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INFRARED SPECTRA FROM SOLID SOLUTIONS OF SPESSARTINE AND YTTRIUM ALUMINUM GARNET

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ABSTRACT

Compositional relationships were established through thin-film spectroscopy for all 17 infrared lattice vibrations in compositions along the binary join spessartine $Mn_3Al_2Si_3O_{12}$ – yttrium aluminum garnet $Y_3Al_2Al_3O_{12}$. Powder-dispersion data yielded similar results, but at lower resolution owing to presence of enhanced overtones, scattering components and interference fringes. Thin-film frequencies of the end members are in excellent agreement with transverse optic modes obtained from single-crystal reflectance spectra. All but a few weak modes are traceable completely across the binary, such that most frequencies depend almost linearly on cell parameter. Different behaviors are seen for the modes assigned to various atomic motions: for example, tetrahedral stretches have two-mode behavior (*i.e.*, both end-member peaks are present with intensities proportional to concentration), which is consistent with the bond strength of Al–O being significantly less (0.83 times) than that of Si–O. Frequencies of the dodecahedral translations increase very slightly, indicating that the increase in average mass as Y^{3+} replaces Mn^{2+} is offset by the increase in bond strength as average valency increases. The observations suggest that the thermodynamic properties of high-pressure garnets with minor tetrahedral substitutions (<4%) will be scarcely affected.

Keywords: IR spectroscopy, yttrium aluminum garnet, spessartine, solid solutions, two-mode behavior.

SOMMAIRE

Nous avons établi, par spectroscopie infra-rouge sur pellicules minces, les dépendances compositionnelles des dix-sept vibrations de réseau du grenat appartenant au système binaire spessartine ($Mn_3Al_2Si_3O_{12}$) – grenat à yttrium–aluminium ($Y_3Al_2Al_3O_{12}$). Les résultats obtenus sur poudres dispersées sont semblables, mais la résolution des spectres est plus faible à cause de la présence d'harmoniques plus intenses, de composantes de diffusion et de franges d'interférence. Les fréquences de vibration des pôles, déterminées sur pellicules minces, concordent très bien avec les modes optiques transversaux obtenus à partir du spectre de réflectance de monocristaux. Sauf pour certains modes dont l'intensité est très faible, nous pouvons tracer tous les modes d'un pôle à l'autre; la plupart des fréquences montrent une dépendance presque linéaire en fonction du paramètre de maille. Les modes qui expriment le mouvement de divers atomes se comportent différemment. Par exemple, l'étirement des tétraèdres fait preuve d'un comportement à deux modes, dans lequel les pics de chaque pôle sont présents, chacun ayant une intensité proportionnelle à la concentration du pôle. Ce comportement concorde avec une liaison Al–O sensiblement moins forte (facteur de 0,83) que la liaison Si–O. Les fréquences de translation des dodécaèdres augmentent très légèrement, indication que l'augmentation moyenne de masse lorsque Y^{3+} remplace Mn^{2+} est compensée par l'augmentation de la force de liaison à mesure qu'augmente la valence moyenne. Ces observations font penser que les propriétés thermodynamiques des grenats de haute pression qui présentent un léger taux de substitution (<4%) dans le site tétraédrique seront peu affectées.

(Traduit par la Rédaction)

Mots-clés: spectroscopie infra-rouge, grenat à yttrium et aluminium, spessartine, solutions solides, comportement à deux modes.

INTRODUCTION

In order to understand the complex dependence of thermodynamic properties on garnet composition, detailed information regarding the effect of cation substitution on the macroscopic and microscopic properties of garnet is needed, as discussed in Hofmeister & Chopelas (1991a, b).

Substitutions in the tetrahedrally coordinated site of a garnet affect its highest frequency modes, which contribute to thermodynamic properties at high temperature. In contrast, substitutions in dodecahedrally coordinated sites induce significant changes in the lowest frequency modes, which severely alters thermodynamic properties over a large range of temperature (*e.g.*, Kieffer 1979). Examination of the complete solid-solutions between synthetic $YAl_2Al_3O_{12}$ (YAG) and spessartine (Yoder & Keith 1951) provides insight into the effect of cation substitution in both tetrahedral and dodecahedral sites. For this coupled substitution ($Y^{3+} + Al^{3+} = Mn^{2+} + Si^{4+}$), effects of these two exchanges are separable because the affected peaks occur at opposite ends of the spectrum (Hofmeister & Chopelas 1991a, Hofmeister & Campbell 1992). Obtaining a suitable system involving the tetrahedral site in natural garnets is problematic because (1) melanite, which does have considerable solid-solution, is commonly non-stoichiometric, and (2) substitution for Si in other garnets is limited to minor amounts of Al, Ti, Fe, P (*e.g.*, Bishop *et al.* 1976, 1978) or to hydrogarnet, where four protons replace one Si (Meagher 1980).

This paper presents thin-film infrared (IR) absorption spectra of high signal-to-noise ratio on spessartine, YAG, and five intermediate compositions synthesized by Yoder & Keith (1951). The powder-dispersion spectra were not used because this technique gives imprecise positions owing to presence of enhanced overtones, longitudinal optic (LO) components and surface modes. The nearly linear dependence of frequency on composition strengthens previous arguments regarding band assignments and provides information on relative force constants and bond strengths. Lastly, effects of minor substitutions involving tetrahedrally coordinated cations on thermodynamic properties are evaluated.

PREVIOUS WORK

Symmetry analysis of IR vibrations

The garnet structure *Ia*3*d* consists of a three-dimensional network of alternate corner-linked slightly elongate octahedra and distorted tetrahedra, both of which share edges with slightly distorted triangular dodecahedra (Euler & Bruce 1965, Novak & Gibbs 1971). (For brevity, these will be referred to as tetrahedra, octahedra and dodecahedra.) As discussed previously (Hurrell *et al.* 1968, Slack *et al.* 1969), this structure has 17 triply degenerate T_{1u} modes active in the infrared. If the vibrational motions of the tetrahedron are mildly perturbed by placing this unit in the garnet structure, then these 17 IR modes should consist of three asymmetric stretching modes of the tetrahedron ν_3, three asymmetric bending modes ν_4, one symmetric bend ν_2, two rotations (librations) R of the tetrahedron, two translations T of the tetrahedron, three translations T_{dod} of the dodecahedrally coordinated cations, and three translations T_{oct} of the octahedrally coordinated cations (Moore *et al.* 1971, Hofmeister & Chopelas 1991a). Note that the contributions of atomic motions from individual sites in garnet do not represent localized vibrations. The intent of the analysis is to establish which atomic motion (if any) dominates a given vibrational mode.

Infrared data

Infrared modes of spessartine and YAG have been completely established through single-crystal reflectance spectroscopy (Hurrell *et al.* 1968, Hofmeister & Chopelas 1991a, Hofmeister & Campbell 1992). Band assignments made on the basis of chemical substitutions in silicate and in rare-earth garnets indicate that mode mixing may occur between ν_2 and the highest-frequency octahedral translation, and also between T and T_{dod}. Frequencies of the internal modes and rotations in garnet are controlled by the size of the unit cell (*e.g.*, McDevitt 1969), which is strongly governed by the mean bond-length of the octahedron. Frequencies of translations are controlled by the mass of the cations, and by the bonding between the cations and the oxygen forming the tetrahedra.

Several solid solutions involving the dodecahedral site in silicate garnets have been investigated through powder-absorption spectroscopy. Mid-IR spectra of compositions from the grossular–almandine, pyrope–almandine (Geiger *et al.* 1989), and pyrope–grossular binaries (Delany 1981) show one-mode behavior, wherein frequency changes smoothly (generally linearly) from one end-member value to the other, which is equivalent to Vegard's law for crystallography. Incomplete far-IR data suggest that T_{dod} translations of pyrope–almandine show two-mode behavior, wherein both end-member peaks are present with *intensities* proportional to the concentration (Hofmeister & Chopelas 1991a, Moore *et al.* 1971). Two-mode behavior generally is related to large differences in mass, leading to the occurrence of local modes within gaps of the phonon spectra; it does not require reduction in symmetry (*e.g.*, Chang & Mitra 1968). Translations of the tetrahedra (but not of the dodecahedra) show two-mode behavior for pyrope–grossular substitutions; this was attributed to differences in force constant (*i.e.*, bond strength) rather than in mass (Hofmeister & Chopelas 1991a). The bonding between the anions of the tetrahedra and the cations is affected by the size of the dodecahedra through edge-sharing.

Substitution of equally charged cations simultaneously in the tetrahedral and in the octahedral sites has been investigated by the techniques of mid-IR absorption (Beregi & Hild 1987) and mid-IR reflection (Zhovanik *et al.* 1982). The synthetic rare-earth garnets that were studied [*e.g.*, $Y_3(Ga,Fe)_5O_{12}$] show one-mode behavior for the internal bands and frequencies that depend nearly linearly on cell volume.

EXPERIMENTAL

The end-members spessartine and YAG, and five binary compositions ranging from 4.3 to 55.3 mole % YAG investigated here were synthesized and characterized through X-ray diffraction by Yoder & Keith (1951). The small grain-size of the garnet crystals (1 to 10 μm) precluded single-crystal IR measurements.

All spectra were collected at room temperature with an evacuated Bomem DA 3.02 Fourier transform interferometer having an absolute accuracy of ± 0.004 cm^{-1} at 2000 cm^{-1}. Powder was compressed into a thin film with a megabar diamond anvil cell (DAC) (*e.g.* Hofmeister *et al.* 1989). For far-IR measurements, type-I diamonds were used, and thicknesses of the films were about 20 μm. For mid-IR experiments, type-IIa diamonds were used, and films were made in the submicrometer range (as confirmed by comparing absorptivity calculated from reflectance data to measured absorbances of peaks: McAloon & Hofmeister 1993). Far-IR absorption spectra were obtained at 1 cm^{-1} resolution from about 100 to 750 cm^{-1} with a helium-cooled Si bolometer and a 3 μm mylar beam-splitter. Mid-IR spectra were obtained at 1 cm^{-1} resolution above 450 cm^{-1} with a liquid-nitrogen-cooled HgCdTe detector and a KBr beam-splitter. An all-reflecting beam condensor was used to increase throughput of the DAC by a factor of four.

Fourier self-deconvolution (Kaupinnen *et al.* 1981) was used to separate overlapping peaks. A pure Lorentzian line shape was assumed. Peak width and peak-narrowing factor were adjusted to avoid side lobes (overdeconvolution). The validity of the deconvolution procedure was established by monitoring the behavior of nearby well-resolved singlet peaks. Positions derived from deconvolution are uncertain by 1–2 cm^{-1} because this is the amount the peaks change if a Gaussian rather than Lorentzian line shape is chosen or if the position of the deconvolution window is changed. The limited-frequency window for the routine (about 200 cm^{-1} wide for the spectral resolution of 1 cm^{-1} used here) prohibited separation of the overlapping stretching modes of Al–O and Si–O, because these cover an extremely wide region from 650 to 1100 cm^{-1}.

RESULTS

Thin-film absorption spectra

The thin-film IR spectra of spessartine, YAG and their solid solutions (Fig. 1) have similar patterns of intensity and frequencies but considerably more peaks than those obtained previously from powder spectra of garnet (Tarte 1965, McDevitt 1969, Moore *et al.* 1971, Slack *et al.* 1969). Fifteen to seventeen peaks are observed, as is typical of single-crystal measurements of the *Ia*3*d* structure (Hofmeister & Chopelas 1991a, Hofmeister & Campbell 1992).

The relative intensities and positions of the peaks for each end-member strongly resemble those of single-crystal reflection measurements (Hurrell *et al.* 1968, Hofmeister & Chopelas 1991a, Hofmeister & Campbell 1992). Correspondence is excellent for peaks that are either weak or well resolved, such that their thin film and transverse optic (TO) frequencies are within 2 cm^{-1} (Table 1). In the regions from 450 to 500 cm^{-1} and from 700–750 cm^{-1}, which have several intense, overlapping peaks, the thin film and reflection spectra are somewhat dissimilar, and the difference in peak positions is slightly larger, 3–8 cm^{-1}. The difference in frequency also is large, 4–5 cm^{-1}, for the two intense high-frequency stretching modes (ν_3) in YAG. The larger difference in peak shape and position for an intense peak is expected, owing to the fact that 1) the absorptivity is related to both the imaginary part of the dielectric function ε_2 and to the real part of the optical function n:

$$a(\nu) = 2\pi\nu\,\varepsilon_2(\nu)/n(\nu) \qquad (1)$$

(*e.g.*, Wooten 1972), and that 2) the *TO* positions are at the maxima in ε_2 but on the sides of the peaks in n.

Thin-film spectra of intermediate compositions along the join $Mn_3Al_2Si_3O_{12}$–$Y_3Al_2Al_3O_{12}$ are transitional in appearance, with patterns much like those of other types of garnet. Most of the expected peaks are resolved in the raw data. Far-IR peaks are distinct, albeit weak and broad (Fig. 1a). Two-mode behavior was observed for the lowest-lying band (assigned as T *versus* T_{dod} by Hofmeister & Campbell 1992). The spectra of intermediate compositions are noisy in the range between 450 and 550 cm^{-1} because both the sample and the type-I diamonds used absorb strongly there. Peaks in this region were resolved through Fourier self-deconvolution (Fig. 2).

Mid-IR spectra of the intermediate compositions are dominated by two-mode behavior of the three highest-frequency stretching modes [the solid solutions have both sets of end-member frequencies, with intensities (Fig. 1b) in proportion to composition]. This phenomenon is associated with large differences in mass or force constant and a large variation in frequency between the end members (*e.g.*, Chang & Mitra 1968; see also Hofmeister & Chopelas 1991a). Structural alterations are unnessary for occurrence of these "local modes". Thus, our data support the results of Yoder & Keith (1951), which are consistent with cubic symmetry.

For the compositions 55.3% and 35.6% YAG, the lower two ν_3 peaks associated with Al^{3+}–O^{2-} stretching are poorly resolved in the raw spectra (possibly because of simultaneous presence of overtones in this region in that the mid-IR spectra of spessartine contain overtones

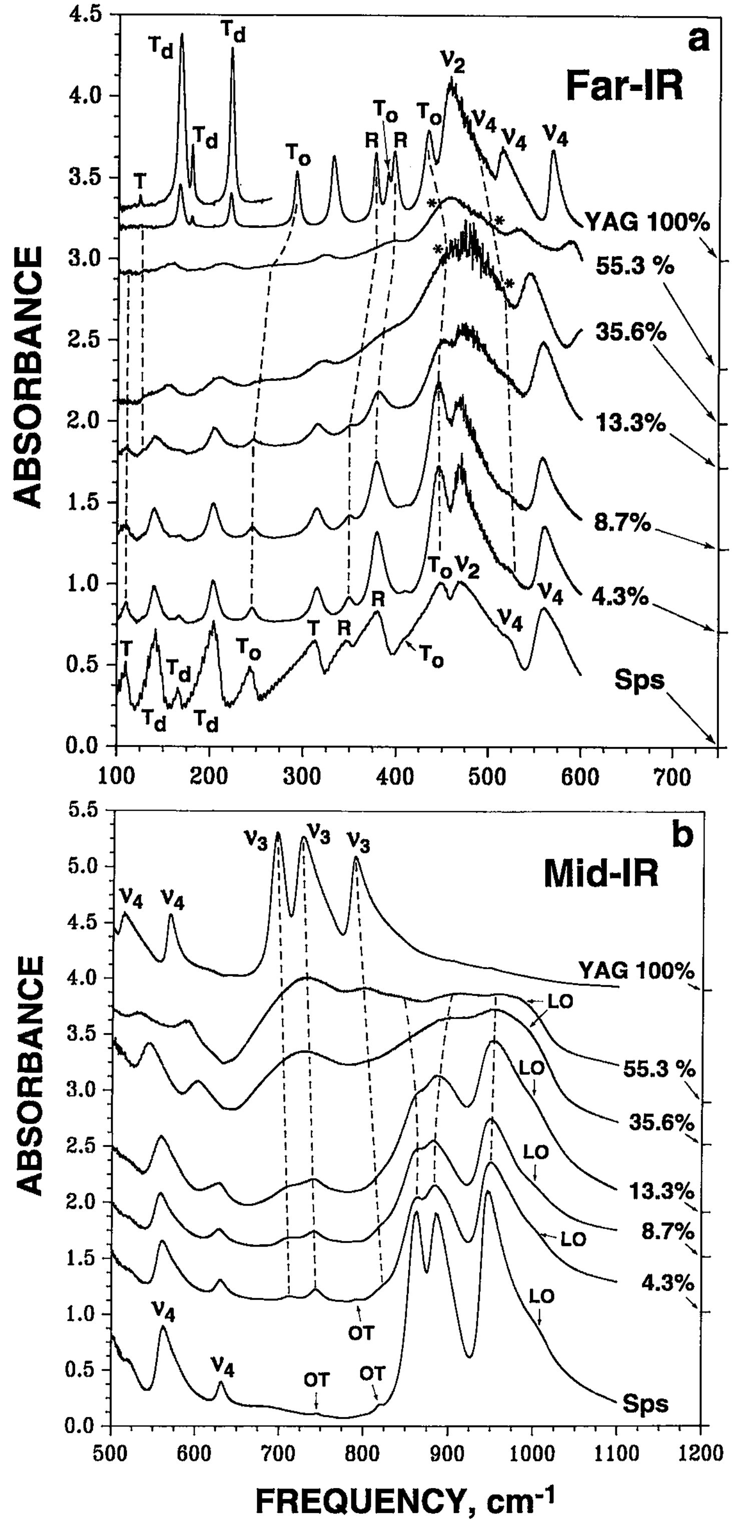

FIG. 1. Thin-film IR absorption spectra of compositions along the binary join $Y_3Al_2Al_3O_{12}$ – $Mn_3Al_2Si_3O_{12}$. The far-IR spectrum of spessartine was taken from a powder dispersion. Spectra are offset for clarity. "Zero" absorbance for each spectrum is indicated on the right. Light dashed lines connect the peaks across the series. (a) Far-IR results. The partial spectrum at the top was taken from a thick film of YAG in order to show the 122 cm^{-1} peak. The noise near 500 cm^{-1} is due to the combined high absorbance of the samples and of the type-I diamonds used for this set of measurements. (b) Mid-IR results. Stars on the peaks for 55.3 and 35.6% YAG indicate peaks resolved by Fourier deconvolution (see text). Overtones or LO components are as indicated (*e.g.*, weak peaks at 750, 818 and 1020 cm^{-1}).

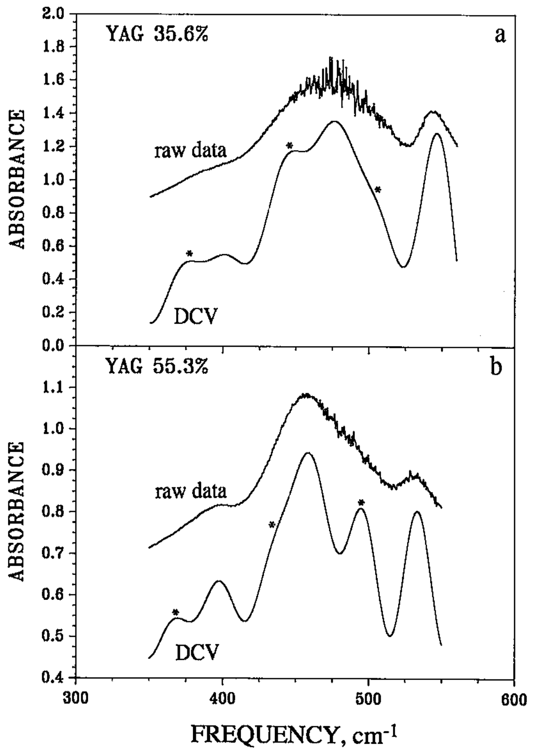

FIG. 2. Examples of Fourier deconvolution. The window for the analysis was roughly centered on the 450 cm^{-1} peak. H of 30 cm^{-1} is the full width at half height. DN of 1.8 is the peak-narrowing factor. A Lorentzian shape was assumed. The peaks revealed through deconvolution marked by the stars correspond to shoulders in the raw data. This procedure does not involve peak fitting; hence, components are not shown. (a) 35 mole % YAG. Raw data, unaltered absorption spectrum. DCV, deconvoluted results. (b) 55 mole % YAG. Raw data, absorption spectrum. DCV, deconvoluted results.

at ~750 cm^{-1} and ~ 818 cm^{-1}). The Fourier deconvolution routine could not separate these peaks because the large breadth of this region exceeded the 200 cm^{-1} window. Peak positions of the overlapping bands were approximately located at the shoulder near 700 cm^{-1}.

Shoulders near 1020 cm^{-1} represent the LO component of the highest frequency peak and are not included in the analysis.

Correlation of the twelve intense peaks along the binary is obvious (Table 1). Four of the weak peaks could also be easily traced across the series (overall, the spectra change in a minor fashion, although not all spectra had every one of these weak bands). An interesting case is the lowest-frequency peak at 108 cm^{-1} in spessartine. It is clearly traceable from 0 to 35 mole % YAG, but lacking at higher YAG contents (Fig. 1a). By default, this band must correspond to the weak, lowest-lying band in YAG at 122 cm^{-1}, which was traceable to 13 mole % YAG, despite its very low intensity (see the inset in Fig. 1a). Note also that the ν_4 peak present in spessartine at 522 cm^{-1} decreases toward 480 cm^{-1} in YAG, in support of previous indications that a weak peak is hidden in this region (Hurrell *et al.* 1968, McDevitt 1969, Hofmeister & Campbell 1992).

DISCUSSION

Band assignments

The results (Table 1) support previous band-assignments inferred from other types of chemical substitution (Hofmeister & Chopelas 1991a, Hofmeister & Campbell 1992), in that each peak with a given assignment in spessartine was found to correlate with a peak with the same particular atomic motion in YAG. Previous assignments were derived through inspection of various chemical substitutions and limited data on solid solutions (see section on previous IR studies).

The three high-frequency peaks (Table 1: 15–17) are associated with asymmetrical stretching of the tetrahedra, as suggested by factor-group analysis and spectra of solutions. The four next-highest-frequency peaks (11–14) are assigned to bending motions of the tetrahedra, such that the lowest frequency and most intense peak of the set, #11, is ν_2. The middle-frequency region contains two intense bands that are assigned to the two rotations. The low-frequency regions contains two intense bands that constitute two of the dodecahedral translations. The remaining translations (T_{dod}, $2T$, and $3T_{oct}$) are associated with weak bands whose positions depend on composition. For T_{oct} or T_{dod}, the primary factor is the mass of the cations, whereas for T, the primary factor is the size of the dodecahedron sharing edges with the tetrahedron (see Hofmeister & Chopelas 1991a, Hofmeister and Campbell 1992).

Some amount of coupling of the IR modes is expected, particularly of the translations, because these are, in general, described as the translation of one unit relative to another, *e.g.*, Y^+ relative to a fixed lattice of AlO_4 and AlO_6 polyhedra, and *vice versa*. For this series, however, extensive mixing of modes is contraindicated by the correlations of the IR bands. The relationships of

TABLE 1. THIN-FILM INFRARED VIBRATIONAL FREQUENCIES FOR THE YAG-SPESSARTINE BINARY

	YAG Content	100%	100%	55.30%	55.30%	35.60%	35.60%	13.30%	8.73%	4.30%	0%	0%
Peak	Assignments	Crystal TO§		Raw data	Deconv.*	Raw data	Deconv.*				**	Crystal TO†
1	T (YAG)	121.7	122.6	128		129±1		126.9	126			
1	T (Sps)			~111		~110		108.4	108.4	108.4	108	111.2
2	T_{dod}	164.2	164.8	157.4		152.9		139.2	139.2	139.2	141.4	140.5
3	T_{dod}	177.9	178.5					166.5	166.5	166.5	165.5	167
4	T_{dod}	219.6	221.3	213.1		209.3		204.2	202.4	202.9	204	203
5	T_{oct}	288.8	291.3	270		257.1		245.2	245.2	245.2	242.6	246
6	T	328.5	330.6	321.5		318.7		313.5	313.5	313.5	313.7	316
7	R	374.3	375.1		367			351.2	349.4	349.4	348	350.5
8	R	395.1	395.6	397¶	397¶	387	387	380.2	378.5	378.5	379.7	379.8
9	T_{oct}	388.3	388.8	397¶	397¶		401		409.3	409.3	410	412
10	T_{oct}	430.6	433.2		435		449	450.3	445.2	445.2	449.1	445
11	ν_2	451	457.1	456.3	458	472.5	476	472.5	467.4	467.4	469.7	461.5
12	ν_4	480#	480#		494		506	518.7	518.7	518.7	522	520
13	ν_4	509.7	513.5	531	533	542.6	546	558	558	559.7	560.6	558
14	ν_4	565	568.3	588.2		600.7		626.4	626.4	629.8	630.9	630
15	ν_3 (YAG component)	690.3	693	697		~700		710.1	710.1	711.8	-	-
15	ν_3 (Sps component)	-		845		~845		862.3	863.9	862.3	862.4	861
16	ν_3 (YAG component)	720.8	725.5	730		727		739.2	740.9	742.6	-	-
16	ν_3 (Sps component)	-		909		896		884.5	881.1	882.8	885.9	884
17	ν_3 (YAG component)	784.9	788.8	799.2		807		~817	~819	~823	-	-
17	ν_3 (Sps component)	-		958.9		952.9		952.9	949.4	949.4	946.4	946

§ Hofmeister & Campbell (1992)
# Hurrell et al. (1968)
* From spectral deconvolution
† Hofmeister & Chopelas (1991a)
~ Indicates shoulders
¶ A doublet occurs because two modes cross at this point on the binary
** Far IR data below 522 cm^{-1} from powder dispersion, mid IR data above 522 cm^{-1} from thin film absorption

frequency with composition or cell parameter, discussed in detail below, show that mode-mixing does occur for two bands: the lowest-lying T and T_{oct}. It is possible that a small amount of mode-mixing occurs between similarly behaving bands such as R, T_{oct}, and ν_2, but changes occurring in the binary system examined here are not an adequate test of this hypothesis. Overall, coupling seems to be weak in spessartine and YAG, and probably is weak for garnet compositions in general.

Structural and compositional trends of thin-film IR modes

Peak positions at middle frequency (~390–650 cm^{-1}) for the $Mn_3Al_2Si_3O_{12}$–$Y_3Al_2Al_3O_{12}$ series decrease as the YAG content of the garnet increases, whereas frequencies from 130 to ~390 cm^{-1} tend to increase, and those above 650 cm^{-1} (and below 130 cm^{-1}) are constant because of two-mode behavior (Figs. 1, 3, Table 1). The cell parameter is one important factor, because these trends approach linearity (Fig. 3). Trends with cell volume are similar (not shown). The direct influence of the unit-cell dimension on frequency is due to the linkage in the garnet structure (Hofmeister & Chopelas 1991a); specifically, the octahedra and tetrahedra form a network, with their bond lengths being affected by the dodecahedra through edge-sharing (Novak & Gibbs 1971). Data on bond lengths for this particular binary join are not available, so that more specific structural relationships cannot be explored.

Most of the trends in Figure 3 are quite flat near the spessartine end-member and then change linearly from 13 to 100 mole % YAG. The sharp bend near 13 % YAG is an artifact of the limited number of compositions tested: a finer-spaced interval is expected to yield smooth trends of frequency with structural parameters. Also, it is possible that a complementary flat trend exists at high YAG contents (such compositions were not available), and that the true trends are s-shaped, as were seen for other binary joins with finely spaced compositional intervals (Hofmeister, Moret, Burns and Hawthorne, in preparation). Two different slopes of frequency *versus* cell parameter are required by the accuracy of the peak positions. We suggest that this difference in slope is related to the fact that frequency depends on a large number of factors such as mass, charge, bond strength, bond length, and compressibility (*e.g.*, Hofmeister & Chopelas 1991a; also see the discussion below) and that all of these factors are compositionally dependent. It may also be possible that near the ends of the binary join, the second component behaves as an "impurity", that is, its local modes are present, but not easily detectable, because of both low intensity and overlap with the bands of the high-concentration end member. This hypothesis is supported by the

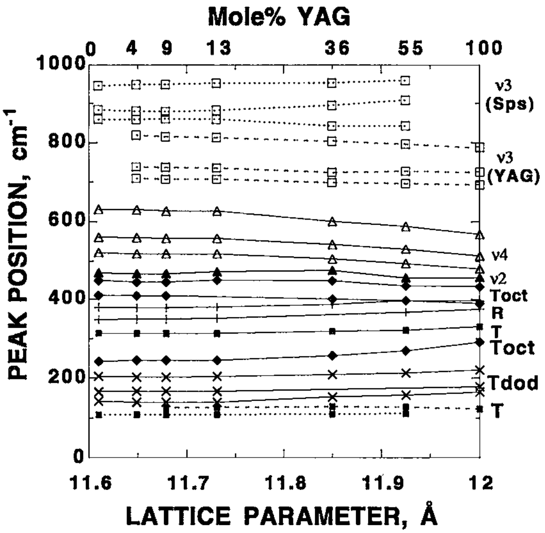

FIG. 3. Frequency obtained from thin films as a function of cell parameter a. Structural parameters were estimated from d_{642} measurements of Yoder & Keith (1951) and from end-member values for a (Euler & Bruce 1965, Novak & Gibbs 1971). For the isometric system, all interplanar spacings are proportional to a. YAG contents are indicated above. For peaks with two-mode behavior, the trends do not extend fully across the compositional axis. Open square, ν_3; open triangle, ν_4; filled triangle ν_2; cross, R; small filled diamond, $T_{\rm oct}$; filled square, translations of the tetrahedron; , $T_{\rm dod}$. Positions from the deconvolutions are used for 55.3 and 35.6% YAG, for which raw data gave imprecise values (Table 1).

linear behavior of all bands that are both well resolved and that clearly exhibit two-mode behavior, as well as by the increase in band width with impurity content (compare 13% YAG with 4.3% YAG in Fig. 1a).

The various behaviors of the IR bands across the binary system are obviously connected with differences in the atomic motions (Figs. 1, 3). As discussed in detail below, the relationships can be used to infer relative force-constants, and all except one octahedral translation behave in a manner that is consistent with band assignments of Table 1, which were derived independently. The exception is inferred to result from mode-mixing.

The frequencies ν of all three bands assigned to dodecahedral translations $T_{\rm dod}$ increase slightly with YAG content or cell parameter. The increase in ν with YAG content at first glance appears contradictory, because

$$\nu^2 = k/\mu, \tag{2}$$

where μ is a reduced mass, and the atomic mass of yttrium, 88.91 amu (atomic mass units), is significantly larger than that of manganese, with 54.94 amu. Obviously, the force constant k changes across the series. Batsanov & Derbeneva (1969) suggested the following relationship:

$$k = b(X_+X_-/r^2)^{3/4} + c, \tag{3}$$

where b and c are constants, and X is the electronegativity (for covalent bonds) or charge (for ionic bonds) of each of the two ions. In the original derivation, r is bond length (Batsanov & Derbeneva 1969); however, for the ν_3 stretching motion in silicates, the cell parameter is the determining factor because of the constraints imposed on expansion of the tetrahedral Si–O bond by the surrounding dodecahedra and octahedra (Hofmeister & Chopelas 1991a). For the case of spessartine-YAG, bond lengths of the dodecahedron should not affect the force constant because the difference between the end members is small: $d_{\rm Mn–O}$ is 2.33 Å (Novak & Gibbs 1971), whereas $d_{\rm Y–O}$ is 2.36 Å (Euler & Bruce 1965), and because the intermediate compositions are expected to lie proportionately between these values, as d_{642} (the spacing of the 642 planes) depends almost linearly on composition (Yoder & Keith 1951). The cell parameter cannot be the important factor because the change from 11.612 Å for spessartine to 12.000 Å for YAG would serve to decrease the frequency with YAG content, not increase it. Instead, it is the difference in charge and mass that accounts for the frequency change. If c in eq. (3) is assumed to be zero, b is assumed to be equal in YAG and spessartine, and the cation is assumed to vibrate against the anions, then the expected ratio of YAG to spesssartine frequency is 1.11, which compares well with the observed ratios of 1.17, 1.07, and 1.08 (Table 1).

The two-mode behavior for the stretching motion of the tetrahedra ν_3 indicates a significant difference in k values, because the change in mass from 28.04 amu for Si to 26.98 amu for Al is quite small. Calculation of the expected ratio of ν_3 for YAG *versus* ν_3 for spessartine as above, but including the effect of cell parameter, gives 0.88 if the electronegativities of 1.8 for Si and 1.5 for Al (Little & Jones 1960) are used, but 0.77 if ionic charges are used. The average ratio of 0.82, as appropriate for the 50% covalent – 50% ionic bonding of Si–O, is close to the frequency ratio of 0.81 observed for all three bands.

The slight decrease in bending frequencies ν_4 and ν_2 can be attributed to lengthening of the bonds across the binary join. A change in force constant due to differences in bonding is not expected, because the bending motion primarily involves O–O repulsion. Whether the bond length of the octahedron or the cell parameter influences the vibrations cannot be ascertained because the relative changes are very similar: Al–O is 1.937 Å in YAG but 1.902 Å in spessartine (Euler & Bruce 1965, Novak & Gibbs 1971). The calculated ratio of frequencies in YAG *versus* spessartine, 0.98, is similar to the observed ratios of 0.98, 0.98, 0.95, and 0.90 for ν_2 and the three ν_4 peaks, respectively.

The two high-frequency translations of the octahedra show slight decreases in frequency similar to those of the bending motions, as expected, because this site is essentially unchanged by the substitution. The only factor likely to affect T_{oct} is changing bond lengths. The calculated ratio of frequencies in YAG *versus* spessartine for T_{oct}, 0.98, is slightly larger than the observed ratios of 0.942 and 0.968. The remaining low-lying translation of the octahedra increases in frequency. This contrasting behavior suggests that this mode (#5) is mixed with translations of the dodecahedra and of the tetrahedra, as suggested by normal mode analysis and by the proximity of the frequencies.

The rotations and one translation of the tetrahedra increase slightly in frequency. This behavior is expected because the bonding of the cation in the dodecahedral site with the anions forming the tetrahedra will increase in strength with the concentration of the trivalent cation, as discussed above, but bonding involving the cation in the octahedral site will be unchanged. The average of the calculated ratio for YAG *versus* spessartine frequencies of rotation, 1.14 (for dodecahedral influence) and 1.00 (for octahedral constancy), is similar to observed ratios of 1.04 and 1.08 for *R* and ratios of 1.04 for *T*.

The lowest-lying band shows classical two-mode behavior, with constant end-member frequencies. The observed two-mode behavior supports strong coupling with T_{dod}, as suggested previously (*e.g.*, Slack *et al.* 1969), in that the ratio of frequencies of the local modes, 1.10, is close to 1.14 calculated as above from equations 2 and 3 by comparing charge and mass of the pair SiO_4 *versus* Mn^{2+} to those of the pair AlO_4 *versus* Y^{3+}. Two-mode behavior also is observed because the lowest-frequency peak is sufficiently weak and narrow that the end-member frequencies do not overlap.

EFFECT OF SUBSTITUTIONS IN THE TETRAHEDRON ON THERMODYNAMIC PROPERTIES

The site occupied by the "impurity" ion will strongly affect the thermodynamic properties. The ions Ti, Al, and Fe are found both in the tetrahedra and octahedra, as summarized by Meagher (1980). Substitution in the octahedra will move these bands proportionately to a lower frequency because the strong dependence of T_{oct} on mass, and will thus increase the density of states at low temperature, yielding a larger heat capacity C_V in this region (Kieffer 1979). The effect will be propagated in the entropy S at higher temperatures because S is related to C_V through an integral.

For a garnet with minor substitution in the tetrahedron, as occurs in eclogites (*e.g.*, Bishop *et al.* 1976, 1978), the main change in the density of states used to calculate heat capacity C_V and entropy S from vibrational spectra (Kieffer 1979) will originate in the two-mode behavior of the stretching bands of the tetrahedron. For Al^{3+}, two-mode behavior is demonstrated to occur, owing to decreased charge. The P^{5+} ion is expected to behave analogously. For Ti^{4+}, doubling of the mass will probably produce the same response. For Fe^{3+}, two-mode behavior for ν_3 is unavoidable, owing to differences in both charge and mass. Frequencies of the other bands are not expected to change appreciably. Given an estimated drop in frequency of ν_3 from about 900 to 750 cm^{-1}, as occurred between spessartine and YAG, the heat capacity will increase over that of the host near 700 to 800 K by roughly the mole % of the substitution times C_V at that temperature. The heat capacity will decrease by the same amount from about 900 to 1000 K. Hence, the change in C_V and S for small substitutions (<4 mole %, which is as observed for high-pressure garnet) is expected to be small.

CONCLUSIONS

Thin-film IR absorption measurements of spessartine and YAG provide satisfactory spectral results given the excellent agreement with the data on single-crystal reflectance. This approach avoids the many difficulties encountered with the powder-dispersion technique, particularly the incorrect relative intensities of the peaks because of sampling of various thicknesses of particles and the incorrect positions of peaks because of presence of surface modes and longitudinal optic components originating through scattering.

Compositional relationships of all 17 IR bands in five garnet compositions along the spessartine–YAG binary were determined. Only a few of the weakest bands could not be traced completely across the series. The smooth, continuous changes corroborate the conclusions of Yoder & Keith (1951), that the *Ia*3*d* symmetry is maintained, and that the changes in structural parameters from spessartine to YAG are monotonic with composition. The trends also support the conclusion of Hurrell *et al.* (1968) that a weak peak is present in YAG at 480 cm^{-1}. The almost negligible changes in frequency from 0 to 13% YAG and the linear change from 13 to 100% YAG suggest that minor substitutions do not measurably affect bonding in the garnet, and that the minor impurities may be acting as local modes, even for bands that follow one-mode behavior (analogous to Vegard's law).

The variation in behavior of the peak positions across the binary is in agreement with assignments of the bands to different types of atomic motion. The presence of both one-mode and two-mode behaviors is consistent with previous, independently derived assignments of bands and consideration of the changes in bonding and mass incurred by Y^{3+} and Al^{3+} replacing Mn^{2+} and Si^{4+}. The change in relative frequency is consistent with calculations of force constant from the formulation of Batsanov & Derbeneva (1969), if cell parameter is used in place of bond length, if bonding within the tetrahedron is taken to be 50% ionic and 50% covalent, and if the octahedral and dodecahedral bonds are assumed to be ionic. The present analysis indicates that edge-sharing in the garnet structure strongly affects its vibrational character. Mode-mixing in spessartine–YAG is indicated only for the lowest-frequency translation of the cation in the octahedral site and the lowest-frequency translation of the tetrahedron, each of which is mixed with the translations of the cation in the dodecahedral site. Coupling of modes in other garnets is suggested also to be weak.

The substitution of Al^{3+} for Si^{4+} in the tetrahedra does not change the frequency of the bands; instead, new bands appear associated with the "impurity" ion, with an intensity proportional to concentration, and the intensity of matrix bands is diminished accordingly. This two-mode behavior results from differences in bond strength between Al^{3+} and Si^{4+}, rather than from differences in mass, as has generally been found to be the case (Chang & Mitra 1968, Hofmeister & Chopelas 1991a). This substitution will affect thermodynamic properties such as C_V and S at high temperatures, above about 800 K, and can be neglected for minor amounts of impurities in the tetrahedral site (*i.e.*, totals of a few %).

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