Infrared Spectrum and Structural Role of Titanium in Synthetic Ti-Garnets

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Abstract. Ti-spessartite, Ti-andradite and its indium homolog, $Ca_3In_2(Si, Ti)_3O_{12}$, have been synthesized and investigated by *infrared* (ir) spectroscopy. The use of isotopic species (^{46}Ti-^{50}Ti) gives the unequivocal proof that some of the additional bands observed in the 800-600 cm^{-1} region are due to TiO_4 tetrahedra. For Si-Ti replacements up to 10 mol%, the localization of Ti on the available tetrahedral sites depends on the nature of the cations. For the In garnet all (or nearly all) Ti is located on tetrahedral sites; in Ti-andradite Ti is distributed over tetrahedral and octahedral sites, tetrahedral sites being thus occupied, in part by Ti (ir band near 700 cm^{-1}) and in part by Fe (ir band near 650 cm^{-1}); in Ti-spessartite the presence of Ti on tetrahedral sites is doubtful, these sites being essentially occupied by Al.

Introduction

Quite a lot of work has been devoted to the crystal chemistry of titanium-bearing andradites $Ca_3Fe_2(Si,Ti)_3O_{12}$, a classical point of concern being the coordination, tetrahedral or octahedral, of titanium.

Previous studies of the infrared spectrum of natural Ti-andradites led one of the present authors to the conclusion that titanium was most probably distributed over tetrahedral and octahedral sites (Tarte, 1965). The experimental data presented at this time were confirmed, but their interpretation was criticized in subsequent papers (Howie and Woolley, 1968; Moore and White, 1971; Dowty, 1971). Indeed, there was no unequivocal proof that some of the observed bands must be assigned to TiO_4 groups; but it should be pointed out that there was also no proof against this assignment.

Such assignment problems may be solved by the study of isotopic species (Tarte and Preudhomme, 1970), and we have accordingly investigated the ir spectrum of synthetic Ti-andradites containing isotopes (either ^{46}Ti or ^{50}Ti) of titanium. The results definitely confirm the conclusions drawn in the 1965 paper.

Table 1. Synthesis conditions

Garnet composition	Starting mixture	Thermal treatment
$Ca_3In_2(Si_{1-x}Ti_x)_3O_{12}$ $x=0,0.02,0.05,0.10$	oxides and $CaCO_3$ $(+ CaCl_2)$	hydrothermal: 550° C, 500 bars, 5 days, followed by dry heating 1000–1050° C, 2 days. Also by solid state reaction at 1170° C
$Ca_3Fe_2(Si_{1-x}Ti_x)_3O_{12}$ $x=0,0.01,0.02,0.05$	oxides and $CaCO_3$ $(+NaCl)$ or glass	hydrothermal: 600° C, 1000 bars, 3 days, followed by dry heating 1050–1100° C, 2 days
$Ca_3Fe_2(Si_{0.98}Ge_{0.02})_3O_{12}$	oxides and $CaCO_3$ $(+NaCl)$	hydrothermal: 600° C, 1000 bars, 3 days
$Ca_3Fe_2(Si_{1-x}Zr_x)_3O_{12}$ $x=0.01,0.02,0.05,0.10$	oxides and $CaCO_3$ $(+CaCl_2)$	hydrothermal: 550° C; 500 bars, 5 days, followed by dry heating 1000–1050° C, 2 days
$Mn_3Al_2(Si_{1-x}Ti_x)_3O_{12}$	oxides	solid state reaction; 1000° C under nitrogen

Experimental

The garnets have been synthesized by well-known procedures (Mill, 1968, 1969) (synthesis conditions in Table 1). Their purity and crystallinity have been checked by X-ray diffraction-technique (monochromatized Co K α radiation). Values of the unit cell parameter a_o have been deduced from the position of high angle peaks. No microprobe analysis was done, and the given garnet compositions are those of the starting mixtures. It should be pointed out that, for orthosilicates at least, the ir spectrum is rather sensitive to the presence of free silica or polysilicates, and thus is by itself a good test of purity (Tarte, 1965). Infrared spectra were obtained by the conventional KBr disc technique, with a Beckman IR 12 spectrophotometer.

Results and Assignments

Indium Garnets $Ca_3In_2(Si_{1-x}Ti_x)_3O_{12}$

We shall first consider the results for the indium garnets, for which the interpretation is reasonably straightforward.

The pure garnet $Ca_3In_2Si_3O_{12}$ gives a typical orthosilicate spectrum, characterized by a transparency window in the $750-600$ cm^{-1} region. On the contrary, samples with the overall composition $Ca_3In_2(Si_{1-x}Ti_x)_3O_{12}$ $(0.01 \leqq x \leqq 0.10)$ exhibit, near 700 cm^{-1}, a supplementary absorption which appears as a partially resolved doublet. The origin of this doublet may be deduced from the following experimental facts: (i) The intensity of these bands increases with increasing titanium content. (ii) The investigation of isotopic compounds with [46]Ti and [50]Ti leads, for these bands, to significant isotopic frequency shifts (Table 2 and Fig. 1), whereas the frequencies of the other bands remain unaffected. This brings the unequivocal proof that the new bands are due to Ti-O vibrations.

Table 2. Supplementary bands observed between 600 and 750 cm^{-1} for $Ca_3In_2(Si_{1-x}Ti_x)_3O_{12}$ compounds

$x=$	Ti^b		^{46}Ti		^{50}Ti		Isotopic shift
	$v(cm^{-1})$	shape[a]	$v(cm^{-1})$	shape[a]	$v(cm^{-1})$	shape[a]	$\Delta v(cm^{-1})$
0.02	710	d	~ 715	d	~ 707	d	8
	699	s	702	s	696	s	6
0.05	708	d					
	698	s					
0.1	710	d	714	sh, d	707	sh	7
	698	s	702	s	695	s	7

[a]   d: diffuse; s: sharp; sh: shoulder
[b]   Natural composition
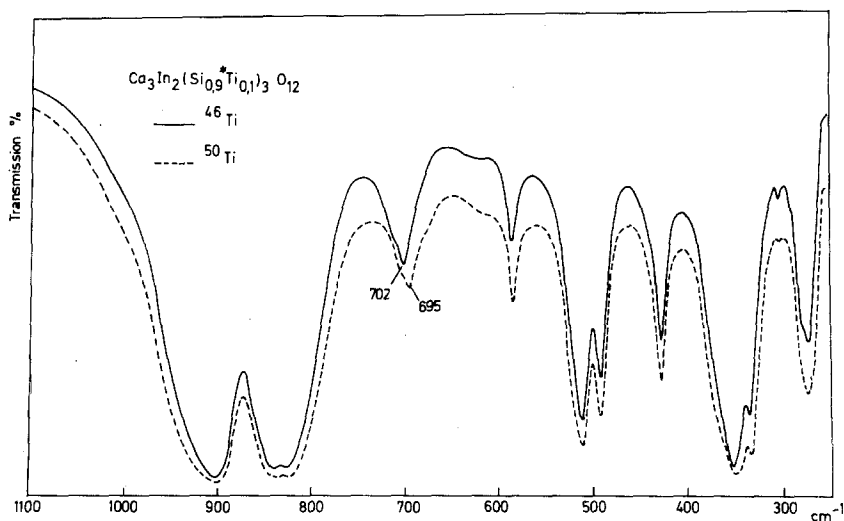
Fig. 1. Typical infrared spectra of synthetic titanium indium garnets

(iii) The formation of a solid solution is proved by the increase of the unit cell parameter a_o with increasing Ti content: $a_o=12.360$; 12.369; 12.382 and 12.410 Å for $x=0$; 0.02; 0.05 and 0.10 respectively (these values are related to samples obtained by solid state reaction at 1170° C. Small discrepancies are observed for hydrothermal samples). (iv) According to previous results on the ir spectra of garnet solid solutions (Tarte, 1965), the shape of the 700 cm^{-1} absorption suggests that it is due to a cation present in solid solution. (v) The frequencies of the new bands (700–710 cm^{-1}) are in full agreement with the frequency range already observed for TiO_4 tetrahedra (750−650 cm^{-1}), either in a pure compound such as Ba_2TiO_4, or in M_2^{II} (Si,Ti)O_4 solid solutions where titanium replaces silicon (Tarte, 1961, 1965). Absorption bands related
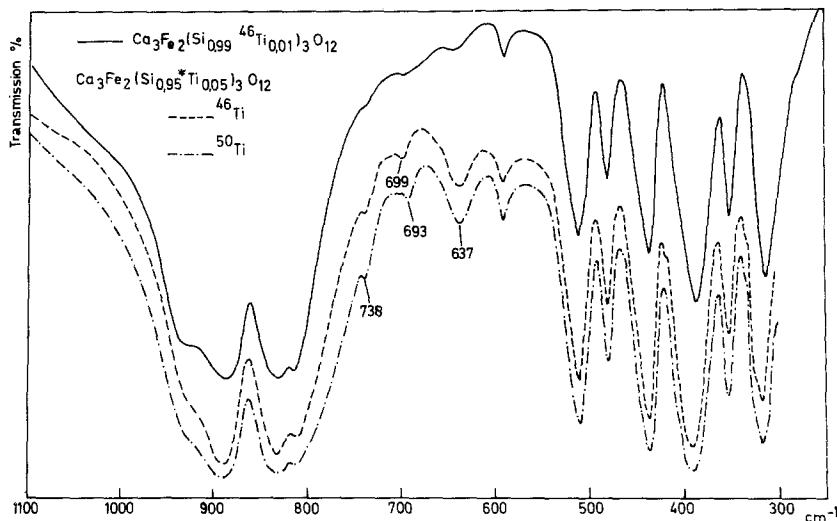
Fig. 2. Typical infrared spectra of synthetic titanium andradites

to TiO_6 octahedra in the garnet structure should be located near or below 500 cm^{-1} (this point will be discussed further on). The sum of these facts brings the definite proof that TiO_4 tetrahedra are able to replace SiO_4, at least in the garnet structure under consideration.

Titanium Andradites $Ca_3Fe_2(Si_{1-x}Ti_x)_3O_{12}$

The discussion of these compositions will be restricted to small Ti contents ($x \leq 0.05$); the case of Ti-rich andradites ($x \geq 0.10$) will be discussed in a forthcoming paper.

It is immediately evident (Fig. 2 and Table 3) that the situation is more complicated than in the case of In garnets, since 3 new bands are related to the introduction of Ti in the structure: 636, 695 and 738 cm^{-1}. Out of these, one band only (695 cm^{-1}) exhibits a frequency and a Ti isotopic shift which are similar to those already noticed for the doublet observed in the spectrum of indium garnets. This band is thus assigned to stretching vibrations of TiO_4 tetrahedra[1]. The broad band near 636 cm^{-1} had already been assigned to vibrations of FeO_4 tetrahedra (Tarte, 1965; Dowty, 1971), in accordance with the fact that FeO_4 tetrahedra give absorption bands in the $650-550 \text{ cm}^{-1}$ region (Tarte, 1965, p. 163). This assignment is fully supported by the lack of any ^{46}Ti-^{50}Ti isotopic shift, and by the fact that a similar band is present in Zr-andradite, but is very weak in Ge-andradite (see below). The existence

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[1]   In fact, this band is asymmetric and probably a doublet; but the high-frequency constituent of this doublet is too weak and too broad to be measured with precision; thus only the low frequency constituent is discussed here

Table 3. Supplementary bands observed between 600 and 750 cm^{-1} for $Ca_3Fe_2(Si_{1-x}Ti_x)_3O_{12}$ compounds

$x =$	Ti[b]		^{46}Ti		^{50}Ti		Isotopic shift
	ν(cm^{-1})	shape[a]	ν(cm^{-1})	shape[a]	ν(cm^{-1})	shape[a]	$\Delta\nu$(cm^{-1})
0.01	738	d	738	sh	738	sh	
	697	sh	~700	sh	~697	sh	
	636	d	635	d	636	d	
0.02	737	s	738	s	738	s	
	{ ~708	sh, d					
	{ 695	s	699	d	692	d	7
	635	d	636	d	636	d	
0.05	737	s	738	s	738		
			{ ~711	sh, d	{ ~702	sh, d	
	695	s	{ 699	s	{ 693	s	6
	637	d	637	d	637	d	

[a] d: diffuse; s: sharp; sh: shoulder
[b] Natural composition

of FeO$_4$ tetrahedra implies that some Ti is located on octahedral sites and thus we reach the conclusion that, in Ti-andradite, the titanium is distributed over tetrahedral and octahedral sites.

The assignment of the 738 cm^{-1} band is a matter of difficulty. This band has been observed in natural Ti-andradites with a low Ti content, where it has been tentatively assigned, either to TiO$_4$ tetrahedra (Tarte, 1965) or to AlO$_4$ or FeO$_4$ tetrahedra (Dowty, 1971; Moore and White, 1971). It must be pointed out that this band is also present in our synthetic samples (which are free from aluminum); thus, in the present case, its assignment to AlO$_4$ tetrahedra is definitely ruled out. On the other hand, since this band is missing in Zr-andradite, the structure of which contains FeO$_4$ tetrahedra (see below), its assignment to FeO$_4$ tetrahedra should also be rejected.

We are therefore left with the assignment to TiO$_4$ tetrahedra, which in turn can be hardly reconciled with the lack of ^{46}Ti-^{50}Ti isotopic shift (Table 3). This latter point, however, cannot be considered as a definite argument against the assignment to TiO$_4$ tetrahedra. The isotopic shifts observed on the 700 cm^{-1} band correspond to an antisymmetric stretch of the TiO$_4$ tetrahedron; but during the corresponding symmetric stretch, the Ti atom is at rest, and no mass effect can be observed. Now, this symmetric vibration is ir-forbidden in a pure garnet. But since selection rules (as deduced from group theory) do not strictly apply to disordered systems such as solid solutions, the assignment to a symmetric TiO$_4$ stretch cannot definitely be ruled out.

Whatever the final assignment of this band, it has no influence on the previous conclusion that, in Ti-andradites with low Ti content, titanium is distributed over tetrahedral and octahedral sites.

Zr-Andradites $Ca_3Fe_2(Si_{1-x}Zr_x)_3O_{12}$

Zr is too large to enter the tetrahedral sites of a silicate garnet. Thus, in Zr-andradite $Ca_3Fe_2(Si_{1-x}Zr_x)_3O_{12}$, Zr is located on the octahedral sites, from which a corresponding fraction of Fe^{3+} cations must be displaced onto the tetrahedral sites: the additional bands in the ir spectrum ($v > 600$ cm^{-1}) are necessarily those of FeO$_4$ tetrahedra. One additional band only is observed near 635 cm^{-1} in the spectrum of these garnets; its relative intensity increases with increasing Zr content, and its assignment to FeO$_4$ tetrahedra is straightforward. No additional band is observed in the 700 cm^{-1} region.

Ge-Andradites $Ca_3Fe_2(Si_{1-x}Ge_x)_3O_{12}$

It has been shown that, whenever Si-Ge or Si-Ti isomorphic replacement is possible in an orthosilicate, the frequencies and shapes of the bands related to GeO$_4$ or TiO$_4$ tetrahedra are nearly the same for a given silicate host lattice (Tarte, 1965, chapter XI). Thus, a comparison of the spectra of Ca_3Fe_2-$(Si_{1-x}Ge_x)_3O_{12}$ and $Ca_3Fe_2(Si_{1-x}Ti_x)_3O_{12}$ solid solutions may bring independent information about the proposed assignments.

Here again, the bands related to the antisymmetric stretching vibrations of the GeO$_4$ tetrahedra are unequivocally identified by ^{70}Ge-^{76}Ge isotopic shifts. For $x = 0.02$, they are observed at 704 (^{70}Ge) and 700 cm^{-1}(^{76}Ge) at nearly the same frequencies as the bands assigned to the TiO$_4$ group. There are, in addition, a very weak shoulder near 740 cm^{-1}, and a very weak band near 650 cm^{-1}. We may tentatively extend the assignments already proposed in the case of Ti-andradites to these bands: GeO$_4$ symmetric stretch (740 cm^{-1}) and FeO$_4$ (650 cm^{-1}). However, these bands are so weak that it is not certain that they belong to the garnet phase.

Ti-Spessartites $Mn_3Al_2(Si_{1-x}Ti_x)_3O_{12}$

Ti-spessartites have been investigated since they are easily synthesized by solid state reaction.

The matter has not been systematically investigated but, here again, some Ti is present in the structure, as evidenced by the increase of the unit cell parameter: $a_o = 11.613$, 11.628, 11.636 Å for $x = 0$, 0.02 and 0.05 (this latter phase not quite pure) respectively.

New, reproducible bands are observed in the ir spectrum at 743, and near 705 cm^{-1}, the latter being broad and very weak. The 743 cm^{-1} band is not shifted by the ^{46}Ti-^{50}Ti replacement and must therefore be assigned to AlO$_4$ tetrahedra. The same isotopic study does not give significant information about the origin of the 705 cm^{-1} band, since this band is too weak and too broad. Thus, in this case, nearly all (if not all) the titanium is located on the octahedral sites.

Discussion

Magnitude of the ^{46}Ti-^{50}Ti Isotopic Shifts

It is useful to check that the observed isotopic shifts have the order of magnitude expected for TiO_4 tetrahedra.

A rigorous mathematical treatment is impossible for several reasons (the TiO_4 tetrahedra are not really isolated; they are distorted, and their bending frequencies are unknown). But a rough approximation (Tarte, 1965, p. 186) leads to the frequency ratio $v_{46Ti}/v_{50Ti} = 1.013$), for the antisymmetric stretch of isotopic TiO_4 tetrahedra, and thus, for a band located at 700 cm^{-1}, to a frequency shift of 9 cm^{-1}. The observed values (Tables 2 and 3) are slightly but systematically smaller, but 2 points should be borne in mind. (i) The ^{46}Ti and ^{50}Ti samples are not isotopically pure; they always contain non-negligible amounts of other Ti isotopes, and the resulting average mass ratio is smaller than 50/46. (ii) The vibrations are not free from interactions with the remainder of the lattice and this should also lead to some lowering of the isotopic shift.

Assignment of the 700 cm^{-1} Band to TiO_4 Tetrahedra

Two points must be considered here: (i) the assignment of this band to Ti-O bonds, which results from ^{46}Ti-^{50}Ti isotopic shifts and is unquestionable; (ii) the assignment to TiO_4 tetrahedra, which is made by analogy with the frequency values already observed for other phases containing TiO_4 tetrahedra. This analogy cannot be considered as a definite proof and has been criticized, particularly by Howie and Woolley (1968) on the following basis.

The ir spectrum of titanite $CaTiSiO_5$ exhibits a broad absorption band of medium intensity between 667 and 700 cm^{-1}. This band must be assigned to Ti-O bonds and to TiO_6 octahedra, since Ti is octahedrally coordinated in titanite. Thus, for bands observed in this frequency region, the assignment to TiO_4 tetrahedra should be considered with caution.

Although apparently correct, this reasoning neglects 2 essential points.

(i) A comparison between the vibrational frequencies of tetrahedral or octahedral groups cannot be made without considering the structural organization of these groups. For a given cation in, say, tetrahedral coordination, the vibrational frequency range will depend on the fact that the tetrahedra are either "isolated" (no common oxygen between tetrahedra) or "condensed" (tetrahedra interlinked by common oxygen atoms), the frequencies being higher for "condensed" than for "isolated" tetrahedra. On the other hand, isolated octahedral groups give lower frequencies than isolated tetrahedral ones; but in relation to the frequency increase observed for condensed groups, the frequency range related to condensed octahedral groups may be similar to that related to isolated tetrahedral groups.

This problem has already been discussed, both from a general point of view (Tarte, 1965), and more specifically in the case of various aluminates

(Tarte, 1967). Thus, the frequency region observed in titanite for condensed TiO_6 octahedra cannot be used as a reference value for the case of garnets, where both tetrahedra and octahedra are isolated.

(ii) The correlation between coordination number and frequency range is valid only in the absence of abnormally short (or long) cation-oxygen distances. This condition is not verified for titanite which has an abnormally short (1.766 Å) Ti-O bond (Speer and Gibbs, 1976). Here again, the comparison with the garnet case is not appropriate.

Finally, the situation may be summarized as follows:

(i) Titanates whose structure contains condensed TiO_6 octahedra with normal Ti-O distances (e.g., $SrTiO_3$, Sr_2TiO_4, ...) give a strong absorption near 600 cm^{-1} (Tarte, 1961, 1965).

(ii) To the best of our knowledge, reliable data on isolated TiO_6 octahedra are missing. But by comparison with other well-investigated cases (AlO_6, GaO_6, FeO_6, ..., Tarte, 1965), it may be deduced that isolated TiO_6 octahedra should give absorption bands near or below 500 cm^{-1}.

(iii) High Ti-O frequencies (near 700 cm^{-1} or more) should be assigned, either to abnormally short Ti-O bonds in TiO_n coordinated groups or to TiO_4 tetrahedra.

In the garnet structure, the octahedral sites, although not regular, do not contain abnormally short cation-oxygen distances. Thus, the Ti-O bands observed near 700 cm^{-1} in some Ti-garnets are necessarily assigned to TiO_4 tetrahedra.

Comparison With Cation Distribution Deduced From Mössbauer Spectra

Several recent papers deal with the structural role of iron in garnets, as deduced from Mössbauer spectra (Huggins et al., 1977a and b; Amthauer et al., 1976, 1977). For pure Ti-andradites (free from other foreign cations), the Ti localization may be deduced from a knowledge of the chemical composition (amount of Si-Ti replacement) and of the Fe^{3+} distribution over tetrahedral and octahedral sites. It is found that Ti is also distributed over tetrahedral and octahedral sites, the amount of tetrahedral Ti increasing with increasing Si-Ti replacement (Huggins et al., 1977a).

For natural garnets containing significant amounts of Al, the same type of information is available, but only for the sum Al+Ti; the individual distributions remain unknown (Huggins et al., 1977b). Thus, Mössbauer studies of pure Ti-andradites lead to conclusions which are in full agreement with our ir findings: Ti must be distributed over tetrahedral and octahedral sites. In this case, the Mössbauer technique has the advantage of giving quantitative results. This is not possible with ir spectroscopy (see below).

In Al-Ti andradites however, no firm conclusion can be deduced from Mössbauer spectra, whereas the existence of TiO_4 groups may still be deduced from the presence of ir absorption bands near 700 cm^{-1}. Paradoxically enough, this band is present for low Ti amounts, but disappears in Ti-rich andradites (Tarte, 1965), despite the fact that Mössbauer data show a continuous increase of TiO_4 tetrahedra with increasing total Ti (Huggins et al., 1977a).

This phenomenon, which precludes a quantitative analysis by ir spectroscopy, is related to vibrational interactions and will be discussed in a forthcoming paper on Ti-rich andradites.

References

Amthauer, G., Annersten, H., Hafner, S.S.: The Mössbauer spectrum of ^{57}Fe in silicate garnets. Z. Krist. **143**, 14–55 (1976)

Amthauer, G., Annersten, H., Hafner, S.S.: The Mössbauer spectrum of ^{57}Fe in titanium-bearing andradites. Phys. Chem. Minerals **1**, 399–413 (1977)

Dowty, E.: Crystal chemistry of titanian and zirconian garnet: I. Review and spectral studies. Am. Mineralogist **56**, 1983–2009 (1971)

Howie, R.A., Woolley, A.R.: The role of titanium and the effect of TiO_2 on the cell-size, refractive index, and specific gravity in the andradite-melanite-schorlomite series. Mineral. Mag. **36**, 775–790 (1968)

Huggins, F.E., Virgo, D., Huckenholz, H.G.: Titanium-containing silicate garnets. I. The distribution of Al, Fe^{3+} and Ti^{4+} between octahedral and tetrahedral sites. Am. Mineralogist **62**, 475–490 (1977a)

Huggins, F.E., Virgo, D., Huckenholz, H.G.: Titanium-containing silicate garnets. II. The crystal chemistry of melanites and schorlomites. Am. Mineralogist **62**, 646–665 (1977b)

Mill, B.V.: Hydrothermal preparation of silicate and germanate garnets in alkaline medium. Russ. J. Inorg. Chem. **13**, 819–821 (1968)

Mill, B.V.: Low temperature limits for the hydrothermal synthesis of silicon and germanium garnets. Inorg. Mater. **5**, 1354–1357 (1969)

Moore, R.K., White, W.B.: Intervalence electron transfer effects in the spectra of the melanite garnets. Am. Mineralogist **56**, 826–840 (1971)

Speer, J.A., Gibbs, G.V.: The crystal structure of synthetic titanite, $CaTiOSiO_4$, and the domain textures of natural titanites. Am. Mineralogist, **61**, 238–247 (1976)

Tarte, P.: Infrared spectroscopic evidence of four-fold coordination of titanium in barium orthotitanate. Nature **191**, 1002–1003 (1961)

Tarte, P.: Etude expérimental et interprétation du spectre infrarouge des silicates et des germanates. Application à des problèmes structuraux relatifs à l'état solide. Acad. R. Belg. Classe Sci.Mém., **35**, N° 4a, 260 p., N° 4b, 134 p. (1965)

Tarte, P.: IR spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra. Spectrochim. Acta **23A**, 2127–2143 (1967)

Tarte, P., Preudhomme, J.: Use of medium-weight isotopes in infrared spectroscopy of inorganic solids: a new method of vibrational assignments. Spectrochim. Acta **26A**, 2207–2219 (1970)