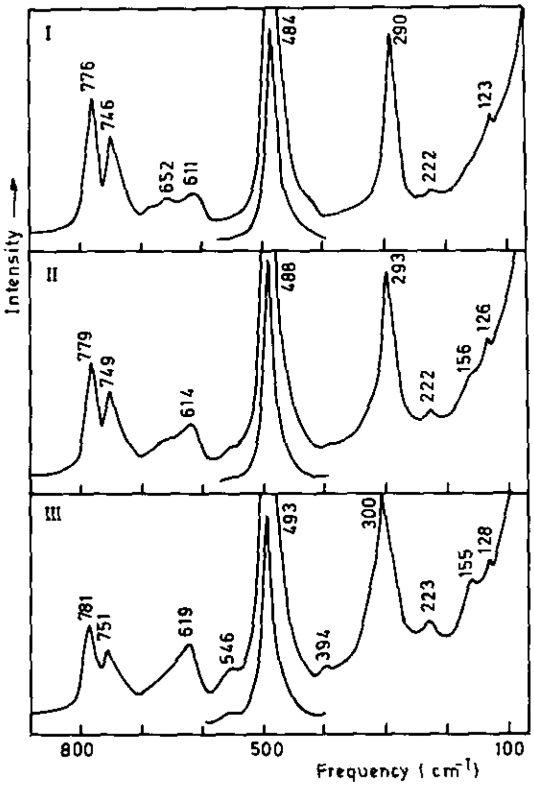

FIG. 3. Raman spectra of the garnet phases for $x = 2.95$ (I), 2.80 (II), and 2.65 (III).

For these last two bands, the actual variations in their relative intensities with composition are in qualitative agreement with these assignments. However, this is not true for the two bands near 780 and 750 cm^{-1}, whose relative intensities remain approximately constant throughout the whole series of solid solutions. This could be tentatively explained by interactions between these two vibrations, which belong necessarily to the same representation A_{1g}, and whose frequencies differ by only 30 cm^{-1}.

DISCUSSION

Cation Distribution and Tin Coordination

In the garnet phases under consideration, the cation distribution is immediately deduced from the overall chemical formula (equal to the nominal composition for the pure solid solutions $2.65 \leq x \leq 2.95$), and from the relative preferences of Ca^{2+}, Sn^{4+}, and Ga^{3+} for the dodecahedral, octahedral, and tetrahedral sites, respectively. Moreover, this distribution is definitely proved, for $x = 2.65$, by the very good confidence factor obtained after refinement of the powder XRD intensities.

The existence of such garnets was rather unexpected since, owing to its medium-sized ionic radius (6), Sn^{4+} is a nearly ideal octahedral cation, at least in its oxygen compounds, and reported examples of either tetrahedral (as in K_4SnO_4 and Na_4SnO_4 (7)) or dodecahedral (as in $Sn(NO_3)_4$ (8)) coordinations are very scarce.

Still more unexpected was the simultaneous occurrence of these three coordinations in a single phase. A few cations can be located on either of the three garnet cationic sites, but this is generally on one type of site only for a given chemical composition (e.g., Li^+ is tetrahedral in $Ln_3Te_2Li_3O_{12}$ (9), octahedral in $Ca_3LiMgV_3O_{12}$ (10), and dodecahedral in $Li_3Cr_2As_3O_{12}$ (11)).

To the best of our knowledge, our solid solutions are the first reported example of the simultaneous occurrence of a cation on the three cationic sites of a single garnet phase. In fact, a similar behavior was suspected in the garnet phases appearing in the system $CaO-Fe_2O_3-SnO_2$ (12), but since these phases were always intimately mixed with impurities, their true composition remained unknown, and no definite conclusion could be drawn about the cation distribution.

Vibrational Spectra

A first point is the fairly different vibrational behavior observed in either the Raman or the IR spectrum. In the former, the GaO_4 and SnO_4 stretching vibrations appear as discrete bands, whereas in the latter, they coalesce into a single broad, asymmetric absorption.

A similar behavior has already been observed in the spectrum of the solid solutions $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ (1), where they have been tentatively explained in terms of symmetry properties of the vibrations and of their role in the occurrence of vibrational couplings: owing to the fact that all IR active vibrations belong to the same representation T_{1u}, extensive vibrational couplings are expected in the IR spectrum, whereas such possibilities are reduced in the Raman spectrum, since the Raman active vibrations are distributed over three representations (A_{1g}, E_g, T_{2g}).

Another point is the great simplicity of the Raman spectra below 600 cm^{-1} (according to the factor group analysis, a total of 25 active modes is predicted in the Raman spectrum). A qualitative explanation is suggested by the Raman spectra of the $Ca_3Sn_{2+x}Ge_{1-x}Ga_2O_{12}$ solid solutions (Fig. 7 of Ref. 1). For the end-member $Ca_3Sn_2GeGa_2O_{12}$ ($x = 0$), the low-frequency (below 600 cm^{-1}) Raman spectrum exhibits, besides the two very strong peaks near 500 and 300 cm^{-1}, a series of very weak, but reasonably sharp peaks in the 450–100 cm^{-1} region. However, for increasing values of x, these peaks are broadened and, since they were already very weak, they merge in a nearly continuous background, as illustrated by the spectrum of the composition $Ca_3Sn_{2.5}Ge_{0.5}Ga_2O_{12}$ ($x = 0.5$; Fig. 7-11 of Ref. 1). This broadening is clearly the result of increasing cationic disorder on the tetrahedral sites. A similar behavior has also been observed in the Raman spectra of other garnet-type solid solutions investigated by the authors (results to be published). It is thus reasonable to extend this explanation to the actual solid solutions (e.g., $(Ca_{2.80}Sn_{0.20})^{VIII}Sn_2{}^{VI}(Ga_{2.40}Sn_{0.60})^{IV}$) with a cationic disorder on both dodecahedral and tetrahedral sites.

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