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Extended library

Volume 1

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Extended library

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## Preface

Infrared (IR) spectroscopy as a method of analysis of molecular structures and identification of chemical compounds was first used at the end of the nineteenth century, when the relationship between absorption of IR radiation and vibrations of atoms in molecules had been established. At present this method is widely used in organic chemistry (for the identification of substances and chemical groups), in polymer chemistry (for the investigation of structural features of macromolecules), in study of surfaces, identification of molecules and investigation of vibration–rotation dynamics in gases, in matrix isolation studies, in the field of semiconductor microelectronics, etc. (see Barnes and Orville-Thomas 1977). However, IR spectroscopy is not widely adopted as a method for the identification of mineral species which is mainly due to the absence of sufficiently complete reference books and databases in this area.

The book “The Infrared Spectra of Minerals” (Farmer 1974) is still the most popular reference book on the IR spectra of minerals. However, as the book was published in 1977, it is now out of date. It contains only several hundred IR spectra of minerals. Since 1977, the number of known mineral species has doubled. At present it is close to 4,800, and every year it increases by 60–100 entries. What is more important, since 1977, there was a substantial expansion of knowledge on many minerals, their crystal chemistry, taxonomy and nomenclature. Many crystal-chemical formulae have been revised.

Recently a library of IR spectra of inorganics (NICODOM IR Inorganics 2006) was published. It contains 600 spectra of minerals from the National Museum in Prague, Czech Republic; the number of mineral species presented in this library is no more than 400. The identity of samples was verified by X-ray diffraction analysis. IR spectra of several hundreds of minerals have been published by H. Mönke (1962–1966), Boldyrev (1976) and Peng Wenshi (1982). However, these publications do not contain any analytical data for reference samples. IR spectra of separate classes, groups or families of minerals and synthetic inorganic compounds are presented in numerous publications (Weir 1966; Nekrasov 1970; Potter and Rossman 1979; Pechkovskii et al. 1981; Melnikova et al. 1985; Chukanov and Kumpanenko 1988, 2012a; Čejka 1999).

The creation of a more representative library of IR spectra of minerals was planned by A.S. Povarennykh, but his untimely decease in 1986 prevented the realization of this project.

This book is the result of an almost 30-year work of the author during which about 150 new minerals have been discovered. The library contains 3,309 IR spectra of about 2,000 minerals (including spectra of 237 holotype samples accompanied by their detailed characterization). The main goal of this book is to present a representative library of IR absorption spectra of mineral species together with additional data on each sample including locality, general appearance and mineral association. In most cases, analytical data (empirical formulae *e.a.*) are given. The library of IR spectra of minerals could be useful for specialists in inorganic chemistry and inorganic materials (cements, ceramics, glasses, microporous materials, etc.). In addition, in the next chapter some modern trends in IR spectroscopy of minerals and some new data and approaches are discussed.

The general theory of vibrational spectroscopy and experimental methodics of infrared spectroscopy as applied to minerals are beyond the scope of this book. These aspects are considered in numerous publications (Farmer 1974; Povarennykh 1978; Smith 1979, Stuart 2004; Nakamoto 2008; Theophanides 2012).

This work would be impossible without the help of numeral researchers. The long-time collaboration with Prof. I.V. Pekov was most important. Reference samples and valuable analytical data were kindly granted by B.V. Chesnokov, A.P. Khomyakov, G.A. Sidorenko, S.V. Malinko, A.V. Voloshin, A.I. Brusnitsyn, A.E. Zadov, D.I. Belakovskiy, Yu. P. Menshikov, R. Ďuďa, V.Yu. Karpenko, L.A. Pautov, P.M. Kartashov, Z.V. Shlyukova, A.G. Bazhenov, D.A. Kleimenov, D. Atencio, V.V. Subbotin, N.V. Ledenyova, A.M. Skrigitil', A.N. Sapozhnikov, E. Jonssen, S. Jancev, M.M. Moiseev, O.A. Ageeva, V.V. Rudnev and many other mineralogists, as well as mineral collectors, of which the contribution of W. Schüller, B. Ternes, G. Blass, R. Allori, M.N. Murashko, A.V. Kasatkin, G. Möhn, C. Schäfer, B. Otter, J. Hyršl and P. Paananen is most appreciated. The collaboration with crystallographers R.K. Rastsvetaeva, S.V. Krivovichev, N.V. Zubkova, D.I. Pushcharovskiy, S.M. Aksenov, E. Tillmanns, S. Merlino, M. Pasero, G. Ferraris, F. Nestola, S.N. Britvin, O.I. Siidra, O.V. Jakubovich, N.A. Yamnova and K.A. Rozenberg, as well as with specialists in different areas of geosciences and analytical methods (G. Raade, P. Voudouris, A. Magganas, A. Katerinopoulos, J. Göttlicher, A.N. Nekrasov, K.V. Van, A.A. Virus, L.A. Levitskaya, O.V. Karimova, A.S. Astakhova, L.A. Korshunova), was especially fruitful. All of them are kindly appreciated.

A significant contribution to the editing of figures was made by A.D. Chervonnyi. Editorial work of S.A. Vozchikova and S.M. Orlova in part of the preparation of illustrations was also significant.

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## 1.1 The Discrete Approach

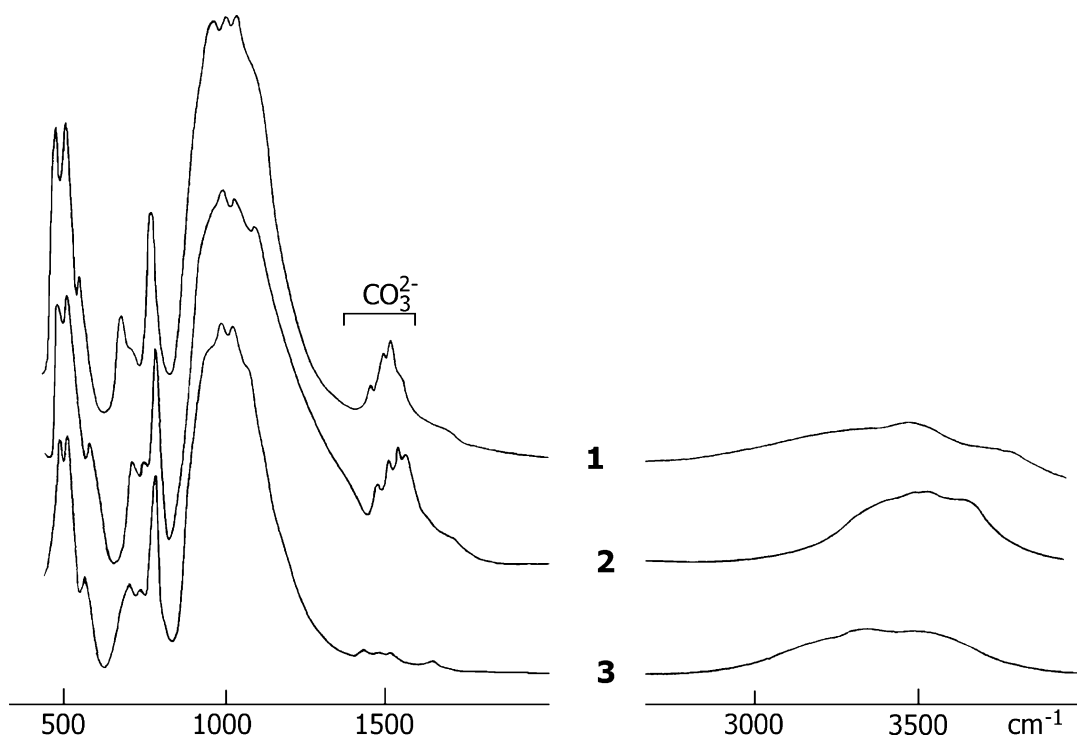
Traditionally, the application of IR spectroscopy in mineralogy is reduced to the determination of wavelengths or frequencies of *discrete absorption maxima*. These values are brought in correspondence with normal vibrations of different chemical bonds or groups of atoms forming covalent bonds – complex anions (e.g.  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SiO}_4^{4-}$ , and  $\text{Si}_2\text{O}_7^{6-}$ ), polyatomic cations ( $\text{H}_3\text{O}^+$ ,  $\text{NH}_4^+$ ,  $\text{UO}_2^{2+}$ , etc.), neutral molecules ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ), as well as lattice vibrations of infinite chains, layers or frameworks as parts of crystal structures of minerals. Another approach, also based on the use of discrete band maxima, is based on correlations between vibration frequencies and different characteristics of minerals (hydrogen bond strengths, degree of isomorphous substitutions, etc.). In this section, we consider several examples of the application of this approach to the investigation of structural features of minerals.

A customary application of IR spectroscopy for the investigation of minerals is the identification of different groups of atoms by their characteristic absorption bands. The ranges of frequencies of characteristic vibrations of most important coordination polyhedra and complex anionic groups are listed by Miller and Wilkins (1952) and Povarennykh (1978). The identification of cationic and anionic isolated groups and polyhedra containing elements with low atomic numbers (H, Li, Be, B, C, O, N) is most important because

the determination of these components by electron microprobe analysis is difficult or impossible. However, in many cases such groups can be easily determined by their absorption in characteristic IR ranges. The individuality of numerous new mineral species approved by the IMA Commission on New Minerals, Nomenclature and Classification during last decades has been first revealed by means of IR spectroscopy. Several examples are given below.

Eudialyte-group minerals are trigonal zircon- and titanosilicates characterized by very complex and variable crystal-chemical features (Johnsen et al. 2003). Their general crystal-chemical formula is  $N(1)_3N(2)_3N(3)_3N(4)_3N(5)_3M(1)_6M(2)_{3-6}M(3)M(4)Z_3[\text{Si}_{24}\text{O}_{72}]\text{O}'_{4-6}\text{X}_2$  where  $N(1-5) = \text{Na}, \text{H}_3\text{O}^+, \text{K}, \text{Sr}, \text{REE}, \text{Y}, \text{Ba}, \text{Mn}, \text{Ca}$ ;  $M(1) = \text{Ca}, \text{Mn}, \text{REE}, \text{Na}, \text{Sr}, \text{Fe}$ ;  $M(2) = \text{Fe}, \text{Mn}, \text{Na}, \text{Zr}, \text{Ta}, \text{Ti}, \text{K}, \text{Ba}, \text{H}_3\text{O}$ ;  $M(3)$  and  $M(4) = \text{Si}, \text{S}, \text{Nb}, \text{Ti}, \text{W}, \text{Na}$ ;  $Z = \text{Zr}, \text{Ti}, \text{Nb}$ ;  $\text{O}' = \text{O}, \text{OH}, \text{H}_2\text{O}$ ;  $\text{X}(1)$  and  $\text{X}(2) = \text{Cl}, \text{F}, \text{H}_2\text{O}, \text{OH}, \text{CO}_3, \text{SO}_4, \text{AlO}_4, \text{MnO}_4$ . Usually these minerals are Cl-dominant in the sites  $\text{X}(1)$  и  $\text{X}(2)$  situated around the axis of threefold symmetry.  $\text{CO}_3^{2-}$ -dominant minerals of this group with different occupation of  $N$ -sites, mogovidite and golyshchite have been discovered recently in the Kovdor massive of alkaline-ultramafic rocks and carbonatites, Kola peninsula (Chukanov et al. 2005a). IR spectra of these minerals contain series of absorption bands in the range from 1,350 to 1,550  $\text{cm}^{-1}$  (Fig. 1.1).

A cancrinite-group mineral kyanoxalite,  $\text{Na}_7(\text{Al}_{6-5}\text{Si}_{6-7}\text{O}_{24})(\text{C}_2\text{O}_4)_{0.5-1}\cdot 5\text{H}_2\text{O}$ , has been



**Fig. 1.1** IR spectra of high-calcium eudialyte-group minerals from alkaline pegmatites of the Kovdor massif: (1) mogovidite ( $\text{CO}_3^{2-}$ -dominant), (2) golyshevite ( $\text{CO}_3^{2-}$ -dominant) and (3) feklichevite ( $\text{Cl}^-$ -dominant)

first determined as a new mineral species different from cancrinite,  $(\text{Na,Ca})_{7-8}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{CO}_3)_{1-2}\cdot 2\text{H}_2\text{O}$ , by characteristic IR bands of oxalate groups at 1,713, 1,373 and  $817\text{ cm}^{-1}$  (Figs. 1.2 and 1.3).

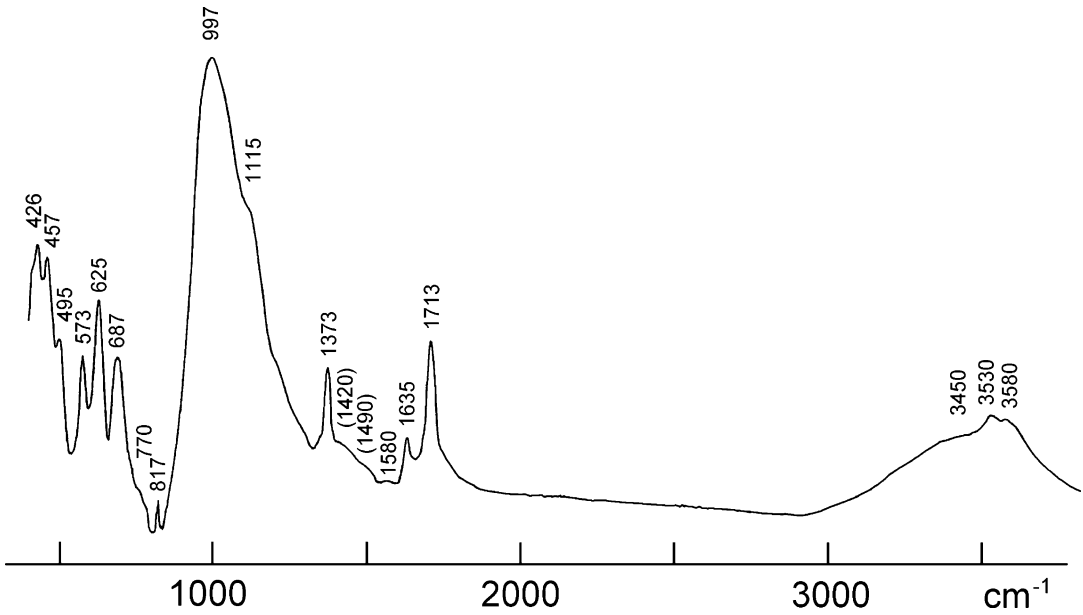
Similarly, the presence of  $\text{NH}_4^+$  groups in the first ammonium arsenate mineral of the autunite group uramarsite discovered in the Bota-Burum U deposit, Southern Kazakhstan, was detected by characteristic bands in the ranges 1,400–1,500 and  $2,800\text{--}3,200\text{ cm}^{-1}$  (Sidorenko et al. 2007, see Fig. 1.4). Earlier this mineral was considered as trögerite.

The *factor group method* for calculation of the symmetry properties, and selection rules for vibrational modes of crystals with known structures, has been reviewed by DeAngelis et al. (1972). The selection rules for each irreducible representation of the factor group are determined by noting the transformation properties for the dipole moment operator (for IR activity) or the polarizability tensor (for Raman activity). This method is effective only in case of simplest structures. In most cases,

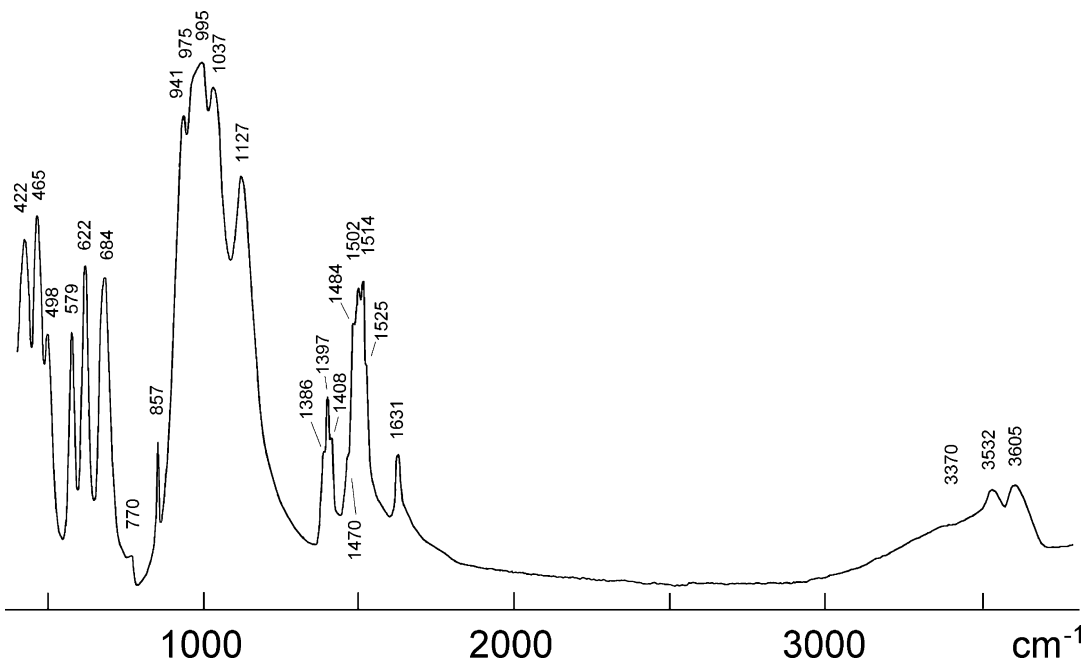
the determination of the number of active modes in IR spectra of minerals is impossible due to the overlapping of spectral bands, resonance splitting and different factors distorting translational symmetry of real crystals (solid solutions involving different complex anions, alteration of different kinds of stacking of layers, local defects, etc.). For this reason, the interpretation of vibrational spectra of crystalline solids has been limited largely to empirical approaches.

The wavenumber range approximately between 400 and  $1,700\text{ cm}^{-1}$  is called the *fingerprint region*. Usually IR spectrum in this region contains very complicated series of overlapping bands. The importance of the fingerprint region is that each mineral species produces a different pattern.

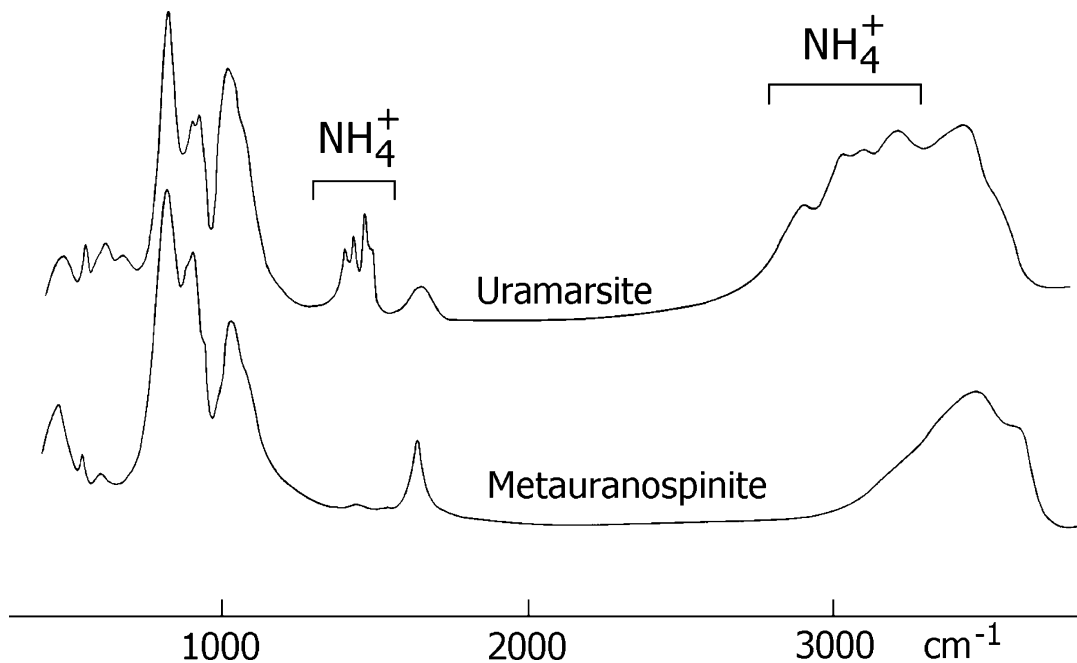
*Symmetry lowering* accompanied by the transformation of structural sites into groups of non-equivalent sites can result in the splitting of corresponding absorption bands. This phenomenon is very typical for IR spectra of minerals. Several examples are considered below.



**Fig. 1.2** IR spectrum of kyanoxalite from Alluaiv Mt., Lovozero alkaline massif, Kola peninsula, Russia (After Chukanov et al. 2011)



**Fig. 1.3** IR spectrum of typical cancrinite from Vishnevye Mts., Urals, Russia (After Chukanov et al. 2011)

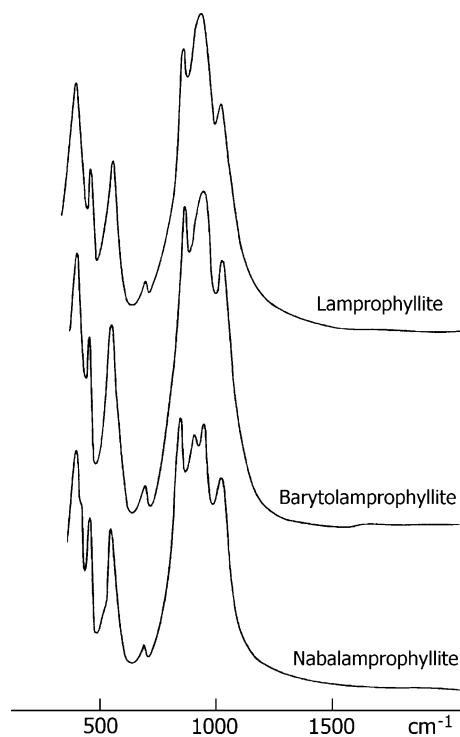


**Fig. 1.4** IR spectra of uramarsite and metauranospinite (After Sidorenko et al. 2007)

IR spectrum of nabalamprophyllite  $\text{Ba}(\text{Na},\text{Ba})\{\text{Na}_3\text{Ti}[\text{Ti}_2\text{O}_2\text{Si}_4\text{O}_{14}](\text{OH},\text{F})_2\}$  (Chukanov et al. 2004) is clearly different from the spectra of lamprophyllite and barytolamprophyllite in a pronounced doublet  $921 + 954 \text{ cm}^{-1}$  in the range of Si–O–stretching vibrations (Fig. 1.5). The splitting of the IR band in this case is a result of lowered symmetry. In centrosymmetric minerals of the lamprophyllite–barytolamprophyllite solid-solution series  $(\text{Ba},\text{Sr})_2\{\text{Na}_3\text{Ti}[\text{Ti}_2\text{O}_2\text{Si}_4\text{O}_{14}](\text{OH},\text{F},\text{O})_2\}$  (space group  $C2/m$ ), the groups  $\text{Si}_2\text{O}_7$  are equivalent, whereas in nabalamprophyllite (space group  $P2/m$ ) there are two types of  $\text{Si}_2\text{O}_7$  groups as a result of the ordering of interlayer cations Na and Ba.

Eveslogite (monoclinic) and yuksporite (orthorhombic) are very close in chemical composition, powder X-ray diffraction patterns and physical properties. However, their identification is easy due to characteristic additional splitting of some bands in the IR spectrum of eveslogite as compared to that of yuksporite (Fig. 1.6) (Chukanov et al. 2008).

The crystal structures of the roscherite-group minerals are based on a heteropolyhedral



**Fig. 1.5** IR spectra of lamprophyllite-group minerals