

The use of infra-red absorption and molar refractivities to check coordination

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With 3 figures

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Auszug

Durch experimentelle Untersuchung der Ultrarot-Absorptionsspektren einiger SiO_2 -Isotope war es möglich, die primäre Koordination, die Atomordnungszahl, das Atomgewicht und die Ionenladung den Absorptions-Wellenlängen der größeren Banden zuzuordnen. Auch die Verwendung der Molarrefraktion zur Voraussage und Bestimmung von Änderungen der (primären und sekundären) Koordination wird erläutert.

Abstract

By an empirical study of the infra-red absorption spectra of some silica isotopes it has been possible to relate primary coordination, atomic number, atomic weight and ionic charge to absorption wave lengths for the major bands. Likewise the utilization of molar refractivity in predicting or determining coordination changes (both primary and secondary) is illustrated.

Introduction

An attempt has been made at using infra-red absorption spectra and molar refractivities to yield information on coordination of cations in simple structures. The fact that infra-red absorption spectra will distinguish phases, which are quite similar crystallographically, is already well known¹, and there is no doubt that the differences in such spectra reflect even minor changes of bond length and configuration. Of course, even in slightly complex uniaxial structures it is difficult to make an intelligent guess at assigning particular frequencies to certain vibration modes.

* Contribution No. 58-123.

¹ RUSTUM ROY and E. E. FRANCIS, On the distinction of sillimanite from mullite by infra-red techniques. *Am. Min.* 38 (1953) 725-728.

The use of infra-red

To proceed from the vibration modes is straightforward even to detect all expected largely, no doubt, to the various cases, such as quartz itself possible to group the absorption cation-anion stretching, cation-anion bending and distortion stretching occurs at the strongest absorption. In a cation-anion bond is the most significant structural change in bond-length changes. Heavily distorted at highest frequency

Moreover, in simple structures hope that certain associations of known-structure materials groups of phases for such as groups of polymorphs.

These same phases, especially value in studying changes in forms, each of which can substance is GeO_2 which exists four-coordinated quartz for

Infra-

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² RUSTUM ROY, Isomorphism Symposium on "Defect structure

Coordination and molar refractivity

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To proceed from the space group symmetry to the permitted vibration modes is straightforward enough; but so far it has been impossible even to detect all expected bands in the spectrum of most solids, due largely, no doubt, to the very broad bands encountered. However in cases, such as quartz itself, which have been studied in detail it is possible to group the absorption bands in the 2-25 μ region into cation-anion stretching, cation-cation stretching and various cation-anion bending and distorting vibrations. Of these the cation-anion stretching occurs at the highest frequencies and constitutes the strongest absorption. In a crystal chemical study of this type this cation-anion bond is the one which can and does reflect the more significant structural changes such as coordination changes resulting in bond-length changes. Hence an examination of the strong absorptions at highest frequency should be of primary interest.

Moreover, in simple structures of high symmetry there is reason to hope that certain associations will be evident when absorption spectra of known-structure materials are compared. The most satisfactory groups of phases for such a study would be groups of isomorphs and groups of polymorphs.

These same phases, especially the polymorphs of GeO_2 , are of value in studying changes in molar refractivity. Not many substances are available which exist in two reconstructively related polymorphic forms, each of which can persist to room temperature. One such substance is GeO_2 which exists in a six-coordinated rutile form and a four-coordinated quartz form.

Infra-red absorption spectra

In our early work² on coesite and GeO_2 data were reported to show clearly the ability to distinguish major coordination changes by absorption spectroscopy. The results in Figs. 1, 2, and 3 summarize the information and deductions to date. The empirical and qualitative nature of these results is emphasized although this may not detract from their usefulness.

The most significant spectra should be those of the GeO_2 polymorphs. Spectra for the polymorphic series SiO_2 quartz, SiO_2 tridymite, SiO_2 cristobalite, SiO_2 glass and SiO_2 coesite are also shown (Fig. 2). The isomorphous series BPO_4 , AlPO_4 , GaPO_4 , FePO_4 , BaAsO_4 , AlAsO_4 and

² RUSTUM ROY, Isomorphism and polymorphism of silica. Mellon Institute Symposium on "Defect structure of quartz and glassy silica", May 22, 1957.

GaAsO₄ in the quartz forms and the GaSbO₄ rutile form are shown in Fig. 3. The following generalizations are made on the basis of these and other spectra:

1. When there is a change of primary coordination of the cation it is clearly reflected in the main stretching frequency. Moreover, the

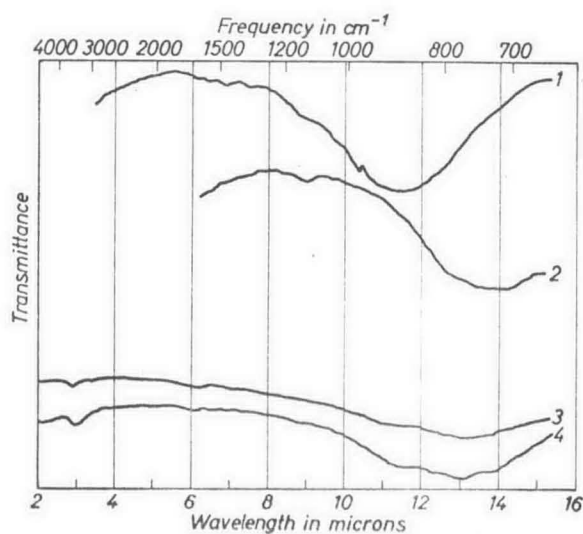


Fig. 1. Infra-red absorption spectra in the 2-15.5 micron region. 1. GeO₂ quartz; 2. GeO₂ rutile; 3. BeF₂ quartz; 4. BeF₂ coesite. (Sample preparation—KBr window, 1-1.5 mg sample in 0.3 g KBr.)

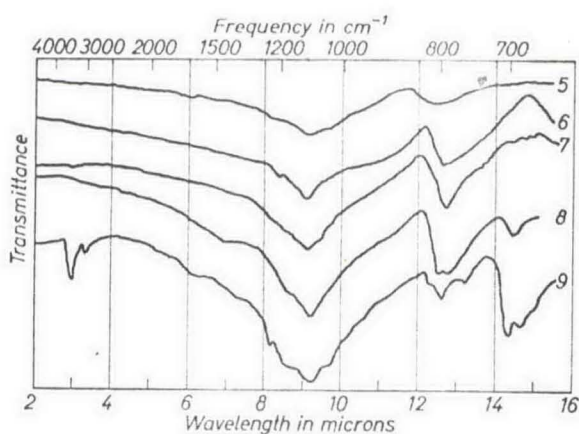


Fig. 2. Infra-red absorption spectra in the 2-15.5 micron region. 5. SiO₂ glass (vitreosil); 6. SiO₂ cristobalite; 7. SiO₂ tridymite; 8. SiO₂ quartz; 9. SiO₂ coesite.

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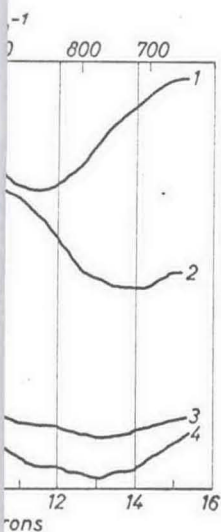
2. The effect of even major changes in secondary coordination (BUERGER's terminology) does not affect the *main* cation-anion stretching absorption band. Thus the patterns of cristobalite, tridymite, quartz and coesite are very similar although there is a 25 per cent volume spread. The coordination of Si⁴⁺ is therefore four in coesite although there may be a greater variety of Si-O distances in coesite than in quartz as indicated by the structure in the main Si-O band. The BeF₂ polymorphs bear out this hypothesis very well (Fig. 1). Hence the increase in density in going from quartz to coesite is realized only by a new packing of tetrahedra and not by increased coordination.

3. The effect of mass on decades in molecular spectra absorption spectra published

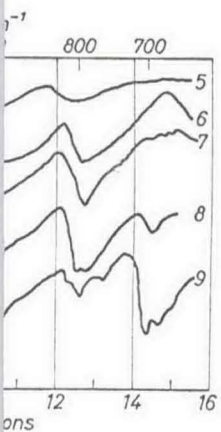
³ F. A. MILLER and C. H. W. frequencies of inorganic ions. *Ann. Z. Kristallogr.* Bd. 111, 6

As₂SbO₄ rutile form are shown in made on the basis of these and

any coordination of the cation it being frequency. Moreover, the



2-15.5 micron region. 1. GeO₂ coesite. (Sample preparation—KBr in 0.3 g KBr.)



2-15.5 micron region. 5. SiO₂ glass; 8. SiO₂ quartz; 9. SiO₂ coesite.

ratio of the squares of the wavelengths, in the case of Ge⁴⁺ changing from four to six coordination, is 1.48, or nearly 6/4. Whether this is mere numerical coincidence or whether it reflects a simple mathematical connection between the effect of coordination on the interionic distance and hence on the force constant, cannot be adequately checked until more examples are at hand.

2. The effect of even major changes in secondary coordination (BUERGER's terminology) does not affect the main cation-anion stretching absorption band. Thus the patterns of cristobalite, tridymite, quartz and coesite are very similar although there is a 25 per cent volume spread. The coordination of Si⁴⁺ is therefore four in coesite although there may be a greater variety of Si—O distances in coesite than in quartz as indicated by the structure in the main Si—O band. The BeF₂ polymorphs bear out this hypothesis very well (Fig. 1). Hence the increase in density in going from quartz to coesite is realized only by a new packing of tetrahedra and not by increased coordination.

3. The effect of mass on absorption frequency has been known for decades in molecular spectroscopy. An inspection of the infra-red absorption spectra published by MILLER and WILKINS³ or by HUNT,

³ F. A. MILLER and C. H. WILKINS, Infra-red spectra and characteristic frequencies of inorganic ions. Anal. Chem. 24 (1952) 1253-1299.

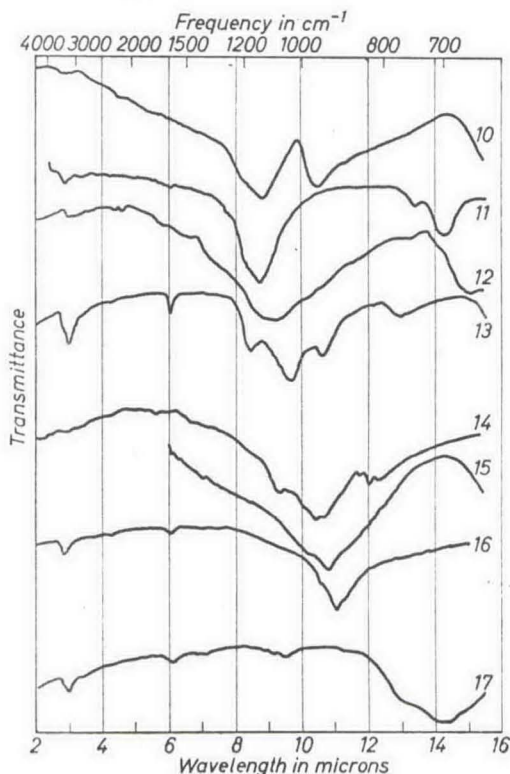


Fig. 3. Infra-red absorption spectra in the 2-15.5 micron region. 10. BPO₄ quartz; 11. AlPO₄ quartz; 12. GaPO₄ quartz; 13. FePO₄ quartz; 14. BAsO₄ quartz; 15. AlAsO₄ quartz; 16. GaAsO₄ quartz; 17. GaSbO₄ rutile.

WISHERD and BONHAM⁴ of solid inorganic compounds shows that a mass relationship must also be operative in related series. For example the sulfate, phosphate, arsenate and tungstate of calcium have major bands which center (at half height) at 8.8, 9.4, 11.9 and 12.3 microns respectively. If these bands are correctly attributed to the stretching frequencies of the S—O, P—O, As—O and W—O pairs of the "anions", a reasonable linear relationship exists between the square of the wavelength and the respective reduced mass. The same is observed for the chlorate, bromate and iodate of sodium and for other series.

Returning to the quartz structures, it is evident that this relation very nearly holds for the GeO₂ and SiO₂ pair, and if the cation and anion charges are considered, also for BeF₂. The agreement is improved by introducing an empirical term for the electron content of the bonds involved⁵.

4. The most generalized case, of course, involves the interaction between coordination (CN), valence ($Z_A \cdot Z_X$), a reduced mass term (μ), the sum of atomic numbers ($A_A + A_X$)^{1/2}, and the absorption wave length. By purely empirical means the following relation was found to hold well for the simple AX₂ compounds (BeF₂, SiO₂, GeO₂) and the GeO₂ rutile form.

$$"K" = \frac{(CN)(\mu) \cdot (A_A + A_X)^{1/2}}{Z_A Z_X \cdot \lambda^2} = 0.168.$$

The agreement for these compounds is within ± 0.002 , or within 2 per cent.

Proceeding from the very restricted selection of AX₂ structures, to the more general ABO₄ compounds of the silica and rutile structures, the agreement does not hold as well, as a study of the figures of Table 1 will show. The "constant" calculated differs from 0.168 by 7.5 per cent on the average for this group, with individual values disagreeing as much as ± 17 per cent. That there exists some agreement even within these limits is of interest in view of the complications introduced by the change from simple binary compounds to ternary ones and the resulting possibilities of ordered and disordered arrangements.

⁴ J. M. HUNT, M. P. WISHERD and L. C. BONHAM, Infra-red absorption spectra of minerals and other inorganic compounds. Anal. Chem. **22** (1950) 1478-1497.

⁵ This electronic effect was found to be proportional to the 1/3 power of the sum of the metal-anion atomic numbers, that is, of the sum of extranuclear electrons. This factor probably can be rationalized as being proportional to the linear electronic density parallel to the stretching directions modifying the vibrations of the mass centers.

The use of

Table 1. Application

Compound	Form
BeF ₂	qtz.
SiO ₂	qtz.
GeO ₂	qtz.
GeO ₂	rutile
BPO ₄	qtz.
BAsO ₄	qtz.
AlPO ₄	qtz.
AlAsO ₃	qtz.
GaPO ₄	qtz.
GaAsO ₄	qtz.
FePO ₄	qtz.
GaSbO ₄	rutile

For the ABO₄ compounds atomic number components calculated as

In Table 2 there are AX₂ and ABX₄ compounds. The values are works^{6,7,8}, and from data purpose here is to show different known forms values of the glass, 3.6 per cent above, and quartz. The total per

⁶ Data on Chemicals Council, Washington, D.

⁷ J. D. H. DONNAY and Memoir 60 (1954).

⁸ Standard X-Ray Diffraction Standards, Washington,

Table 1. Application of empirical equation in the calculation of "K"

Compound	Form	Main absorption wavelengths (λ , microns)	"K"	Per cent difference from average
BeF ₂	qtz.	13.1	0.167	- 0.6
SiO ₂	qtz.	9.15	0.170	+ 1.2
GeO ₂	qtz.	11.5	0.169	+ 0.2
GeO ₂	rutile	14.0	0.166	- 1.2
Average			0.168	
BPO ₄	qtz.	8.92	0.141	-16.0
BAsO ₄	qtz.	10.45	0.151	-10.0
AlPO ₄	qtz.	8.9	0.172	+ 2.4
AlAsO ₃	qtz.	10.56	0.159	- 5.3
GaPO ₄	qtz.	9.55	0.197	+17.2
GaAsO ₄	qtz.	11.25	0.166	- 1.2
FePO ₄	qtz.	9.7	0.179	+ 6.5
GaSbO ₄	rutile	14.4	0.171	+ 1.8

For the ABO₄ compounds, arithmetical averages are used for the cation mass or atomic number components. A weighted average is used for the cation charge, calculated as

$$Z_{(A \cdot B)} = \frac{Z_A^2 + Z_B^2}{Z_A + Z_B}$$

Molar refractivities

In Table 2 there are presented molar refractivities (R_m) of a few AX₂ and ABX₄ compounds having mainly the silica and rutile structures. The values are calculated from data in standard reference works^{6,7,8}, and from data newly obtained in this laboratory. The main purpose here is to show the order of magnitude and trend of R_m in the different known forms of the compounds. Thus for SiO₂ the R_m values of the glass, low cristobalite and low tridymite are about 3.6 per cent above, and that of coesite, 1.8 per cent below the value for quartz. The total percentage difference is very close to that found

⁶ Data on Chemicals for Ceramic Use. Bulletin 118, National Research Council, Washington, D. C. (1949).

⁷ J. D. H. DONNAY and W. NOWACKI. Crystal Data. Geol. Soc. Am., Memoir 60 (1954).

⁸ Standard X-Ray Diffraction Powder Patterns. Circular 539, Nat. Bu. Standards, Washington, D. C., Vols. 1-7 (1953-1957).

between the glass and coesite forms of BeF_2 . The R_m for the cristobalite and quartz forms respectively of BPO_4 , BAsO_4 , AlPO_4 , AlAsO_4 also are approximately within 3 per cent of each other. A decrease of the

Table 2. Comparison of molar refractivities

Compound	Form	Density	Average* refractive index	$\frac{R_m^{**}}{(A \cdot B) X_2}$	Per cent*** difference
SiO_2	glass	2.203	1.458	7.45	+ 3.6
SiO_2	<i>l</i> -crist.	2.325	1.486	7.42	
SiO_2	<i>l</i> -trid.	2.262	1.470	7.41	
SiO_2	quartz	2.648	1.548	7.19	
SiO_2	coesite	2.90	1.598	7.06	- 1.8
BeF_2	glass	1.986	1.275	4.07	+ 1.7
BeF_2	quartz	2.38	1.328	4.00	
BeF_2	coesite	2.55	1.345	3.93	- 1.7
BPO_4	crist.	2.80	1.597	6.41	+ 2.6
BPO_4	quartz	3.07	1.642	6.24	
BAsO_4	crist.	3.64	1.682	7.75	+ 3.5
BAsO_4	quartz	4.00	1.738	7.49	
AlPO_4	crist.	2.285	1.465	7.36	+ 3.4
AlPO_4	quartz	2.62	1.526	7.12	
GaPO_4	crist.	3.27	1.560	8.15	+ 2.5
GaPO_4	quartz	3.54	1.603	7.95	
MnPO_4	crist.	2.87	1.482	7.56	+ 4.7
MnPO_4	quartz	3.20	1.528	7.22	
GeO_2	glass	3.628	1.6081	9.90	+ 2.8
GeO_2	quartz	4.228	1.707	9.63	
	rutile	6.239	2.015	8.46	-12.2

Abbreviations: crist. = cristobalite, trid. = tridymite.

* Average refractive index calculated as $\sqrt[3]{N_3^2 N_2}$. The comparative values of R_m , in general, are not sensitive to manner of calculating the average refractive index.

** $\frac{R_m}{(A \cdot B) X_2}$ equals the R_m of AX_2 or $1/2$ of ABX_4 compounds. R_m normally reported in cm^3 per mole.

*** Percentage difference relative to the R_m value of the quartz polymorph of each series.

The same order is observed in these compounds. The effect of the anions although they are differently packed in the structural arrangement of the refractive index "ing" of the ions. The effect of a clearly in the of the quartz and the density of the refractive index on the other hand this value is the forms differing correlatable with. In addition, the allows the calculation of the complex compound ordination of val and SILVERMAN Al in 4 and 6 values differ by quartz-rutile polymorph in 4 and 6 coordination differ by 12 per cent that, if the measured by 12 ± 2 per cent be predicted.

The usefulness reached via infrared are tetrahedral

⁹ H. W. SAEI
J. Am. Ceram. Soc.

¹⁰ RUSTUM ROY
Soc. 72 (1950) 33

¹¹ These author communications) also significant changes values differ by c

for the cristobalite
 PO_4 , AlAsO_4 also
 A decrease of the

$\frac{n^{**}}{b) X_2}$	Per cent*** difference
.45	+ 3.6
.42	
.41	
.19	
.06	- 1.8
.07	+ 1.7
.00	
.93	- 1.7
.41	+ 2.6
.24	
.75	+ 3.5
.49	
.36	+ 3.4
.12	
.15	+ 2.5
.95	
.56	+ 4.7
.22	
.90	+ 2.8
.63	
.46	-12.2

same order is evident for the glass-quartz forms of GeO_2 . In all of these compounds the A and B cations are tetrahedrally coordinated by the anions although the polyhedra may be more or less distorted and are differently packed. The constant differences between the different structural arrangements of the tetrahedra demonstrate the sensitivity of the refractivity data in reliably describing the "efficiency of packing" of the ions, even where primary coordination is not disturbed. The effect of a change from 4 to 6 coordination is brought out very clearly in the densities, refractive indices and molar refractivities of the quartz and rutile forms of GeO_2 . Relative to the quartz form, the density of the rutile is 48 per cent greater, and the average refractive index 18 per cent greater. The molar refractivity decrease, on the other hand, amounts to only 12.2 per cent. However, since this value is *three times* the maximum change noted for the various forms differing only in secondary coordination, such a change is correlatable with an integral change of primary coordination. In addition, the additive nature of Rm is especially important as it allows the calculation of the refractivities of components in complex compounds and thereby provides a tool for testing the coordination of various cations of a multicomponent system. SAFFORD and SILVERMAN⁹ give values which they obtained for Al_2O_3 with Al in 4 and 6 coordination as 12.30 and 10.53 cm^3/mole . These values differ by 14 per cent in the same direction as for the GeO_2 quartz-rutile pair. ROY¹⁰ has calculated values for MgO with Mg in 4 and 6 coordination, 5.18 and 4.54 respectively, which also differ by 12 per cent¹¹. Thus one may generalize with caution that, if the molar refractivity "contribution" of an oxide increases by 12 ± 2 per cent, a change of coordination from 6 to 4 may be predicted.

The usefulness of molar refractivity in supporting our conclusions reached via infra-red data that the cations in coesite (SiO_2 and BeF_2) are tetrahedrally coordinated, is evident. It also supports indirectly

⁹ H. W. SAFFORD and A. SILVERMAN, Alumina-silica relationship in glass. *J. Am. Ceram. Soc.* **30** (1947) 203-211.

¹⁰ RUSTUM ROY, Magnesium in fourfold coordination in glass. *J. Am. Chem. Soc.* **72** (1950) 3307.

¹¹ These authors and others (N. J. KREIDL and K. FAJANS, personal communications) also list values of Rm for many minerals and their glasses where no significant changes in cation coordination are expected, and these respective values differ by only one or two per cent.

comparative values
 ating the average re-

pounds, Rm normally

he quartz polymorph

the assignment^{12,13,14} of 16 molecules to the coesite cell—that is, the measured density is compatible with the 16 molecule unit and with the *Rm* value calculated. If the coesite cell contained 18 molecules the measured density would be considerably in error (2.90 vs. 3.26) and the *Rm* based on the higher density would be almost 12 per cent lower than for quartz, suggestive of 6-coordinated Si, and of a rutile structure, which clearly coesite does not have.

Acknowledgment

This work forms a part of a study in crystal chemistry supported by the Chemical Physics Branch, U.S. Army Signal Corps, under contract No. SC-71214 and SC-74951.

¹² TIBOR ZOLTAI and M. J. BUEGER, The crystal structure of coesite, the dense, high pressure form of silica. *Z. Kristallogr.* **111** (1959) 129–141.

¹³ L. S. RAMSDELL, The crystallography of coesite. *Am. Min.* **40** (1955) 975–982.

¹⁴ FRANK DACHILLE and RUSTUM ROY, High pressure region of the silica isotypes. *Z. Kristallogr.* **111** (1959) 451–461.