

Database of Standard Raman Spectra of Minerals and Related Inorganic Crystals*

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Establishing a standard Raman spectral database for minerals and related inorganic crystals is a very important basis for further increasing the applications of Raman spectroscopy in the geosciences. However, the Raman spectral pattern of a crystal is a function not only of its composition and structure but also of the scattering geometry during the measurement. Therefore, the standard Raman spectrum of a crystal must be measured under well-defined standard conditions. It would be of great interest to establish a standard measuring configuration with which the characteristic Raman spectra of all mineral crystals could be obtained. Factor-group analysis of the main types of minerals indicates that almost all of them possess a Raman-active totally symmetric (TS) vibrational mode. Therefore, we propose a scheme to measure standard Raman spectra under a scattering geometry set up on the basis of these TS modes. Using this scheme, we were able to establish a database for standard Raman spectra of minerals and related inorganic crystals.

Index Headings: Raman spectroscopy; Database; Minerals and inorganic crystals.

INTRODUCTION

Before 1975, the application of Raman spectroscopic techniques to the geosciences had been limited by the intrinsic weakness of the Raman signal and by the requirement of optically high-quality bulk samples for Raman measurement.^{1,2} The latter factor was particularly problematic because geological samples are usually inhomogeneous and impure, and often fluorescent. The situation was changed by the advent of the micro-Raman spectroscopic technique.^{3,4} Its micro-spatial analytical capability largely relaxed the requirement for bulk optical quality of samples. With a spatial resolution of 1 μm , the technique requires a minimum weight of analyzed sample of about 10^{-9} to 10^{-12} g. Therefore, not only can the spectra of inhomogeneous geological samples be obtained more easily, but many micro-phases in these samples, such as fluid inclusions, local phase transitions, micro-scale exsolution, etc., also can be studied. Their compositional and structural characteristics reveal very interesting information about the geological processes that occurred in the past. For this reason, the application of Raman spectroscopic techniques to geological research developed at full speed after the creation of the micro-Raman technique in 1975 (Fig. 1). In addition to its successful applications to mineralogy, petrology, gemology, and paleontology, the micro-Raman technique has been

widely used in high-pressure and high-temperature (high P-T) phase-transition experiments, especially for studies using diamond anvil cells. It has become one of the two most powerful techniques (together with synchrotron X-ray diffraction) that actually realize *in situ* measurements of the high P-T phases that may exist in the core of the Earth or on the other planets, while they are still sealed in a diamond anvil cell.⁵⁻¹¹

However, because the Raman spectrum of any compound is a characteristic "finger print", the successful application of Raman spectroscopy in the geosciences has further increased the requirement for establishing a database of standard Raman spectra of minerals and related inorganic crystals.¹² The main difficulty in building this database is to decide what type of measuring scheme should be used, in order to assure that the spectra obtained can be used as standards. It is well known that the Raman spectral pattern of a crystal is a function not only of its composition and structure but also of the scattering geometry adopted during the measurement, i.e., the reciprocal orientation of its crystallographic axis with the electric vector *E* of the exciting radiation. Therefore, the chosen scheme for measuring standard spectra must ensure that (1) the recorded spectral patterns of crystals are characteristic; (2) there is a good reproducibility of these patterns; (3) the spectra can be compared with the spectra taken from ordinary geological samples.

Two frequently suggested measuring schemes for standard Raman spectra are (1) polarized measurements on certain orientations of a crystal sample and (2) nonpolarized measurement on the powder of a sample. The first scheme permits one to collect all Raman-active vibrational bands of a crystal and to obtain their intrinsic relative scattering intensities. Obviously, this scheme requires both high crystallographic quality of the standard mineral samples and a huge number of standard measurements for building a database. In addition, ordinary geologic samples are usually difficult to orient, partly because of their state (often polycrystalline) and size and partly because of their location (e.g., in thin section, intergrown with other mineral phases, included inside a host crystal, and even sealed in high P-T equipment). Therefore, the Raman spectra of ordinary geological samples are rarely comparable with the standard spectra obtained by using the first scheme. The advantage of measuring a powdered sample is that randomly oriented micro-particles theoretically express all Raman-active vibrational bands of a crystal structure in one measurement. However, there is a contradiction in the requirement for the particle size in a powdered sample. A truly "randomly" oriented powder sample requires the particle size to be

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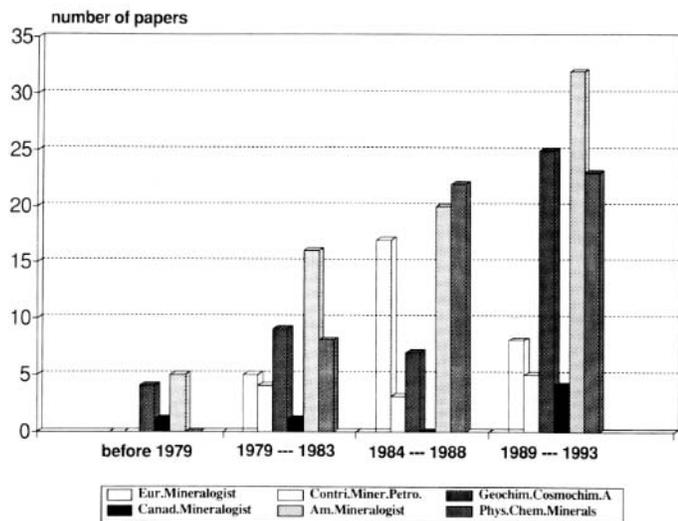


FIG. 1. Published geological research papers using Raman spectroscopy in six journals (checked from the database of Chemical Abstracts and of Georef).

as small as possible, whereas the high signal-to-noise (S/N) ratio requirement for standard Raman spectra relies on large particles, in that the intensity of Raman scattering is closely related to the long-range ordering in the crystal lattice and, thereby, related to the particle size. Therefore, this scheme also is not very practical.

On the basis of factor-group analysis by use of the correlation method¹³ for the main types of mineral crystals, we propose a practical measuring scheme for establishing a standard Raman spectral database of minerals and related inorganic crystals. This scheme permits the establishment of a scattering geometry for the micro-crystals based on their totally symmetric vibrational modes. The Raman spectra obtained in this way contain the main spectral characters of the crystals and can be reproduced and compared with the spectra taken from ordinary geological samples. By using this proposed scheme, we measured over five hundred standard samples (minerals and related inorganic crystals) and set up a database including the measured spectral data and the spectral data of over seven hundred minerals and inorganic compounds collected from the literature. The arrangement of the spectral data and their mineralogical information in this database follows a traditional mineral classification.¹⁴ A search/match program was also made which allows phase-determination of unknown geological samples on the basis of their Raman spectra.

MEASUREMENTS PROCEDURE FOR OBTAINING STANDARD RAMAN SPECTRA

Figure 2 shows a micro-Raman measurement procedure that has been very widely used for analysis of geological samples. The most important step in this procedure is to find the strongest band in the characteristic spectral region of the sample and to record the entire spectrum under the scattering geometry for which that band attains its maximum intensity. Actually, in most cases for mineral samples, this strongest band corresponds to the totally symmetric vibrational mode (TS mode) of the strongest covalent bond in the crystal struc-

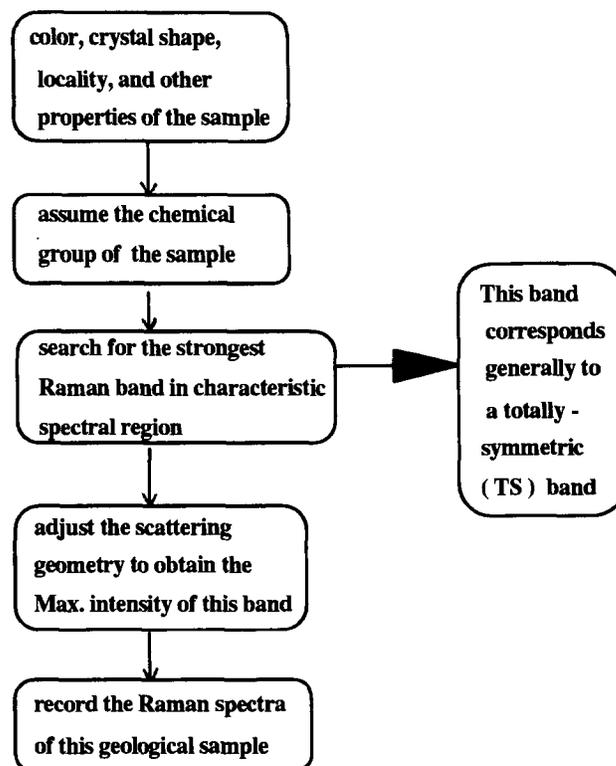


FIG. 2. A commonly used micro-Raman measurement procedure for geological samples.

tures. The measuring scheme that we have proposed is, therefore, to set up a standard scattering geometry based on the strongest TS mode of each crystal sample. This scheme is in agreement with the commonly used measuring procedure for ordinary geological samples; therefore the obtained spectra are comparable. In addition, the feasibility of this measuring scheme is related to two main factors: (1) the existence of at least one TS vibrational mode for each mineral; (2) the characterization of the obtained spectra.

Existence of the TS Vibrational Mode in Minerals. The TS mode, which produces the strongest Raman band in the spectrum of a chemical compound, is often related to the most covalent chemical bond of the anionic unit in its structure. Therefore, in the following discussion, the minerals have been divided into four groups according

TABLE I. The separation of main mineral types into four groups.

Group I minerals having a (XO ₃) ⁿ⁻ unit	Group II minerals having a (XO ₄) ⁿ⁻ unit	Group III minerals having a polymer of units	Group IV minerals having no obvious unit
Carbonate	Sulfate	Soro-silicate	Element
Nitrate	Phosphate	Ring-silicate	Oxide
Borate	Tungstate	Chain-silicate	Halide
Iodate	Molybdate	Layer-silicate	Sulfide
Arsenite	Chromate	Tecto-silicate	Hydroxide
Tellurite	Vanadate	Some borate	
Selenite	Arsenate	Vanadate	
	Tellurate	Chromate	
	Selenate	...	
	Ortho-silicate		

TABLE II. Correlation of the A_1' mode of the D_{3h} point group to site symmetry and to crystal symmetry.

In D_{3h} point group	In site symmetry	In crystal symmetry	
A_1'	$A'(C_{3h})$	$A_{1g} + A_{2g} + B_{1u} + B_{2u}$	(D_{6h})
	$A_1(D_3)$	$A_g + B_u$	(C_{2h})
	$A_1(C_{3v})$	A	(C_3)
	$A(C_{2v})$	A'	(C_2)
	$A(C_2)$	A	(C_2)
	$A(C_3)$		
	$A'(C_3)$		

to the anionic unit that they possess (Table I); then the factor-group analysis is performed separately.

The minerals of group I have the anionic unit $(XO_3)^{n-}$ which belongs to D_{3h} symmetry. For these minerals, the chemical bonds in the $(XO_3)^{n-}$ unit are usually far more covalent than the bonds which connect these anionic units to cations. This means that the totally symmetric stretching vibrational mode of the $(XO_3)^{n-}$ group has the most intense Raman band in the spectra of these compounds. In an isolated $(XO_3)^{n-}$ unit, this mode belongs to the A_1' symmetric species of the D_{3h} point group. In a crystal, the symmetry of the vibrational modes of a $(XO_3)^{n-}$ group is affected both by the symmetry of the site where it is located (site effect) and by the symmetry of the entire crystallographic network (coupling effect). As far as the site effect is concerned, Table II shows that, regardless of the site symmetry of the $(XO_3)^{n-}$ anionic group, its A_1' mode always transforms into the corresponding TS mode of the site symmetry. But for the coupling effect, Table II shows that the transformation of the A_1' mode will depend on the type of crystal symmetry: if it is lower than that of the site symmetry (e.g., C_3 , C_s , C_i for C_{3h} site symmetry), the A_1' mode transforms directly into the corresponding TS mode of the crystal symmetry; whereas if the crystal symmetry is equal to, or even higher than, that site symmetry (e.g., D_{6h} , C_{2h} for C_{3h} site symmetry), the A_1' mode of the $(XO_3)^{n-}$ group will split into several vibrational modes, including at least one TS mode. Therefore, this analysis indicates that all minerals of group I which possess $(XO_3)^{n-}$ anionic units will have at least one TS vibrational mode in their Raman spectra. Table III shows the characteristic spectral region where this TS mode is located for the common minerals of group I (data from our measurements and literature).

Table IV shows the same analysis for the minerals of group II, which possess $(XO_4)^{n-}$ anionic units (T_d symmetry). They also have at least one TS mode. Table V shows the characteristic spectral region where this TS mode is located for the common minerals of this group.

In the crystal structures of the minerals of group III, the above units $(XO_3)^{n-}$ or $(XO_4)^{n-}$ exist but form different polymerized species by sharing their corner oxygens,

TABLE III. Characteristic spectral regions for common minerals of group I.

Minerals	Anionic unit	Characteristic spectral regions (cm ⁻¹)
Carbonate	$[CO_3]^{2-}$	1030-1130
Nitrate	$[NO_3]^-$	1040-1060
Iodate	$[IO_3]^-$	750-800

TABLE IV. Correlation of the A_1 mode of the T_d point group to site symmetry and to crystal symmetry.

In T_d point group	In site symmetry	In crystal symmetry	
A_1	$A(T)$	$A_{1g} + A_{2g} + A_{1u} + A_{2u}$	(O_h)
	$A_1(D_{2d})$	$A_g + A_u$	(T_h)
	$A_1(C_{3v})$	$A_1 + A_2$	(O)
	$A(S_4)$	A	(D_2)
	$A(D_2)$	A	(C_3)
	$A_1(C_{2v})$	A	(C_2)
	$A(C_3)$	A	(C_2)
	$A(C_2)$		
	$A'(C_2)$		

such as $(Si_2O_7)^{6-}$, $(B_2O_5)^{4-}$, etc. Therefore, besides the symmetric stretching vibrational mode of $X-O_{nb}$ bonds (where O_{nb} denotes a nonbridging oxygen and NBO represents the number of them per anionic unit), there exists also the symmetric stretching vibrational mode of the $X-O_b-X$ bond(s) (where O_b denotes the bridging oxygen that connects the anionic units). The frequency of this latter vibrational mode is always much lower than that of the $X-O_{nb}$ vibration, for example, 1150-850 cm⁻¹ for $Si-O_{nb}$ and 750-450 cm⁻¹ for $Si-O_b-Si$. Its scattering intensity depends on the number of bridging oxygens (**BO**) per anionic unit. Table VI shows the typical Raman spectra of silicates having different polymeric types of $(SiO_4)^{4-}$ units. A direct correlation between the relative intensities of the two TS modes and the NBO/BO ratio can be found. For the silicates having $NBO < 2$, the symmetric stretching band of $Si-O_b-Si$ has much stronger intensity than that of the $Si-O_{nb}$ stretching band. Therefore, it should be easier to use this $Si-O_b-Si$ TS stretching mode in order to devise the scattering geometry for those types of minerals, such as mica, amphibole, etc.

It is difficult to select a more covalent ionic unit in the crystal such as oxide, hydroxide, halide, and sulfide compounds (group IV). The existence of a TS vibrational mode in these crystals will depend only on the symmetry of the sites that are occupied by the ions. By checking the character tables,^{2,13,15} one can divide the 32 site symmetries into two types: A (10) and B (22) (Fig. 3). The translations of the ions that occupy an A -type site in a crystal can give a TS mode because, for these ions, at least one component of its three translations (T_x , T_y , T_z) belongs to the totally symmetric species (e.g., for an ion at the C_2 site, its T_z belongs to A). In contrast, the ions that occupy a B -type site in a crystal cannot produce any TS mode. Given that each space group has a limited number of site

TABLE V. Characteristic spectral regions for common minerals of group II.

Minerals	Anionic unit	Characteristic spectral region (cm ⁻¹)
Sulfate	$[SO_4]^{2-}$	950-1100
Tungstate	$[WO_4]^{2-}$	900-940
Molybdate	$[MoO_4]^{2-}$	870-940
Chromate	$[CrO_4]^{2-}$	~880
Phosphate	$[PO_4]^{3-}$	900-1100
Arsenate	$[AsO_4]^{3-}$	800-900
Vanadate	$[VO_4]^{2-}$	820-900
Ortho-silicate	$[SiO_4]^{4-}$	850-950

symmetries, the 230 space groups of crystals also can be divided into two types (Fig. 3). Eighty-five space groups possess only *A*-type site symmetry. Hence, all crystals (of group VI) belonging to these space groups have at least one TS mode in their Raman spectra. The remaining 145 space groups possess the site symmetries of both *A* and *B* types. The existence of a TS mode for these crystals will depend on the occupancy of the *A*-type sites (Fig. 3). Table VII shows the results of the factor-group analysis made for 23 typical structures representing 49 minerals of the group IV. It can be seen that most of these minerals have at least one TS mode. As the exception, there are six structures for which all ions are located on highly symmetric *B*-type sites and hence have no TS mode. An interesting ramification is that these minerals either have no Raman-active vibrational modes at all or have only one Raman-active vibrational mode that can be used to set up the scattering geometry. Therefore, these exceptions do not invalidate the proposed measuring scheme. The characteristic spectral regions of the common minerals of group IV are shown in Table VIII.

From the above analysis, we can conclude that almost all minerals have at least one totally symmetric vibrational mode, which can be used to set up the scattering geometry for recording their standard Raman spectra.

Characterization of the Obtained Spectra. The aim of proposing this measuring scheme is to obtain a "characteristic" Raman spectrum from one special measurement. However, whether the spectra obtained can be used as standards depends on three factors: the quantity of spectral information that these spectra contain, the reproducibility of the spectral pattern, and the ability to compare them with the spectra obtained from ordinary geological samples.

On the basis of the symmetry properties of the polarizability tensor α of different crystals, the direction of the electric vector **E** of the exciting radiation that permits the appearance of a Raman-active vibrational mode in the spectrum can be deduced from the equation $\mathbf{P} = \alpha \cdot \mathbf{E}$. Table IX shows the analyzed results for monoclinic crystals. It can be seen that the scattering intensities of TS modes (A , A' , A_g) of monoclinic crystals are always nonzero regardless of the **E** direction. In contrast, the nonzero intensities of the non-TS modes (B , A'' , B_g) require special **E** directions. Table X assembles similar results for all seven crystal symmetric types. In this table, Raman-active modes are divided into three groups according to the **E** direction required for their observations. All TS modes for all seven crystal symmetric types (also E and E_g modes for cubic crystals) are included in the "common" modes, because they appear in the Raman spectra of crystals without any special requirement for the **E** direction. This property of TS modes is the basis of the proposed measuring scheme and makes it a very practical one. Some vibrational modes of trigonal, tetragonal, and hexagonal crystals are classified as "quasi-common" modes, because they appear in most cases except when **E** is parallel to the *c* axis of the crystal. The modes that require quite strict **E**-direction conditions are called "less-common" modes.

To summarize, the measuring scheme that we propose is to fix a crystallographic axis of the crystal or micro-crystal sample in the coordinates of a micro-Raman spec-

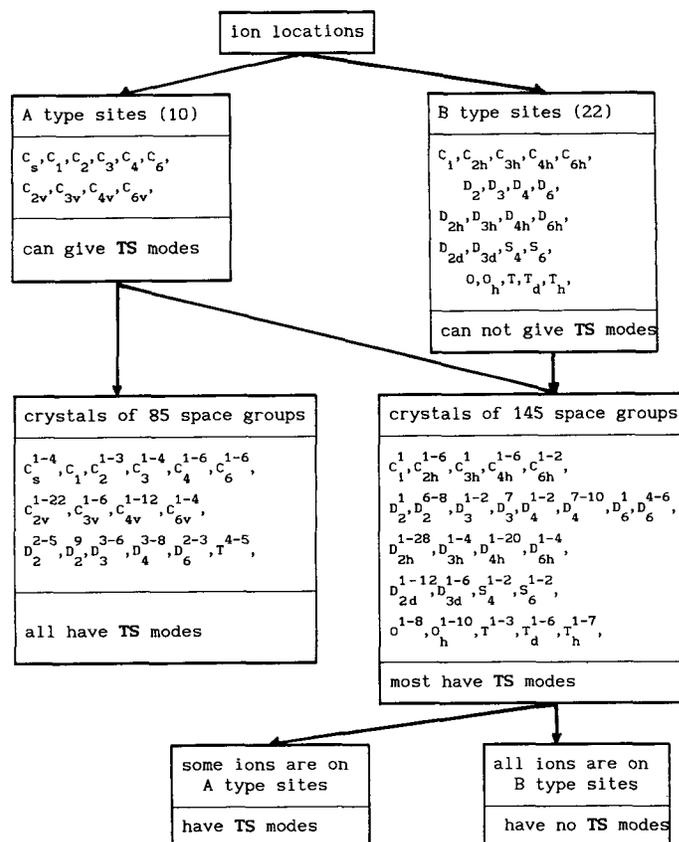


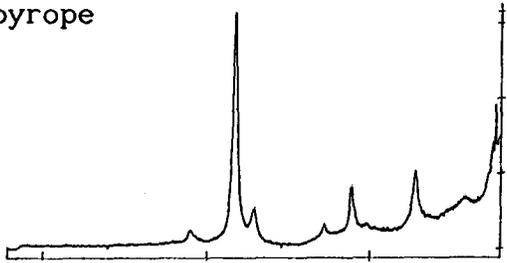
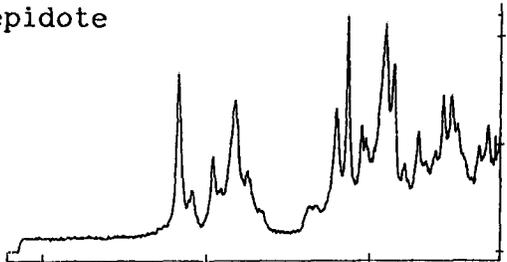
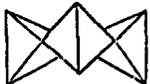
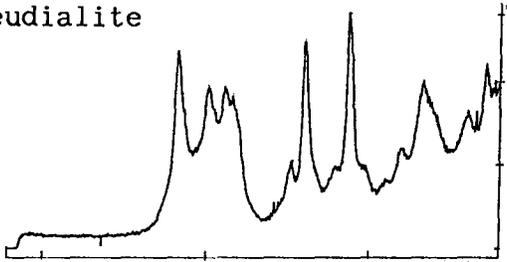
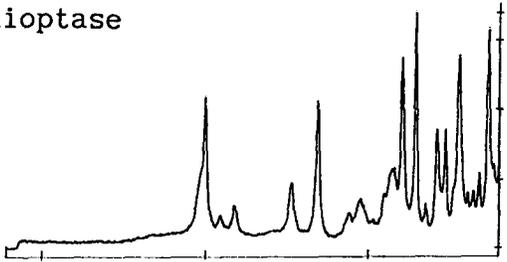
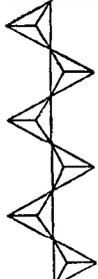
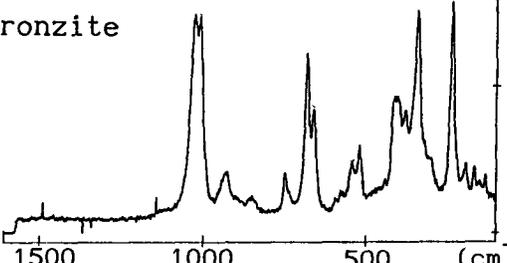
FIG. 3. Existence of the TS mode in the minerals of group IV.

trometer, by means of visual observation of the edges of euhedral crystal or the orientation of a cleavage, then to adjust the **E** direction of the incident laser beam until the TS band appearing in the characteristic spectral region attains its maximum intensity, and finally to record the entire spectrum. The last three lines in Table X show, for three types of Raman modes, the probability of their occurrence in the spectra, as well as the reproducibility of the band positions and intensities. The data indicate that the spectrum obtained with the use of the proposed measuring scheme will contain the main spectral characters of a crystal, i.e., it contains most Raman-active modes ("common" modes, "quasi-common" modes, and in certain cases some "less-common" modes), and has a good reproducibility in terms of the band positions and band intensities of the main bands. Although this spectrum cannot compare, in all details, with a set of polarized spectra measured on the totality of the reciprocal orientations of that crystal, it is more comparable with the spectrum recorded from an ordinary geological sample, because the latter is usually measured by using the same procedure. Therefore, in practice, this kind of characteristic Raman spectra will be able to be used as standard spectra for mineral phase determinations in geoscientific applications.

ESTABLISHMENT OF A DATABASE

The measuring scheme is the main factor that directly affects the quality of a standard Raman spectra database. Other factors concerned are the choice of the standard

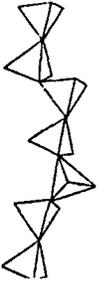
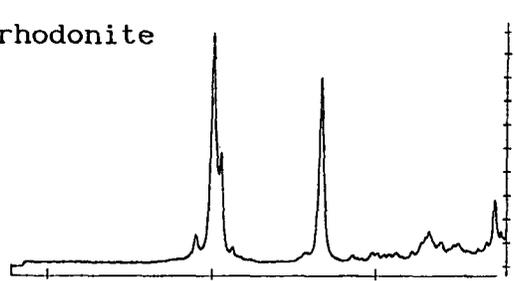
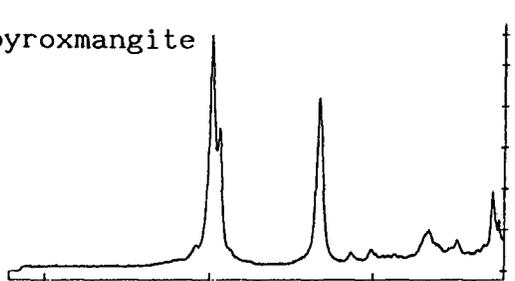
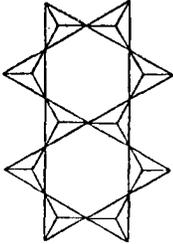
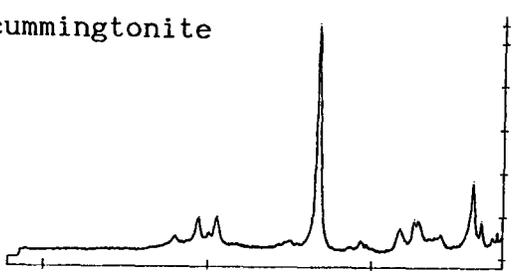
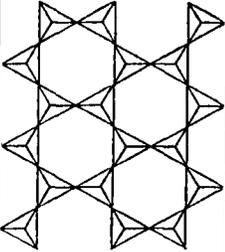
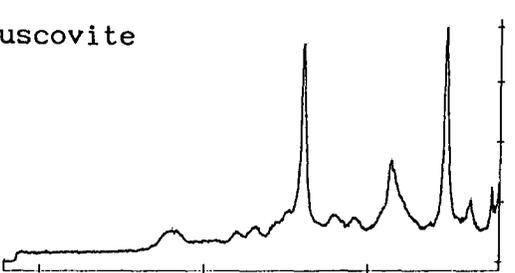
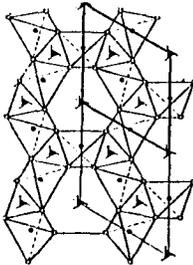
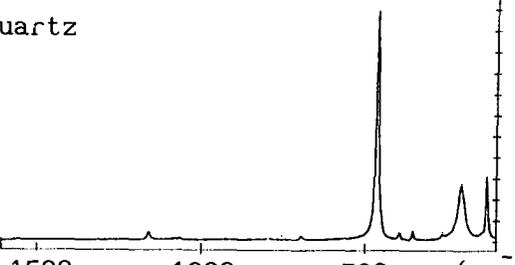
TABLE VI. Totally symmetric vibrational mode (TS) of silicates.

mineral types	structural unit	form of polymer	NBO	BO	typical Raman spectra Si-O _{nb} TS mode Si-O _b -Si TS mode
ortho-silicate	[SiO ₄] ⁴⁻		4	0	pyrope 
soro-silicate	[Si ₂ O ₇] ⁶⁻		3	0.5	epidote 
ring-silicate	[Si ₃ O ₉] ⁶⁻		2	1	eudialite 
	[Si ₆ O ₁₈] ¹²⁻		2	1	diopase 
chain-silicate	[Si ₂ O ₆] ⁴⁻ _∞		2	1	bronzite 

mineral samples, the calibration of the Raman spectrometer, the search/match method employed, and the structure of the database. These considerations will be discussed separately.

Standard Mineral Samples. Obviously, the mineral samples of this database should include, at least, all the common minerals (about 300) and cover most of the different structural types in each mineral group. Over five

TABLE VI. Totally symmetric vibrational mode (TS) of silicates (continued).

mineral types	structural unit	form of polymer	NBO	BO	typical Raman spectra	
					Si-O _{nb} TS mode	Si-O _b -Si TS mode
chain silicate	$[\text{Si}_5\text{O}_{15}]_{\infty}^{10-}$		2	1	rhodonite 	
	$[\text{Si}_7\text{O}_{21}]_{\infty}^{14-}$		2	1	pyroxmangite 	
	$[\text{Si}_4\text{O}_{11}]_{\infty}^{6-}$		1.5	1.25	cummingtonite 	
layer-silicate	$[\text{Si}_4\text{O}_{10}]_{\infty}^{4-}$		1	1.5	muscovite 	
tecto-silicate	$[\text{SiO}_2]_n$		0	2	quartz 	

hundred mineral samples were chosen from the collection (more than 3000 specimens) of the Infrared Spectroscopy Laboratory of the Chinese Academy of Geological Sciences. They were all identified with the use of an infrared

spectroscopic technique. Most of them were also checked by X-ray diffraction and electron microprobe analysis. As a complement, some synthetic inorganic crystals also were used, such as nitrates, halides, and hydroxides. Generally,

TABLE VII. Results using group theory analyses for 23 structures of group IV.

Structural types	Typical comp.	Space group	Occupied sites	Raman-active modes (TS mode)
Zincite (2)	ZnO	C_{6v}^4	C_{3v}, C_{3v}	$A_1 + E_1 + 2E_2$
Corundum (4)	Al_2O_3	D_{3d}^5	C_3, C_2	$2A_g + 2E_g$
Arsenolite (2)	As_2O_3	O_h^7	C_{3v}, C_{2v}	$2A_{1g} + 2E_g + 5F_{2g}$
Rutile (4)	TiO_2	D_{4h}^4	D_{2h}, C_{2v}	$A_{1g} + B_{1g} + B_{2g} + E_g$
Anatase (1)	TiO_2	D_{4h}^9	D_{2d}, C_{2v}	$A_{1g} + 2B_{1g} + 3E_g$
Paratellurite (1)	TeO_2	D_4^4	C_{2v}, C_1	$5A_1 + 6B_1 + 5B_2 + 6E$
Ilmenite (3)	$FeTiO_3$	S_6^2	C_3, C_3, C_1	$5A_g + 5E_g$
Perovskite (2)	$CaTiO_3$	D_{2h}^6	C_3, C_{2v}, C_1	$5A_g + 4B_{1g} + 5B_{2g} + 4B_{3g}$
Spinel (8)	$MgAl_2O_4$	O_h^7	T_d, D_{2d}, C_{3v}	$A_{1g} + E_g + 3F_{2g}$
Pseudobrookite (3)	Fe_2TiO_5	D_{2h}^{17}	$C_3, C_{2v}, C_1, C_{2h}, C_2$	$4A_{1g} + 4B_{1g} + 3B_{2g} + 4B_{3g}$
Wolframite (2)	$FeWO_4$	C_{2h}^4	C_2, C_1, C_1	$4A_g + 4B_g$
Scheelite (1)	$CaWO_4$	C_{2h}^2	S_4, C_1	$3A_g + 5B_g + 4E_u$
Brucite (1)	$Mg(OH)_2$	D_{3d}^3	D_{3d}, C_{3v}	$2A_{1g} + 2E_g$
Diaspore (1)	$AlO(OH)$	D_{2h}^6	C_3, C_1	$5A_g + 4B_{1g} + 5B_{2g} + 4B_{3g}$
Bochmite (1)	$AlO(OH)$	D_{2h}^{17}	C_{2v}, C_{2h}	$3A_g + 2B_{1g} + B_{2g} + 3B_{3g}$
Pyrite (1)	FeS	T_h^8	S_6, C_3	$A_g + E_g + 3F_g$
Wurtzite (1)	ZnS	C_{6v}^4	C_{3v}, C_{3v}	$A_1 + E_1 + 2E_2$
Cuprite (2)	Cu_2O	O_h^4	D_{3d}, T_d	F_{2g}
Fluorite (3)	CaF_2	O_h^5	O_h, T_d	F_{2g}
Sphalerite (1)	ZnS	T_d^2	T_d, T_d	F_2
Periclase (5)	MgO	O_h^5	O_h, O_h	
Halite (3)	NaCl	O_h^5	O_h, O_h	
Uraninite (2)	UO_2	O_h^5	O_h, T_d	F_{2g}

a crystalline micro-grain of each standard mineral sample was chosen for Raman measurements. In some cases (clay minerals, etc.), fine powders also were used. The micro-grain used as the sample of Raman measurement was carefully selected under an optical microscope, to be sure that it had the typical color and crystal form of that mineral. Any sample that yielded a doubtful Raman spectrum was re-examined by the infrared technique with the use of the same micro-grain. If doubt remained after this step, the Raman spectrum was eliminated. The Raman spectra of some clay minerals had a very poor S/N ratio; they were also eliminated. In the end, 418 standard Raman spectra from mineral samples and 46 spectra from synthetic inorganic crystals were obtained.

Calibration of the Raman Spectrometer. The measurements of standard Raman spectra were performed on a Spex 1403 double-monochromator spectrometer. A monochannel detector (photomultiplier) was used. The 514.5-nm line of an Ar^+ laser was the exciting source. For all standard spectra, the recording spectral step was 1 cm^{-1} with an integration time at each wavenumber of 1 s. The low-frequency limit for all standard spectra was fixed at 100 cm^{-1} , whereas the high-frequency limit that was chosen depended on the mineral groups analyzed: 800 cm^{-1} for oxide, halide, and sulfide; 1300 cm^{-1} for silicate; 1500 cm^{-1} for sulfate, etc. The spectra in the

TABLE VIII. Characteristic spectral regions for common minerals of group IV.

Minerals	Characteristic spectral region (cm^{-1})
Oxide	300–700
Sulfide	200–500
Halide	100–400
Hydroxide	3500–3800

$3000\text{--}4000\text{ cm}^{-1}$ region were also recorded for the samples containing hydroxyl and structural water. The width of the spectral slits was chosen according to the strength of the Raman signals of the different mineral groups.

A systematic calibration was performed on this Raman spectrometer before the measurements of standard spectra. This calibration included the determination of the accuracy and reproducibility of the wavenumber, the spectral responses with polarized and nonpolarized incident light, the slit function, the spectral resolution, and the spurious bands produced by instrumental elements. The following observations were made on the basis of this calibration:

1. The wavenumber accuracy of this spectrometer is within $\pm 0.5\text{ cm}^{-1}$ in the $0\text{--}2000\text{ cm}^{-1}$ spectral region corresponding to the 514.5-nm line; hence, no correction has to be done for the spectra recorded in the $100\text{--}1500\text{ cm}^{-1}$ region. The error is $< 1.7\text{ cm}^{-1}$ in the

TABLE IX. Properties of Raman-active vibrational modes of monoclinic crystals and the electric vector E direction of laser radiation (x, y, and z correspond to the a, b, and c axes of the crystal).

Raman properties:	for A	a 0 d	for B	0 e 0
	A'	$\alpha = 0\ b\ 0$	A''	$\alpha = e\ 0\ f$
	A_g mode	d 0 c	B_g mode	0 f 0
E direction	Scattering intensity	Induced dipole moment	Scattering intensity	Induced dipole moment
$(E_x\ 0\ 0)$	Nonzero	$(P_x\ 0\ P_z)$	Zero	
$(0\ E_y\ 0)$	Nonzero	$(0\ P_y\ 0)$	Zero	
$(0\ 0\ E_z)$	Nonzero	$(P_x\ 0\ P_z)$	Zero	
$(E_x\ E_x\ 0)$	Nonzero	$(P_x\ P_x\ P_z)$	Nonzero	$(P_x\ P_x\ P_z)$
$(0\ E_y\ E_y)$	Nonzero	$(P_x\ P_y\ P_z)$	Nonzero	$(P_x\ P_y\ P_z)$
$(E_x\ 0\ E_z)$	Nonzero	$(P_x\ 0\ P_z)$	Zero	
$(E_x\ E_y\ E_z)$	Nonzero	$(P_x\ P_y\ P_z)$	Nonzero	$(P_x\ P_y\ P_z)$

2000–4000 cm⁻¹ spectral region, and a correcting formula was deduced as follows:

$$\nu_{\text{corr}} = \nu_{\text{meas}} - 5.2 \times 10^{-4}(\nu_{\text{meas}} - 519).$$

- The wavenumber reproducibility is good, but a shift of the origin (0 cm⁻¹) was observed. Since the Raman spectrum of a single crystal of silicon was recorded every day, the observed position shift of its 519.5-cm⁻¹ band was used to correct the wavenumber of standard spectra recorded in the same day.
- The spectral responses of this spectrometer are shown in Fig. 4. It can be seen that the responses of this spectrometer for polarized incident light (\parallel or \perp) are very different. However, since the standard spectra were recorded without an analyzer put in front of the entrance slit of the spectrometer, only the nonpolarized response was taken into account for relative band-intensity correction. It shows that the change in the spectral response is very small ($R = 0.96$ – 0.93) in the 0–1500 cm⁻¹ spectral region. Therefore the measured band intensities for fundamental vibrational modes of minerals are good. In contrast, that in the 3000–4000 cm⁻¹ region needs to be corrected by using the following formula:

$$I_{\text{corr}}(\nu) = [1.3 + 3.0 \times 10^{-4}(\nu - 3000)]I_{\text{meas}}(\nu).$$

- Spurious bands exist in some of the recorded Raman spectra, especially those having a low S/N ratio. They are likely to originate from the fluorescence of the glue used for fixing the lenses of the microscope objective used in this spectrometer. They were eliminated in the later treatment of standard spectra.

Search/Match Method in the Database. The database was established in a form that permitted it to be run on IBM-PC/AT or compatible computers. For phase identification, the method of comparing an entire sample spectrum with the standard spectra was not chosen for the three following reasons: (1) commonly existing cation substitution in mineral structures can introduce slight frequency shifts of the Raman bands; (2) fluorescence produced by contaminants may raise the spectral background and degrade part of the spectrum; (3) spurious bands can modify some spectra. Instead, selected parameters of the spectral bands (band position, relative band intensity, and bandwidth) are used for comparison. With the selection of these parameters for each spectrum in a peak-search program, the influences of background and spurious bands can be eliminated immediately. The possible frequency shift in band position due to cation substitution can be put into consideration by setting up an “error window” in the wavenumber match program. Another argument in favor of the use of band parameters for comparison of Raman spectra is that the latter often contain sharper and more separated bands than do the corresponding IR spectra.

Structure of the Database. In this database, three types of data were put into three sub-bases. The original data files of standard spectra along with the measuring conditions were organized in the first “original spectral sub-base” according the codes given to samples. The code of each mineral sample corresponds to its position in the Strunz classification (Strunz 1978). This classification was

TABLE X. The three types of Raman-active vibrational modes and the required electric vector E directions for their appearances in the spectra. Notice that the appearance of the TS mode does not need any special scattering geometry for any crystal. This property is the basis of the proposed measurement scheme (x, y, and z correspond to the a, b, and c axes of the crystal).

Crystals	Common modes		Quasi-common modes		Less common modes	
	Mode	Required E direction	Mode	Required E direction	Mode	Required E direction
Triclinic crystal	A_1, A_g	Any			B, B'', B_g	In (xoy), (yoz) plans
Monoclinic crystal	A_1, A', A_g	Any			B_1, A_2, B_{1g}	In (xoy) plan
Orthorhombic crystal	A_1, A_1', A_g	Any			B_2, B_1, B_{2g}	In (xoz) plan
					B_3, B_2, B_{3g}	In (yoz) plan
Trigonal crystal	A_1, A_g, A_1, A_{1g}	Any	E, E_g	$\neq z$	E, E_g	In (xoz), (yoz) plans
Tetragonal crystal	A_1, A_g, A_1, A_{1g}	Any	B, B_g	$\neq z$	B_2, B_{2g}	In (xoy) plan
Hexagonal crystal	A_1, A_g, A_1, A_{1g}	Any	E_2, E', E_{2g}	$\neq z$	E_2, E'', E_{1g}	In (xoz), (yoz) plans
Cubic crystal	A_1, A_g, A_1, A_{1g}	Any	F, F_g, F_{2g}		F, F_g, F_{2g}	In (xoz), (yoz), (xoy) plans
Using proposed scheme						
Probability of appearing in spectrum	In any cases				In some cases	
Reproducibility of band position	Good				Good	
Reproducibility of band intensity	Good				Not sure	

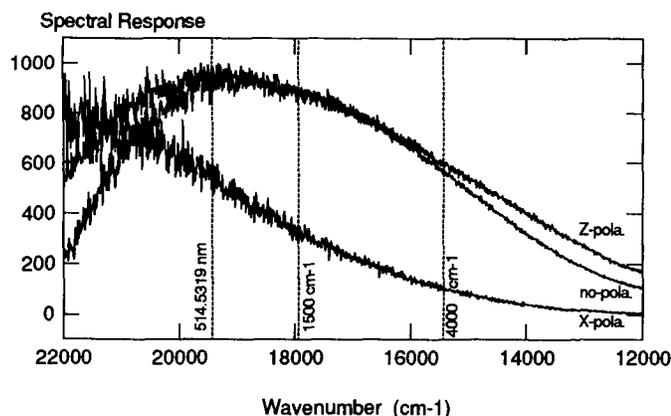


FIG. 4. Spectral response of the Spex 1403 Raman spectrometer, where spectral response $R(\nu)$ is equal to $I^{\text{exp}}(\nu)/I^{\text{cal}}(\nu)$, in which $I^{\text{exp}}(\nu)$ is the normalized emission intensity of the spectrum of a tungsten band lamp recorded by this spectrometer, $I^{\text{cal}}(\nu)$ is calculated by using Planck's blackbody formula (also normalized), and z-pola and x-pola represent the polarization directions.

chosen because it demonstrates well the common and individual character of mineral samples in terms of their composition and structure features. A corresponding file including all Raman band parameters for each standard spectrum was obtained by using a peak-search program. These files were put into a "band parameters sub-base" that uses the same codes. Besides the measured spectral data, this sub-base also includes the band parameters of the spectra of 740 minerals and related inorganic compounds collected from the literature. Sixty-nine of them were chosen among the publications issued by Sadler Research Laboratory;¹⁶ some were selected from *Infrared and Raman Spectra of Inorganic and Coordination Compounds*;¹⁷ and the remaining ones were collected from the following journals: *Spectrochimica A: Molecular Spectra*, *European Journal of Solid State and Inorganic Chemistry*, *Physics and Chemistry of Minerals*, *American Mineralogist*, *Canadian Mineralogist*, *European Journal of Mineralogy (Bulletin de Min rologie)*, and *Mineralogical Magazine*. The files of literature data can be distinguished from those of measured data by the last letter "R" in their codes. The third sub-base contains the mineralogical parameters for all mineral samples (including those of literature data). It contains: mineral name, chemical formula, space group, number of molecules per unit cell, and the references where these parameters were found. Figure 5 shows the procedure established for the phase determination based on the Raman spectrum recorded from an unknown geological sample.

CONCLUSION

A database for standard Raman spectra of minerals and related inorganic crystals has been established. The standard spectra were obtained under a practical measuring scheme, which was devised on the basis of the vibrational mode analysis for the main types of minerals. The spectral measurements were performed on a Raman spectrometer that was systematically calibrated before use. All recorded spectra were carefully corrected and examined. The standard samples used in this database cover the main types of minerals in terms of composition and structure. The spectral data collected from the literature

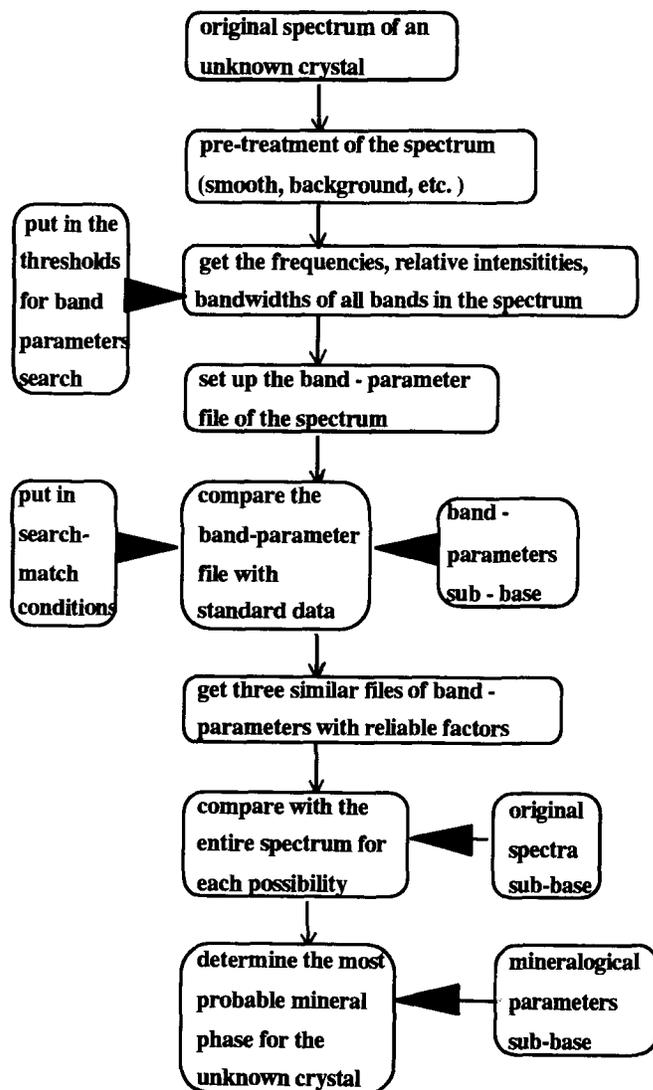


FIG. 5. Phase-identification procedure by using this standard Raman spectra database.

were used to compensate for some of the lack of data due to experimental difficulties. This database and its search/match program have been written to be run on IBM-PC/AT or compatible computers. After data format standardization, the Raman spectra recorded on any commercial Raman spectrometer could be used directly to compare with the standard data of this database.

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