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Review

MINERALS FROM MACEDONIA
XXVIII. A TRIBUTE TO ACADEMICIAN GLIGOR JOVANOVSKI[◆]

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The present review covers the contributions of Academician Gligor Jovanovski and his co-workers in the field of minerals: their spectra, their structure and their investigations with analytical techniques. All together 60 entries were covered, starting with an early spectroscopic paper and ending with the beautiful book entitled MINERALS FROM THE REPUBLIC OF MACEDONIA WITH AN INTRODUCTION TO MINERALOGY.

The contributions are reviewed chronologically in each of the sections entitled ***Spectroscopic Papers*** and ***Other Papers Devoted to Minerals***. Some of the entries contain illustrations (25 in number), primarily, parts of the recorded infrared and/or Raman spectra. The cover of the above mentioned book is shown in Fig. 25.

In the list of references, complete titles are included so that a simple look at a given reference enables the reader to grasp the essentials of the content of the paper or a conference contribution.

Keywords: infrared (IR) and Raman spectroscopy; Fourier transform infrared (FTIR); atomic absorption spectrometry (AAS); atomic emission spectrometry with inductively coupled plasma (AES-ICP); neutron activation analysis; powder X-ray diffraction

МИНЕРАЛИ ОД МАКЕДОНИЈА
XXVIII. ОМАЖ ЗА АКАДЕМИКОТ ГЛИГОР ЈОВАНОВСКИ

Во овој прегледен труд се анализирани објавените прилози на академик Глигор Јовановски и неговите соработници од областа на минералите: нивните спектри, нивната структура и нивното изучување со аналитички техники. Опфатени се вкупно 59 статии и соопштенија и една книга, почнувајќи со една рана статија и завршувајќи со прекрасната книга чиј наслов е MINERALS FROM THE REPUBLIC OF MACEDONIA WITH AN INTRODUCTION TO MINERALOGY.

Во секоја од секциите (нивните наслови на англиски се ***Spectroscopic Papers***, т.е. *спектроскопски статии* и ***Other Papers***, т.е. *други статии*) прифатените трудови се разгледувани хронолошки. За некои опфатени трудови се дадени и слики (вкупно 24), предимно делови од снимените инфрацрвени или рамански спектри. Корицата на погоре спомнатата книга е покажана на Fig. 25.

Во листата на цитирани трудови се дадени нивните целосни наслови, така што со еден поглед читателот може да ги долови битните елементи содржани во дадената статија или соопштение.

Клучни зборови: минерали од Република Македонија; инфрацрвена (IR) и раманска спектроскопија; фурие трансформна инфрацрвена спектроскопија (FTIR); атомска апсорпциона спектрометрија (AAS); атомска емисиона спектрометрија со индуктивно спрегната плазма (AES-ICP); неутронска активациона анализа; прашкаста рендгенска дифракција

[◆] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

1. PROLEGOMENA

It is both rewarding and difficult to write a review article about the contributions of Academician Gligor Jovanovski to the study of minerals from Macedonia.

It is rewarding because these contributions are exceptional scientifically and, in addition, serve as a clear sign for the existence of a country named, despite denials from some quarters, Macedonia or, more fully, the Republic of Macedonia.

On the other hand, it is difficult to briefly summarize the content of around 60 scientific papers, published mainly in distinguished international journals and cited many, many times in the scientific literature.

Since this review article is published in the present special issue dedicated to Academician Gligor Jovanovski, accepting the challenge I now try my best to give the reader a fair presentation of the content of the papers on minerals from Macedonia and a deserved tribute to their author.

It should be noted that the work on the minerals from Macedonia does not cover all research interests of Academician Jovanovski and that the reviewed papers deal with studies in several scientific fields. The early papers dedicated to the study of minerals from Macedonia are spectroscopic in nature (at first by conventional infrared spectroscopy and later enriched by the use of Raman and FTIR spectroscopy). Such a state of matters is a natural consequence of the availability of spectroscopic equipment, on the one hand, and the active spectroscopic work at the Institute of Chemistry of the Faculty of Science, on the other. Needless to say, a number of co-workers from the Institute of Chemistry actively participated throughout in the studies by Academician Jovanovski as may be seen in the list of references given below.

Without having X-ray diffraction instrumentation on hands, Jovanovski devoted a respectable portion of his research of minerals to crystallographic (X-ray) studies. Clearly, such studies would not have been possible without the openhanded cooperation of researchers from Zagreb and Uppsala and the perseverance of Jovanovski himself.

As the instrumental basis of the Institute of Chemistry grew and diversified and as an active research practice using the corresponding techniques took place, in his portfolio Jovanovski included the work with atomic absorption spectrometry (AAS), atomic emission spectrometry with inductively coupled plasma (AES-ICP) and neutron activation analysis. Again, some of these studies were carried out in cooperation with researchers from institutions where the corresponding equipment was available.

2. SPECTROSCOPIC PAPERS

The early spectroscopic papers dealt mainly with minerals found in the ore deposit Alšar (or Allchar,) of which lorandite (Fig. 1) is the most interesting one. The importance of this mineral, reach in thallium, stems from the expectation that it can be used as a suitable dosimeter for solar neutrinos and, as a consequence, the large-scale international project LOREX (from ***Lor***andite ***Ex***periment).

Fig. 1. Lorandite

Thus, in the paper by Trajkovska, Šoptrajanov, Jovanovski and Stafilov [1] the infrared spectra (Fig. 2) recorded at room temperature (RT) and the boiling point of liquid nitrogen (LNT) and the RT Raman spectra of lorandite, as well as those of realgar and orpiment, were recorded and discussed.

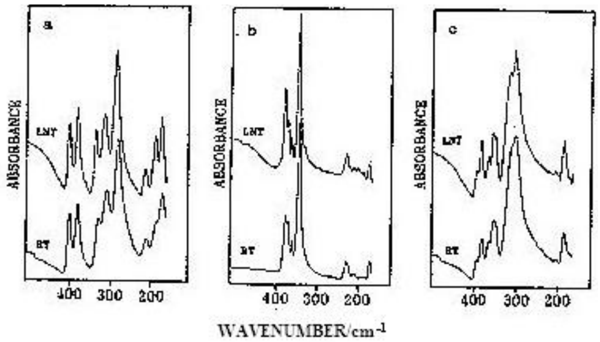

Fig. 2. IR spectra of lorandite (a), realgar (b) and orpiment (c)

The novelty in the paper concerns the interpretation of the temperature shifts of the bands at

401 and 381 cm^{-1}, on the one hand, and that of the trio of bands at lower frequencies, on the other. The higher-frequency band was assigned to vibrations with mainly As–S$_{t}$ character, whereas the bands at lower frequency are likely to result from vibrations with mainly As–S$_{b}$ character (the subscripts "t" and "b" refer to "terminal" and "bridging" role of the sulfur atoms in the structure). In another paper by the same group of authors [2], studied were the infrared spectra of lorandite and realgar recorded from KBr pellets on a conventional infrared instrument and from CsI pellets on a Fourier transform infrared (FTIR) one (Fig. 3).

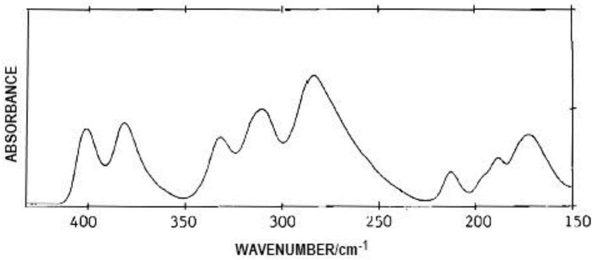

Fig. 3. Fourier-transform infrared spectrum of lorandite

Considering the AsS$_3$ pyramids in the structure as the simplest vibrational units, assignments were made for the As–S$_{t}$ stretches and for the symmetric and antisymmetric S$_{b}$–As–S$_{b}$ stretchings (the description being only approximate). It should be noted that the modes described, tentatively, as S–As–S deformation could, perhaps, be equally well described as As–S–As bendings.

The vibrational (infrared and Raman) spectra of $\text{M}^{\text{I}}\text{M}^{\text{III}}\text{S}_2$ type synthetic minerals (with M^{I} = Tl or Ag and M^{III} = As or Sb) were recorded and compared with the corresponding spectra of $\text{M}^{\text{III}}{}_2\text{S}_3$ type minerals, orpiment (As$_2$S$_3$) and stibnite (Sb$_2$S$_3$) [3]. The spectra of the three As-containing minerals (orpiment, lorandite and smithite (AgAsS$_2$)) are rather similar, as are those of the three Sb-containg minerals (stibnite, weissbergite – TlSbS$_2$, and miargyrite – AgSbS$_2$), despite differences in the crystal structures. The spectra of this group of compounds were reinvestigated much later in [4].

The Raman study of sulfide minerals (stibnite, realgar, orpiment and lorandite) from the Alšar deposit [5] revealed differences between the spectra of single crystals of stibnite and those of the polycrystalline samples. It was concluded that the differences in the appearance could be ascribed to either different polarization effects or to the extent of grinding.

Infrared spectroscopy was used in [6], as a suitable method to estimate the lorandite content in natural minerals of realgar and of the realgar content in crystals of lorandite.

After the end of the LOREX project (one of the reasons for this was the fact that the quantity of lorandite selected from the ore was not nearly that which was, theoretically, required), the studies on lorandite by Jovanovski and coworkers ceased. However, the studies on vibrational spectra of **minerals** were far from being abandoned.

Thus, the vibrational spectra of natural gypsum and barite were studied and interpreted in [7] and those of some phosphate minerals were investigated in the communication [8]. The latter communication is important since the FTIR spectrum of a mineral believed to be struvite is, in fact, of newberyite so that the sample identity was wrongly determined.

The FTIR spectra of calcite (1) and aragonite (2) were recorded (Fig. 4) [9]. Because of the operation of selection rules, a band at 1083 cm^{-1} is present in the spectrum of aragonite in a spectral region where calcite shows no absorption. This band was used to determine the content of calcite in aragonite and of aragonite in calcite. A linear relationship exists between the integrated band intensities of mixtures of calcite and aragonite and the mass fraction of the "foreign" component in mixtures of the two minerals.

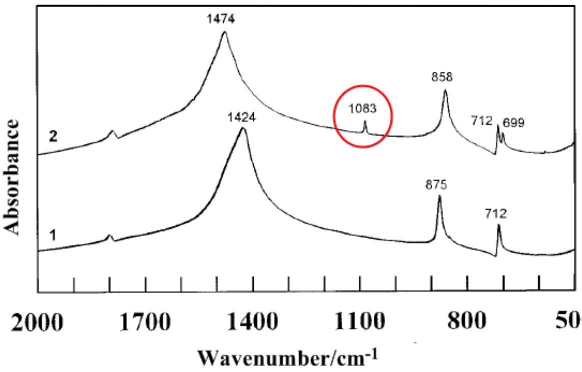

Fig. 4. Infrared spectra of calcite (1) and aragonite (2)

The discrimination between some carbonate minerals by Fourier transform infrared spectroscopy was the main goal of paper [10].

Gypsum, barite and their synthetic analogues were studied by FTIR and Raman spectroscopy in [11]. It was found that the spectra of natural and synthetic CaSO$_4\cdot$2H$_2$O were very similar, whereas slight frequency differences were present when the spectra of natural and synthetic BaSO$_4$ were compared.

The difficulties connected with the selection, separation, purification, identification and characterization of several sulfide minerals (galena – PbS, sphalerite/wurzite – (Zn,Fe)S, pyrite – FeS_2, and chalcopyrite – $CuFeS_2$) from the Sasa, Bučim, Zletovo and Toranica localities in Macedonia were discussed in [12]. The identification was based on the comparison of the results from the study in question (obtained by the use of infrared and Raman spectroscopy and powder X-ray diffraction) and the relevant literature data on the corresponding mineral species originating from all over the world. The Raman spectra of galena, wurzite, pyrite and chalcopyrite from the localities in eastern Macedonia were studied in the communication [13].

The rhombohedral carbonates originating from Macedonia were studied by Fourier transform infrared spectroscopy in ref. [14]. In the FT spectra of the calcite-group minerals (calcite – $CaCO_3$; magnesite – $MgCO_3$ and siderite – $FeCO_3$), on the one hand, and those of the dolomite one [dolomite – $CaMg(CO_3)_2$, and kutnahorite – $CaMn(CO_3)_2$], on the other, significant frequency differences were observed, especially in the case of the infrared active ν_4 mode (cf. Fig. 5 for some data).

Mineral	Characteristics of the cation			Average cation–oxygen distance / Å	Covalent character of the cation–oxygen bond / %	Vibrational frequencies / cm^{-1}		
	Effective radius / Å	A_r	CN			ν_3	ν_2	ν_4
Magnesite $MgCO_3$	0.72	24.31	6	2.14	29	1450	887	748
Dolomite $CaMg(CO_3)_2$	$(0.86)_{av}$	32.20	6	2.25	24	1438	881	729
Siderite $FeCO_3$	0.78	55.85	6	2.18	31	1422	866	737
"Siderite" $FeCO_3$ with 46.2% $MnCO_3$						1415	866	732
Calcite $CaCO_3$	1.00	40.08	6	2.37	19	1424	875	712
Aragonite $CaCO_3$	1.18	40.08	9	2.49	19	1474	858	712

Fig. 5. Spectroscopic data of the studied rhombohedral carbonates

Identification of the silicate varieties and their localities using FTIR spectroscopy was attempted in the paper [15] by G. Jovanovski, B. Boev, P. Makreski, M. Najdoski and G. Mladenovski. An overview of the basic morphological, physicochemical and crystallographic characteristics of the most typical silicates is given and colored pictures of all studied silicate minerals are presented.

Six sulfate minerals were identified by infrared and Raman spectroscopy in [16]. It turned out that a mineral, previously characterized as anhydrite is actually gypsum, although its outside appearance is quite different from that of samples of gypsum collected at various locations in Macedonia including Debar where the wrongly identified mineral was found.

The infrared spectra at room temperature (RT) and the boiling temperature of liquid nitrogen (LNT) of $M^I_3M^{III}S_3$ type minerals where M^I is either Tl or Ag and M^{III} is As or Sb were studied in [17] and reinvestigated by P. Makreski, G. Jovanovski, B. Minčeva-Šukarova, B. Šoptrajanov, A. Green, B. Engelen and I. Gržetić in ref. [18] where the vibrational (Raman and far infrared) spectra of two thallium synthetic minerals, ellisite (Tl_3AsS_3) and stibioellisite (Tl_3SbS_3), were recorded and analyzed. To facilitate the interpretation, two further synthetic minerals, proustite (Ag_3AsS_3) and pyrargyrite (Ag_3SbS_3) were included in the study. The spectra of all four synthetic minerals were compared with the spectra of naturally occurring orpiment (As_2S_3) and stibnite (Sb_2S_3).

The article [19] (tenth in the series with a common main title MINERALS FROM MACEDONIA) is interesting mainly because in it the FTIR spectroscopy was combined with atomic absorption spectrometry (AAS), atomic emission spectrometry with inductively coupled plasma (AES-ICP)[*] and powder X-ray diffraction. The combination of four powerful instrumental techniques and classical chemical analysis was employed in the processes of separation and identification of a number of oxide minerals (hematite, Fe_2O_3; magnetite, Fe_3O_4; limonite, FeOOH; goetite, α-FeOOH; corundum, Al_2O_3; rutile, TiO_2; chromite, $FeCr_2O_4$). The analyzed samples were collected from eight mineral deposits (Pehčevo, Alšar, Raduša, Veselčani, Sivec, Košino, Ržanovo and Damjan).

The dependence of the color of quartz and opal on the composition of trace elements was

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[*] It is strange that the term *emission atomic spectrometry with induced coupled plasma* was used in the abstract.

studied in [20] by AAS spectrometry and by FTIR and micro-Raman spectroscopy.

It was shown that the infrared spectra could not give indications about the variations of the color of different quartz samples, but the complete chemical analysis showed that the trace elements are those responsible for the color of the mineral samples. Thus, for example, the red color of the quartz and opal specimens is connected with the presence of Fe, the green ones contain significant amounts of Ni, the milky appearance is due to Ca and light or dark brown to black color originates from the presence of Al, Pb and Mn trace elements.

Fourier transform infrared spectroscopy was used in paper [21] to identify ten collected minerals from the Sivec mineral assemblage.

A series of articles deals with the vibrational spectra of silicates (nesosilicates [22], pyroxenes and pyroxenoids [23], amphiboles [24], sorosilicates [25], sheet silicate minerals [26], phyllosilicates [27], and cyclosilicates [28] collected from various localities in the Republic of Macedonia. As a rule, the recorded vibrational (infrared and Raman) spectra of various silicates were discussed and interpreted in terms of their structural characteristics. The most important crystallographic data (crystal system, unit cell parameters, number of structural units in the primitive unit cell and unit cell volume), as well as numerically presented powder X-ray diffraction patterns, were included [22–28] and discussed. Sometimes the detailed chemical composition of the studied minerals was also given. In all cases, assignments of the recorded and graphically presented infrared and Raman spectra were given.

Seven nesosilicate minerals: almandine – $Fe_3Al_2(SiO_4)_3$, spessartine – $Mn_3Al_2(SiO_4)_3$, zircon – $ZrSiO_4$, titanite – $CaTiOSiO_4$, olivine – $(Mg,Fe)_2SiO_4$, kyanite – Al_2OSiO_4, and staurolite – $Fe_2Al_9O_6(SiO_4)_4(OH)_2$, have been studied by infrared and Raman spectroscopy in [22]. The spectra were recorded (as examples, in Figure 6 and Figure 7 the IR and Raman spectra of almandine and spessartine are given and in Figure 8 the IR spectra of kyanite and staurolite are shown).

The spectra were interpreted, in terms of the vibrations of the SiO_4 structural units and by comparing the spectra of the samples collected in Macedonia (Pelagon, Lojane, Kozjak, Dunje, Ržanovo, Štavice) with the published data on the respective minerals collected in areas all over the world (the reasons behind such comparison lie in the belief that in naturally occurring minerals impurities may cause observable differences).

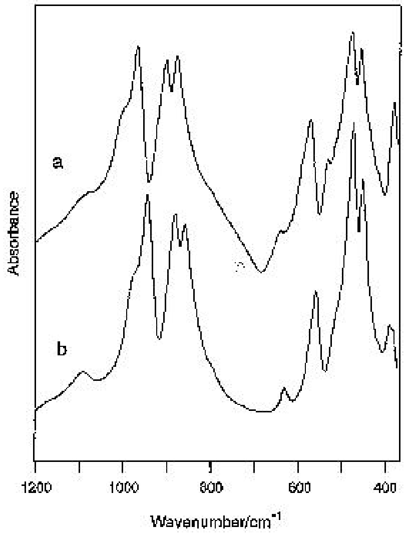

Fig. 6. IR spectra of almandine (a) and spessartine (b)

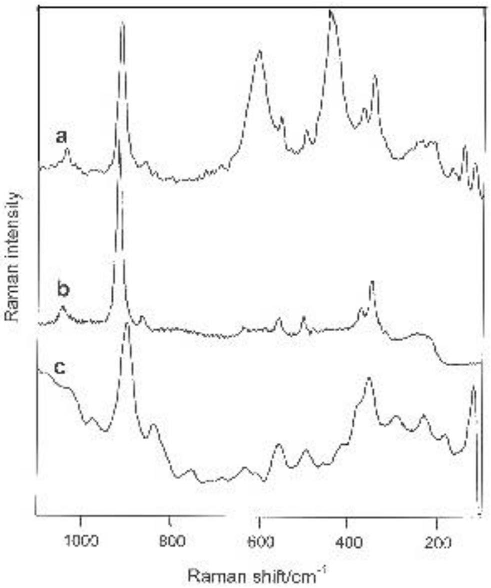

Fig. 7. Raman spectra of almandine (a and b) and spessartine (c)

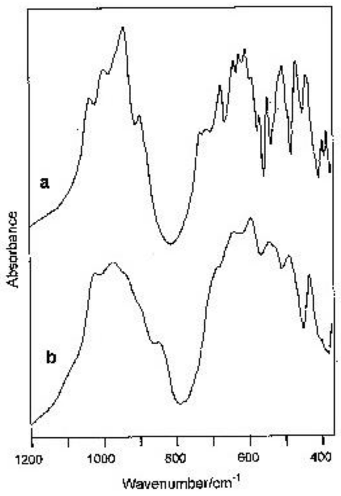

Fig. 8. IR spectra of kyanite (a) and staurolite (b)

Staurolite is unique among the studied minerals of this group because only in its structure OH groups are present and, understandably, the O–H stretching region (Fig. 9) was worth studying in the case of this mineral.

The most important crystallographic parameters of all seven minerals were listed and the structural differences and/or similarities were emphasized.

Since the bonds within the SiO_4 tetrahedra in the structure of the orthosilicates are considered to be much stronger than those between the silicate groups and the "outside" cations, it was reasonable to consider the SiO_4 groups as the main vibrating units and assign the spectra accordingly. Then the infrared bands at the highest frequencies (above 700 cm^{-1} or so) would be interpreted as due to the antisymmetric SiO_4 stretch, ν_3, while the strong Raman band around 900 cm^{-1} (when present) would certainly originate from the symmetric ν_1 stretch. The strong infrared bands originating from the bending ν_4 mode appear below 700 cm^{-1} and in the region below 500 cm^{-1} weak IR bands or shoulders due to the ν_2 bending mode are found in the spectra of almandine, spesartine, zircon, titanite and kyanite. Rather surprisingly, to this mode a *strong* band (at 417 cm^{-1}) is assigned in the infrared spectrum of olivine.

Expectedly, the infrared spectrum of staurolite is different from those of the other studied minerals, especially in the O–H stretching region where bands are present in the spectrum of this mineral (Fig. 9), but in the spectra of the remaining six studied minerals the region is empty.

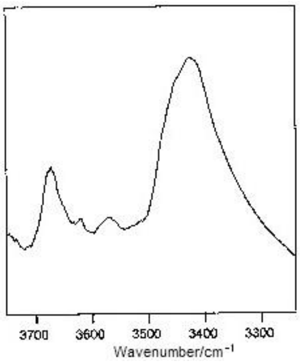

Fig. 9. The O–H stretching region in the IR spectrum of staurolite

The IR spectra of the pyroxenes augite – (Ca,Na)(Mg,Fe,Mn.Al)$(SiAl)_2O_6$, ferrojohannsenite Ca(Fe,Mn)Si_2O_6, and of carpholite $MnAl_2Si_2O_6(OH)_4$, [23], compared with the spectrum of quartz are shown in Figure 10.

The broad spectral bands were subjected to curve fitting, a clever procedure making it possible to "resolve" overlapped bands and determine the individual frequencies of the components which would be impossible to do otherwise.

This procedure has been employed in other cases as well (see below).

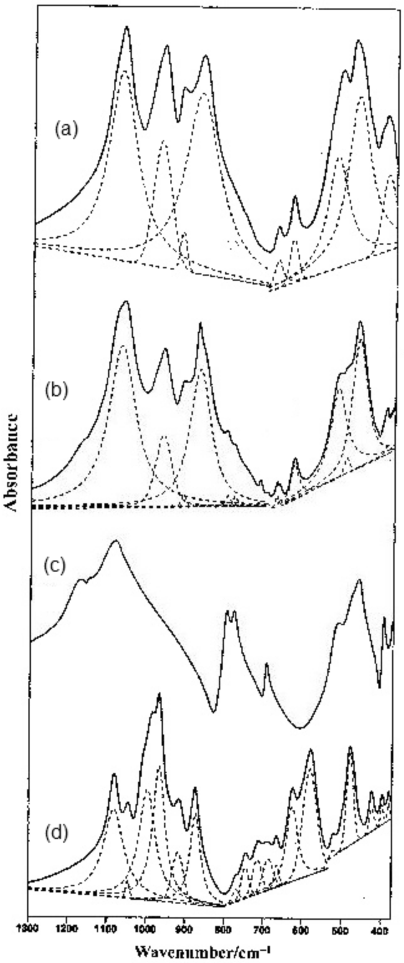

Fig. 10. Infrared spectra of augite (a), ferrojohannsenite (b), quartz (c) and carpholite (d). The spectrum of quartz is given for comparison and curve fitting has been performed in the case of the other three minerals.

The spectrum of carpholite is for the first time studied in some details in [23]. It should be noted that this mineral is the only studied pyroxene which contains OH groups as is evident from the spectrum in the O–H stretching region (Fig. 11).

Some commonly appearing amphiboles with a general formula $W_{0–1}X_2Y_5Z_8O_{22}(OH)_2$ were studied in ref. [24]. It was shown that the intensity and the number of IR bands in the O–H stretching region, especially after curve fitting, could serve for exact mineral identification.

Vibrational spectroscopy (IR and Raman) was used [25] to identify and characterize three sorosilicate minerals: epidote – $Ca_2Al_2(Fe^{3+}, Al)(SiO_4)(Si_2O_7)O(OH)$, collected from the Dunje locality, hemimorphite – $Zn_4(Si_2O_7)(OH)_2{\cdot}H_2O$, and ilvaite – $CaFe_2^{2+}Fe^{3+}(Si_2O_7)O(OH)$, picked up from the samples collected from the Sasa locality.

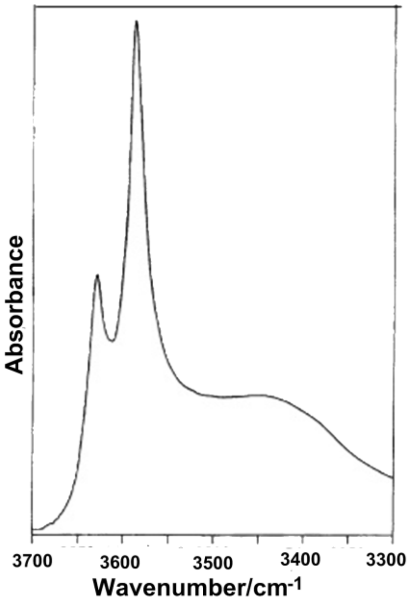

Fig. 11. Carpholite: the O–H stretching region

It should be mentioned that the Raman spectrum of ilvaite has not, apparently, been recorded so far, whereas spectra of the other two minerals are available, but not properly analyzed and discussed. Unfortunately, the recorded by us Raman spectrum of ilvaite is of poor quality and thus of little use for identification purposes. On the other hand, the intensity and especially the frequency of the IR bands in the O–H stretching region could serve as a reliable tool for discrimination between epidote and the isomorphous, but Fe-free, clinozoisite.

IR and Raman spectroscopy were used [26] as an identification tool for some sheet silicate minerals: chrysotile – $Mg_3Si_2O_5(OH)_4$, antigorite – $(Mg,Fe^{2+})_3Si_2O_5(OH)_4$, talc – $Mg_3Si_4O_{10}(OH)_2$, clinochore – $(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$, cymrite – $BaAl_2Si_2O_8{\cdot}H_2O$, and montmorillonite – $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$.

On the basis of the recorded vibrational spectra it is possible to distinguish between isomorphous chrisotile and antigorite and the presence or absence of a peak at ≈ 1630 cm^{-1} attributed to the H–O–H bending vibrations (Fig. 13) is indicative of presence or absence of H_2O molecules in the structure. Thus, cymrite and/or montmorilomite would not be mixed with minerals in whose spectra there are bands in the O–H stretching region (chrysotile, antigorite, talc or clinochore), but no band exists around 1630 cm^{-1}.

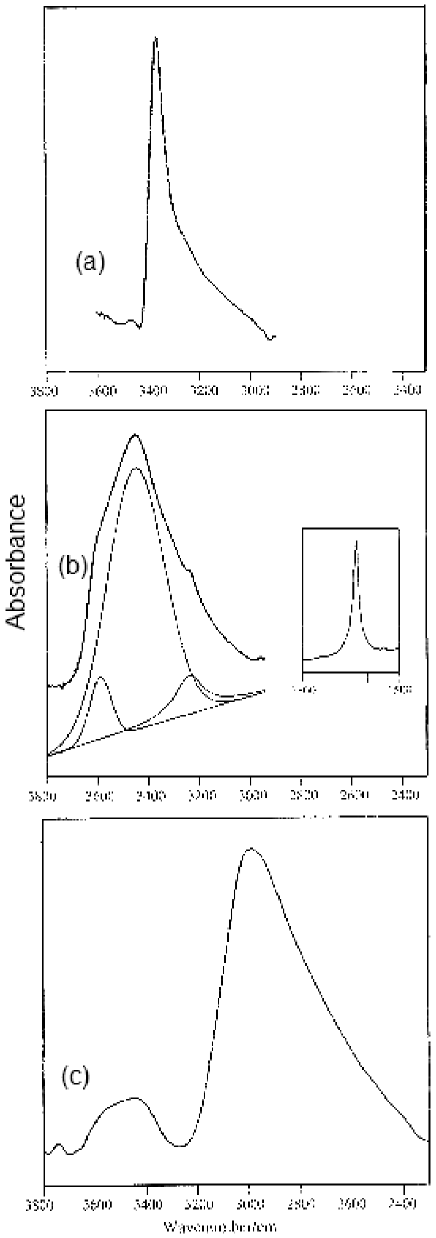

Fig. 12. Infrared spectra of epidote (a), hemimorphite (b) and ilvaite (c)

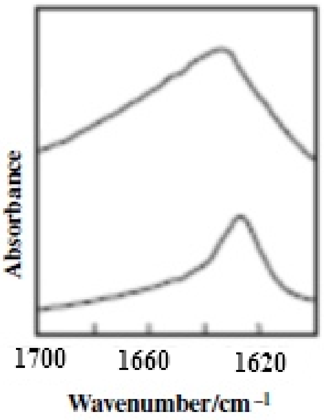

Fig. 13. Cymrite (top) and montmorillonite: the δ(HOH) region

The phyllosilicate minerals biotite – $K(Mg,Fe^{2+})_3$; muscovite – $KAl_2(Si_3Al)O_{10}(OH,F)_2$; phlogopite – $KMg_3(Si_3Al)O_{10}(F,OH)_2$; clinochore – $(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$ collected from various localities in the Republic od Macedonia (Dunje, Nežilovo, Pelagon, Čanište, Sivec) were studied by IR and Raman spectroscopy in [27]. The results of the study showed that Raman spectroscopy is more sensitive to compositional changes than IR.

Samples of beryl – $(Be,Mg,Fe)_3Al_2Si_6O_{18}$, and the tourmaline mineral schorl – $Na(Fe,Mg)_3Al_6(BO_3)_3Si_6O_{18}(OH,F)_4$, collected from Čanište (beryl) and Bonče (schorl) localities were studied in ref. [28]. The crystals were mechanically separated from the ore.

Although beryl is nominally anhydrous, the infrared spectra clearly show (Fig. 14) that water molecules are present in the existing channels of the structure of the mineral. In fact, two types of water molecules (type I and type II) have been identified and the bands attributable to the vibrations of these water types are marked correspondingly in Figure 14. In the inset of Figure 3 of ref. 28 (not shown here) a clear band due to the HOH bending of water type II is present, once again confirming the existence of such molecules in the channels of the structure.

The IR spectra of the mineral schorl in the 1500–850 cm^{-1} and 850–400 cm^{-1} regions are given as Figure 15. As seen, curve fitting was performed and four bands were identified in the former region and quite a number in the latter one.

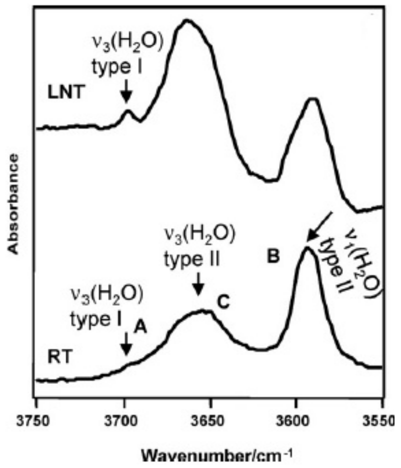

Fig. 14. The O–H stretching region in the IR spectrum of beryl

The frequencies of the bands together with their assignments and a comparison with the IR data of various tourmalines are given in a table in ref. [28].

Two papers [29, 30] bear the wording “spectra–structure characterization” or “spectra–structure correlation” in their titles. This may be a little misleading since the correlations between the spectroscopic and crystallographic data were present in the majority of previously discussed contributions.

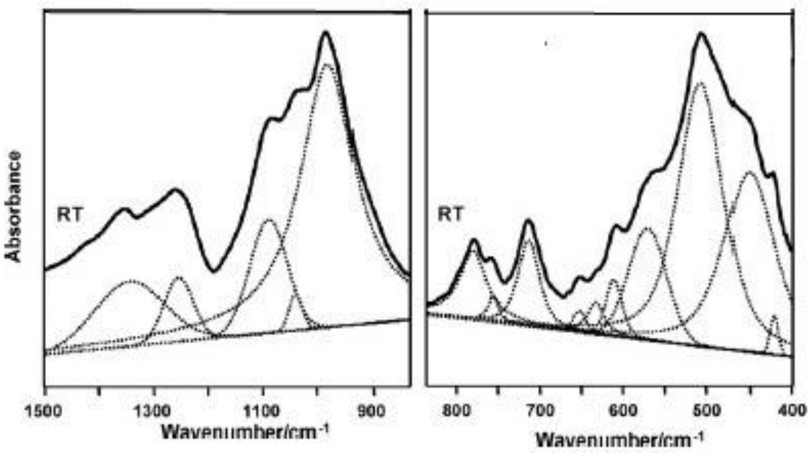

Fig. 15. Curve fitting of the features in the 1500–850 cm^{-1} (left) and 850–400 cm^{-1} regions (right) of the infrared spectra of the cyclosilicate schorl; the curve-fitting results are shown as dashed lines

In the first of these two papers [29] the spectra of the alkali feldspars albite – $NaAlSi_3O_8$, microcline – $KAlSi_3O_8$, and sanidine – $(K,Na)(Al,Si)_4O_8$, were recorded (Fig. 16). Also studied were the IR and Raman spectra of the zeolite type mineral stilbite – $NaCa_4Al_8Si_{28})_{72}\cdot 30H_2O$.

Despite their common structural characteristics, the appearance of the vibrational spectra of the three studied alkali feldspars makes it possible to discriminate between them (Fig. 16). At least some of the differences reflect the degree of disorder on going from microcline (highly ordered feldspar with well-resolved peaks in the spectrum) to sanidine (disordered feldspar and broad, ill-resolved peaks). Thus, the band around 650 cm^{-1} shifts the lower wavenumber values with increasing Al/Si disorder, whereas the band near 540 cm^{-1} shows an opposite trend being positioned at higher frequency in the spectrum of mineral in which the structural disorder is largest.

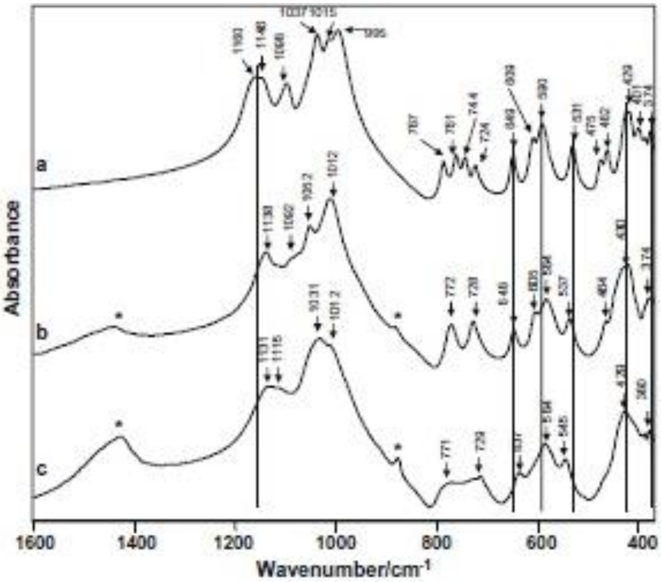

Fig. 16. Infrared spectra of tectosilicates: (a) albite, (b) microcline, (c) sanidine; the bands marked with asterisks originate from calcite impurities

In the case of the two isomorphous minerals grossular – $Ca_3Al_2(SiO_4)_3$, and uvarovite – $Ca_3Cr_2(SiO_4)_3$ sharing a common general chemical formula, $Ca_3Y_2(SiO_4)_3$, the most prominent spectral differences [30] are mainly due to the difference in the nature of the trivalent cations (Al^{3+} and Cr^{3+}). It seems that two different effects (different cation crystal field stabilization energy and the effect of cation masses and radii) working in opposite directions are responsible for the observed shifts of the SiO_4 stretching Raman band (blue shifted) and the corresponding infrared band (red shifted).

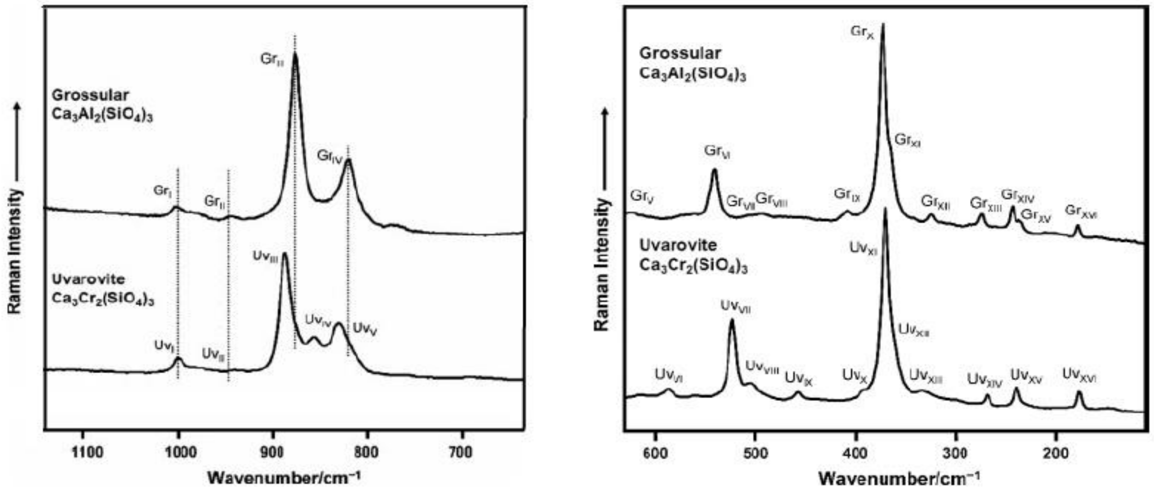

Fig. 17. Raman spectra of grossular and uvarovite (nesosylicates)

The vibrational spectra of the endemic mineral nežilovite (present only in the Nežilovo locality) were studied experimentally and theoretically in [31]. The Raman spectra were excited by two lines: 532 nm from a Nd:YAG laser and 632.8 nm from a He:Ne laser, whereas the IR spectra were recorded at transmittance mode. The theoretical basis for the assignment of the spectra was based on a pseudopotential plane-wave density functional theory (PW-DFT). The Raman spectra, as well as the higher-frequency region of the infrared spectra, resemble the corresponding spectra of the magnetoplumbite-group minerals, whereas the lower-frequency part of the IR spectra is similar to the corresponding region of barium ferrite.

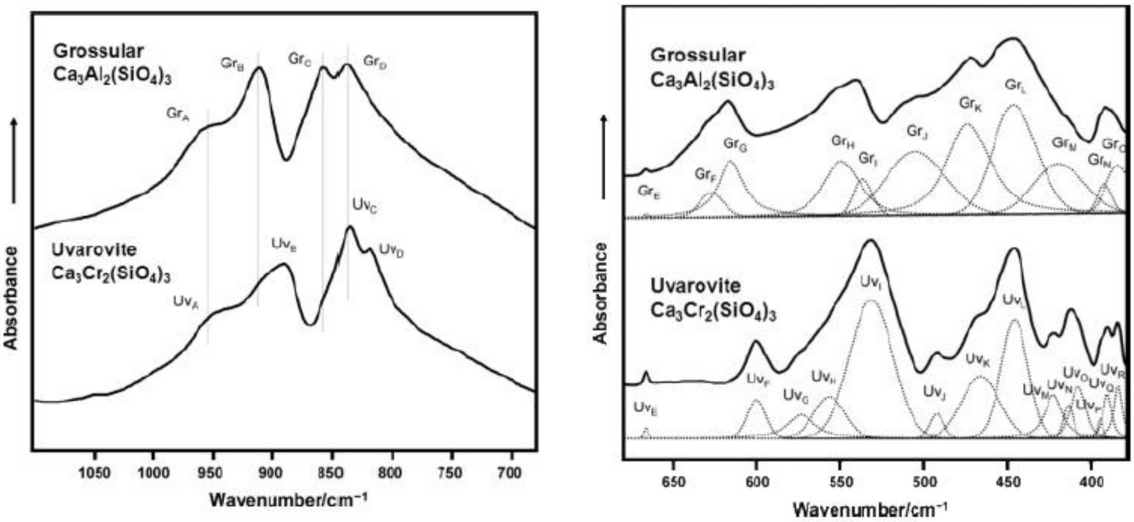

Fig. 18. Infrared spectra of grossular and uvarovite

The micro-Raman spectra of four extremely rare and endemic thallium sulfosalts, namely fangite (Tl_3AsS_4), vrbaite ($Tl_4Hg_3As_8Sb_2S_{20}$), raguinite ($TlFeS_4$) and rebulite ($Tl_5Sb_5As_8S_{22}$), from the Alšar deposit were presented (Fig. 19) for the first time ever (the minerals themselves are known for over 30 years) and discussed in the paper by P. Makreski, G. Jovanovski and B. Boev [32]. The composition of the investigated minerals, together with those of lorandite ($TlAsS_2$) and parapierrotite ($Tl(Sb,As)_5S_8$) were determined by scanning electron microscopy and energy dispensive spectrometry.

In spite of the structural differences between them, the spectra of the studied minerals exhibit rather high similarity, mainly because of the existence of XS_3 pyramidal and/or XS_4 tetrahedral vibrational units (X = As, Sb, Fe) as the main building blocks in their structures and by the rather close X–S distances in the XS_3 and/or XS_4 structural units. Yet, some spectral differences have been observed. Namely, the existence of only one type of FeS_4 tetrahedra (in raguinite) and one type of AsS_4 tetrahedra (in fangite) is manifested by the appearance of only one band due to the $\nu_1(XS_4)$ mode in their spectra, whereas the presence of two different types of As and Sb polyhedra (AsS_3 and SbS_3/SbS_4) in the structure of rebulite and AsS_3 and SbS_3 in vrbaite is manifested by the appearance of two bands related to the $\nu_1(XS_4)$ modes in their spectra.

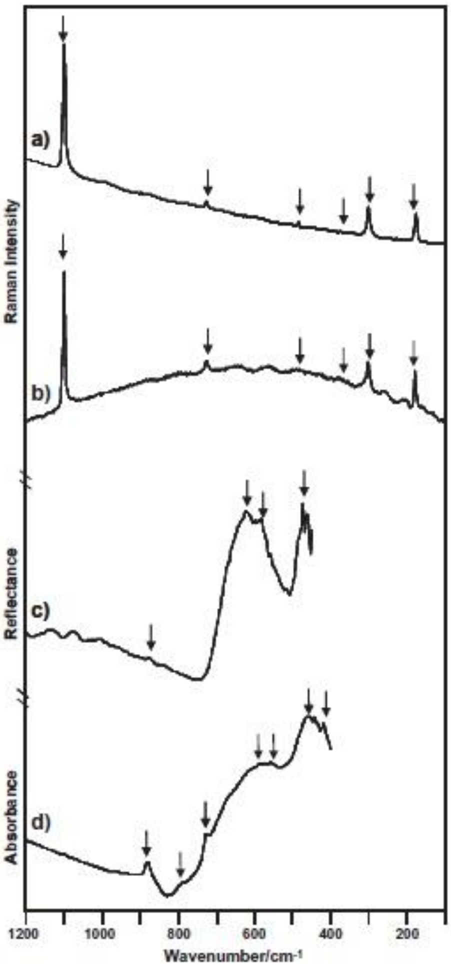

Fig. 19. Raman spectra of nežilovite, 532 nm excitation (a) and 632.8 nm excitation (b); IR spectra (c) and (d)

When recording Raman spectra (Fig. 20), care had to be taken to properly adjust the laser power/density. This was necessary since if this was not done, the sample would photodegrade into a series of other products. Laser-induced solid-state transformation was registered in synthetic Tl-sulfosalts as well.

The vibrational spectra of two arsenate hydroxyl-bearing minerals, sarkinite – $Mn_2(AsO_4)(OH)$ and adamite – $Zn_2(AsO_4)(OH)$, were thoroughly studied both experimentally (by FTIR and Raman techniques) and theoretically (using the periodic density functional theory, DFT) [33]. The FTIR spectra of the white and green adamite and that of sarkinite have been recorded at two different temperatures (298 K and 113 K) and are presented here as Figure 21. The shift of the O–H stretching band in white adamite with gradual temperature changes has also been studied and the results are presented in Figure 22. The presence of only one O–H stretching band in the spectrum of adamite is consistent with the existence of a only one independent OH ligand in the structure of adamite. On the other hand, the existence of four independent OH ligands present in the structure of sarkinite is reflected in the more complex appearance of the bands in the O–H stretching region of the spectra of this mineral.

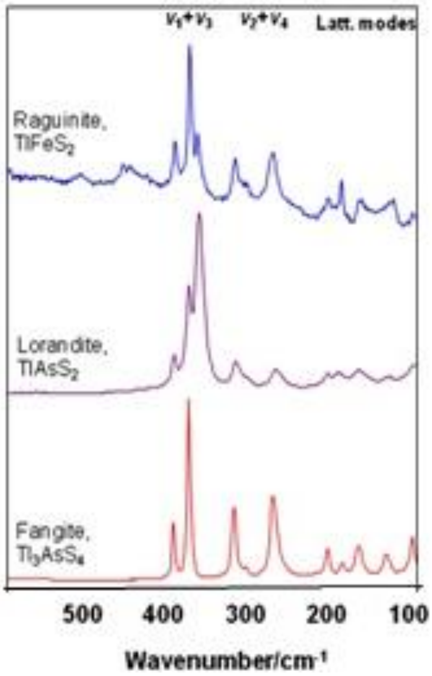

Fig. 20. Raman spectra of some thalium sulfosalts

Qualitatively speaking, the agreement between the band assignments based on theory and on experiment was satisfactory, the trends being, in most cases, reproduced. On the other hand, the existing differences are being due to the fact that the theoretical frequencies refer to transversal optical modes only, whereas the experimental band contours contain information about both transversal and longitudinal modes.

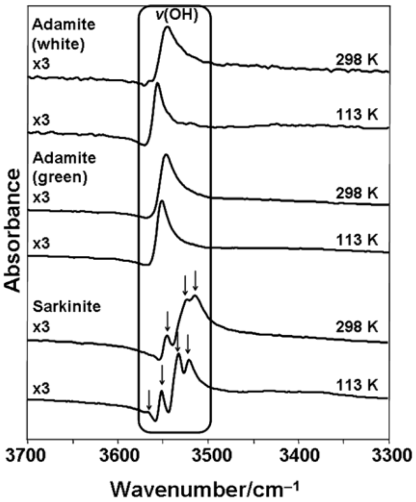

Fig. 21. Infrared spectra of white adamite and sarkinite

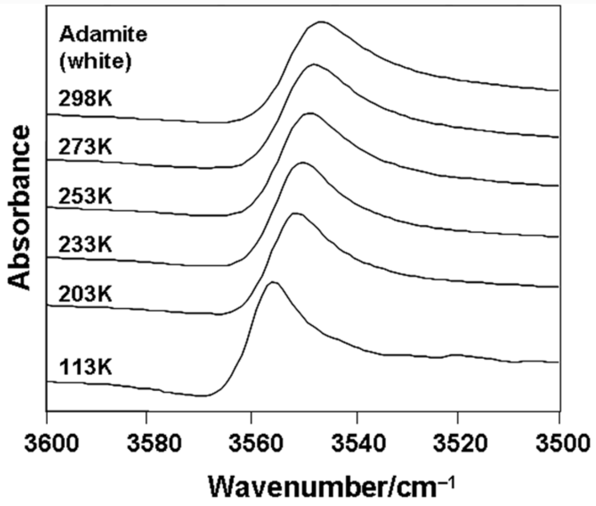

Fig. 22. Gradual temperature changes in the O–H stretching region of the spectrum of white adamite

Two papers [34, 35] deal with the laser-induced changes in the spectral features of some minerals (such effects were briefly discussed in ref. [32]).

In the first of the two [34], the appearance of two strong laser-induced fluorescence bands (at 446 and 607 cm^{-1}) in the FT-Raman spectrum of samples (collected from the Staro Bonče locality) of the mineral almandine, $Fe_3Al_2(SiO_4)_3$, when the spectrum was excited with the 1064 nm line of the Ng:YAG laser. Such bands were absent in the dispersive Raman spectrum obtained using 488, 514.5 and 532 nm excitation.

In the second paper [35] studied were the laser-induced transformations of stibnite (Sb_2S_3) and other related sulfosalts containing Sb_2S_3 structural units. In addition to the natural stibnite and parapierrotite ($TlSb_5S_8$) from the Alšar locality, several synthetic sulfosalts – stibnite, stibioellisite (Tl_3SbS_3), miargyrite ($AgSbS_2$) and weissbergite ($TlSbS_2$), were included in the study. The transformation products were compared with those obtained by the independently carried out thermal degradation of stibnite.

A simple and efficient method for the detection of traces of rare earth elements in minerals by Raman spectroscopy was proposed in ref. [36]. It has a lower detection limits for the rare earth traces in minerals (analytically important), but can even be extended to serve as a convenient experiment for undergraduate and postgraduate laboratory courses.

A review on the complementary use of vibrational spectroscopy and X-ray powder diffraction for detection and identification of silicate minerals from Macedonia is given in [37] and a more complete review (in which other types of minerals are also treated) is presented by Gligor Jovanovski and co-workers in [38].

A long (77 pages) and very well documented (89 references) review paper by Jovanovski, Makreski, Šoptrajanov, Kaitner and Boev [39] summarized the complementary use of vibrational spectroscopy and X-ray diffraction for identification and detection purposes in the research of minerals from Macedonia. The article is adorned by 28 color pictures of minerals collected by some of the authors. It may have been (and almost certainly was) the seed of the extraordinary book *Minerals from the Republic of Macedonia* to which the last section of this review is devoted.

Paper [40] concerns the study of the properties, free-volume characterization and anti-cancer effects of various arsenic sulfide (As_4S_4) nanoparticles prepared by milling. Structural changes are studied using Raman and FTIR spectroscopic methods and positron annihilation lifetime method. The anticancer effects are tested using flow cytometry and western blotting analysis. The effects of milling are associated with the formation of arsenic sulfide crystalline nanoparticles and the fragmentation of the corresponding free-volume entities. The anticancer effects of the nanosuspensions are verified on the human cancer H460 cell line, in which case DNA damage and greater numbers of apoptotic cells are observed.

Recently the results of the study of arsenate water-bearing minerals hörnesite [$Mg_3(AsO_4)_2 \cdot 8H_2O$], and symplesite ($Fe_3(AsO_4)_2 \cdot 8H_2O$), by vibrational (IR and Raman) spectroscopy and X-ray powder diffraction were published by Makreski, Stefov, Pejov and Jovanovski [41]. Although their spectra exhibit evident similarity, yet, some spectral differences have been observed due to the differences between their crystal structures and this enables to discriminate between the studied minerals. Otherwise, the authors observed that the Raman spectrum of hörnesite does not show any band in the water stretching region. It confirms once more the very well known fact that the Raman technique is not reliable enough to detect the presence of water molecules in the studied samples due to their low polarizability.

3. OTHER PAPERS DEVOTED TO MINERALS

The communication [42] (Fig. 23) is important in several ways. Namely, it was the *first* of the long series of papers with a general title “MINERALS FROM MACEDONIA”.

16. Конгрес на хемичарите и технолозите на Македонија, Скопје, 28-30 октомври, 1999

MINERALS FROM MACEDONIA: I. ANALYTICAL APPLICATION OF POWDER X-RAY DIFFRACTION PATTERNS OF CALCITE AND ARAGONITE

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Fig. 23. The upper part of the first page of ref. [42]

Furthermore it marked, for the first time, the presence, as a co-author, of Branko Kaitner from Zagreb, a researcher whose contributions to the study of minerals from Macedonia were of great importance, not only because of the fact that he worked in Laboratory of General and Inorganic Chemistry, Faculty of Science in Zagreb, where X-ray diffraction instruments were on disposal to the Macedonian researchers (especially to Gligor Jovanovski, an MS and PhD student of this institution). If only for these reasons, the groundbreaking importance of [42] is great, despite the fact that it was a communication presented to a congress of the chemists and technologists of Macedonia rather than to be a contribution to a scientific journal.

As for the scientific value of this communication it lies in possibility to use powder X-ray diffraction methods to detect calcite impurities in aragonite or aragonite impurities in calcite. This was possible due to the fact that a strong diffraction maximum exists in the powder X-ray diagram of calcite where aragonite exhibits no diffraction and, on the other hand, the rather strong diffraction maximum at $2\theta = 27.620°$ is present in the diffraction diagram of aragonite and none exists in the corresponding region of the calcite diffraction pattern. It was shown that, from an analytical point of view, the X-ray diffraction method is more sensitive than FTIR and, consequently, superior to the spectroscopic one.

Vibrational spectroscopy and X-ray diffraction (assisted in some cases by atomic absorption spectrometry (AAS) and atomic emission spectrometry with inductively coupled plasma (AES-ICP) were, no doubt, the techniques Gligor Jovanovski and his coworkers most often used. However, when needed (and available) other techniques were also employed among which neutron activation analysis should certainly be mentioned.

The AAS and AES-ICP techniques were employed in [43] to determine the content of trace elements (Ag, Cd, Co, Cr, Mn. Ni, Pb and Zn) in some iron minerals, namely hematite (Fe_2O_3); limonite ($FeO{\cdot}OH$); magnetite ($FeO{\cdot}Fe_2O_3$); marcasite (FeS_2); pyrite (FeS_2); siderite ($FeCO_3$) and vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$].

Since one of the major problems in electrothermal atomic absorption spectrometry (ETAAS) and the atomic emission spectrometry with inductively coupled plasma (AES-ICP) is the matrix interference, a method for elimination of iron by extraction with isoamyl acetate and the subsequent determination of the investigated trace elements in the inorganic phase.

The content of the trace elements Cd, Co, Cr, Mn, Ni and Zn in some copper minerals was determined by flame absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) in [44]. To avoid the interference of the matrix element, a method for electrolytic separation of copper was proposed. For chalcopyrite a method of extraction of iron by isoamyl acetate in HCl solutions proved to be effective. The content of Cd, Co and Cr was found to be very low in brochantite, chalcantite, covellite and native copper.

The results of the determination by flame atomic absorption spectrometry (FAAS) and ETAAS of trace elements in iron minerals (pyrite – FeS_2, from Bučim and Sasa, chalcopyrite – $CuFeS_2$, also from Bučim and Sasa, and hematite – Fe_2O_3, from Damjan and Ržanovo) were presented in [45]. For better results, a method for separation of the chloride complex of iron by extraction with diisopropyl ether from an acidified medium was proposed and employed. The extraction method was optimized.

The authors of the first paper in which the k_0-method of instrumental neutron activation analysis (k_0-INAA) was used [46] were Radojko Jaćimović, Petre Makreski, Vekoslava Stibilj, Trajče Stafilov and, of course, Gligor Jovanovski. Its subject was the characterization of some iron minerals, namely pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and hematite (Fe_2O_3). The number of elements simultaneously determined was thirty nine. It was found that the content of the major constituents in all samples is significantly lower than the value calculated on the basis of the chemical formula. Thus the theoretical value for iron in pyrite is 46.5 %, while the experimental one was found to be only 34.0 %, the corresponding values for iron in chalcopyrite are 30.4 % and 24.2 % and those in hematite are 69.9 % and 60.3 %. The situation of copper in chalcopyrite is similar: 34.6 % theoretically and 25.7 % experimentally.

The k_0-INAA method was used [47] to determine the composition of four copper minerals from Macedonia, namely brochanite [$Cu_4SO_4(OH)_6$], chalcantite ($CuSO_4{\cdot}5H_2O$), chalcopyrite ($CuFeS_2$) and native copper, while the fifth mineral, covellite (CuS) was from Bor in Serbia. It was found that in the native Cu from Bučim most of the investigated elements (39 in number) are present in the order of a few mg/kg, while the content of iron is higher than that of the other elements. The contents of As, K, Na and U in brochantite is higher than that of the other determined elements, the situation with the content of Ca, Co, Na and Zn in chalcantite, of Ag, As, Se and Zn in chalcopyrite and of As and Se in covellite being similar. Significantly lower than the theoretical value (100 %) was the content of copper in native Cu (89.45 %).

The content of trace elements in iron minerals hematite, pyrite and chalcopyrite was determined [48] by instrumental neutron activation analysis (k_0-INAA) and radiochemical neutron activation analysis (k_0-RNAA). The determination of the content of the trace elements was performed after the extraction of iron by isoamyl acetate and diisopropyl ether.

Instrumental neutron activation analysis was also used in the determination of trace elements in chalcopyrite after the removal of matrix elements [49].

The k_0-neutron activation analysis was used in [50] to determine the trace elements in brochantite from Sasa and native copper from Bučim. In brochantite the contents of As, Fe, K, Na, Se, U and rare-earth elements are higher than that of the rest of investigated elements (44 in number).

The question whether the removal of copper by electrolysis from copper minerals is an appropriate method for determination of trace elements which is found in the title of ref. [51] was answered positively.

The discrete solid-state process with steady-state X-ray diffraction was visualized in [52] and the linkage isomerization of As_4S_4 clusters during the protoinduced transition of realgar to pararealgar was the subject of [53] (see Fig. 24).

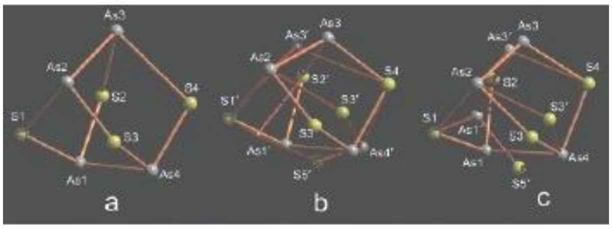

Fig. 24. Structure and topology of the As_4S_4 cluster before (a), during (b) and after (c) irradiation with visible light

The geological setting, lithologies and identification of the minerals from the Ržanovo Fe–Ni deposit were the subject of the paper by Boev, Jovanovski and Makreski published in the *Turkish Journal of Earth Sciences* [54]. A detailed review is given of the mineralogy, petrology and petrological evolution of the Ržanovo deposit which is situated in the western ophiolite belt of the Vardar zone. Two maps and twelve tables of data are included. A particular attention was given to the mineral identification by vibrational spectroscopy, the detailed text being enriched by seven figures of infrared and Raman spectra and seven tables.

The geology and mineralogy of the Alšar Sb-As-Ti-Au deposit is being treated in paper [55]. Three maps and three tables with data were included. Basic data for 44 minerals found in the Alšar deposit were listed in the paper and a list of 70 references was given.

A paper by Boev, Bermanec, Serafimovski, Lepitkova, Mikulčić, Šoufek, Jovanovski, Stafilov and Najdoski [56] contains a detailed description of the Alšar mineral assemblage.

A text on the minerals from Macedonia [57] was published in the informative-professional review "*Macedonian Minery and Geology*". Twelve color photos of minerals and a map with the locations from which mineral samples were collected is included.

A long (22 pages) entitled "Minerals from the Republic of Macedonia with an Introduction to Mineralogy" [58] was included in the publication "*Ukrainian-Macedonian Scientific Proceedings (number 5)*" published in Kiev. As the title suggests, a rather detailed review was given on the two related subjects, a list of 109 references and a mineral index containing a list of minerals studied by the authors (and some other ones mentioned in the text) is included.

A review on the crystallography in Macedonia and the collaboration between Macedonian and Croatian crystallographers was published [59] in the book of papers presented at the scientific meeting "*Crystallography in Croatia"*. Seven color pictures of either minerals or the determined crystal structures were included.

4. THE BOOK "MINERALS FROM THE REPUBLIC OF MACEDONIA"

A detailed, scientifically excellent and beautifully presented book with the title given above [60] may be considered as a crown on the work of Gligor Jovanovski on minerals.

Fig. 25. The cover of the book *Minerals from the Republic of Macedonia with an Introduction to Mineralogy*

Although the two other authors (Petre Makreski and Blažo Boev) have undoubtedly seriously contributed to this jewel of scientific publication in Macedonia and the role of Robert Jankuloski (photographs) and Ladislav Cvetkovski (design) is preeminent, there is no doubt in the mind of the present author that nothing of the sort could have been accomplished if it were not for the leadership of Gligor Jovanovski. With due modesty, it may be mentioned that the authors of the book included a statement reading “with the continued contribution of Branko Kaitner, Trajče Stafilov and Bojan Šoptrajanov”.

Let us look forward to new and equally exciting contributions of Academician Jovanovski!

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