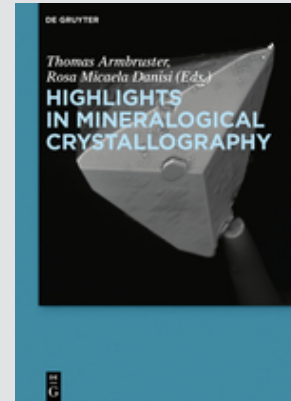*Thomas Armbruster, Rosa Micaela Danisi (Eds.)*

HIGHLIGHTS IN MINERALOGICAL CRYSTALLOGRAPHY

"Highlights in Mineralogical Crystallography" presents a collection of review articles with the common topic: structural properties of minerals and synthetic analogues. It is a valuable resource for mineralogists, materials scientists, crystallographers, and earth scientists. This book includes:

▶ An introduction to the RRUFF database for structural, spectroscopic, and chemical mineral identification.
▶ A systematic evaluation of structural complexity of minerals.
▶ *ab initio* computer modelling of mineral surfaces.
▶ Natural quasicrystals of meteoritic origin.
▶ The potential role of terrestrial ringwoodite on the water content of the Earth's mantle.
▶ Structural characterization of nanocrystalline bio-related minerals by electron-diffraction tomography.
▶ The uniqueness of mayenite-type compounds as minerals and high-tech ceramics.

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1 The power of databases: The RRUFF project

1.1 Introduction

In today's world, many people rely on the availability of databases to perform daily activities such as checking meteorological forecast, finding a recipe, or verifying the spelling of a word. These are examples of actions that anyone can do quickly, routinely, and often at little cost, because of access to the Internet and the development of extensive databases.

The science community has always relied on databases, which in the earlier years were only available through collations of journals, books and data records. The analogic nature of these data resources dramatically limits the process of searching records and establishing relations between datasets. Nowadays, digital scientific databases and the World Wide Web have changed the way we can do science. This new generation of databases not only provides access to information, but allows data sharing between multidisciplinary research projects and make it possible to cross-link diverse types of data.

Minerals are very important to both the world economy and research science, they supply the raw materials necessary for the development of modern societies and their study provides knowledge of our planet, the solar system, and the very nature of the universe. As such, their identification and characterization is critical to many fields. However, only a few experts can accurately identify minerals without analytical instruments and their complementary databases. In general, minerals are uniquely characterized by both chemistry and crystal structure, or their derivative properties. For instance, the derivative property, color, can be a function of chemistry, or crystal habit a function of structure.

The characterization and differentiation of minerals in the 19th century was largely based on chemical composition and crystal forms. This led to the appearances of compendia of minerals and their diagnostic properties in the form of books that become the earliest publicly available databases of minerals, such as Dana's System of Mineralogy (1837–1997) [1], Hintze's Handbuch der Mineralogie (1897–1933) [2], or Goldschmidt's Atlas der Krystallformen (1913–1923) [3] containing drawings of all recognized crystals forms of minerals.

The discovery of X-ray diffraction techniques in 1912 brought about a dramatic change in the way minerals could be characterized because the diffraction pattern of a given mineral species remains consistent without regard to the crystal form, habit, color, or other variability in properties. This has led to a large amount of definitive data that is used to help identify and characterize minerals. Subsequent technological innovations have increased the speed and volume of data acquisition, and therefore, the need of databases to organize and make available all this information.

In addition to chemical and diffraction techniques, spectroscopy has proven to be a valuable derivative methodology used to identify and characterize minerals. In particular, Raman spectroscopy has shown itself to be a competitive technique because Raman spectra of minerals depend fundamentally on their chemistries and structures. Moreover, this technique is generally nondestructive, requires little sample preparation, it is quick and holds the promise of low cost. Infrared spectroscopy is another popular technique that is complementary to Raman and is capable of providing distinctive spectra suitable for search/match routines. Both spectroscopy techniques are undergoing major instrumentation changes towards portable and handheld systems (e.g. [4–7]).

Mineral identification using Raman spectroscopy is normally performed by search/match routines that compare the acquired spectrum with reference spectra from a database. The purpose of the RRUFF project is to develop such a Raman database by measuring the chemistry, X-ray diffraction patterns, Raman, and infrared spectra of the known minerals and to make these data readily and freely available to the scientific community, industry, and the general public. RRUFF database currently contains about 7000 mineral samples representing 3500 mineral species. The power of the RRUFF database is that its data is not collected from disparate publications and procedures but rather is collected with the same methodology, on the same set of samples and with the same instrument.

Although they are not currently included in RRUFF, there are other analytical and spectroscopy techniques that aid in the characterization of minerals [8]. For example, Laser-Induced Break-down Spectroscopy (LIBS) provides chemical composition by measuring all the elements present in a mineral sample. Mössbauer spectroscopy is also extensively used in mineralogy to examine the various valence states and the type of coordination polyhedron occupied by iron atoms.

1.2 A brief history of the RRUFF project

Until recently, Raman spectroscopy was only accessible to specialists because it required complex instruments worth hundreds of thousands of dollars. In 2003, the Hamilton Sundstrand Sensor Systems company (CA, USA) and the University of Arizona (USA) were funded by NASA to develop a miniaturized high performance Raman system for Mars surface studies [9, 10]. The success of this project demonstrated that inexpensive small Raman instruments had the capability to make Raman spectroscopy a popular stand-alone field tool for routine and unambiguous identification of minerals and other materials by non-experts and thus, would eventually become available to the broad public.

Mineral identification using Raman spectroscopy needs reference spectra, so anticipating the increasing use of the technique, Pr. Downs at the University of Arizona built a Raman spectral database for minerals by obtaining representative samples of

minerals that are also characterized and identified by X-ray diffraction and chemical composition. There are a couple of models that can be used to fund database development. One is to charge an annual license, such as the funding model used by International Centre for Diffraction Data (ICDD) (http://www.icdd.com/). However, if the cost of Raman instruments become so inexpensive that it is less than the cost of a license, then the ICDD model of funding is not reasonable. The RRUFF project database is based on the model of paying upfront for database development and providing the data for free.

Mr. Michael Scott, the founding president of Apple Computers, provided the funding to begin the project and create a proof of concept. He named it the RRUFF Project [11]. With this funding, the project developed procedures for validation and verification and the purchase of required instruments, including X-ray diffractometers and Raman spectrometers.

A requirement from Mr. Scott was that all the data collected by the RRUFF project would feed an open-access Raman spectral database not only for geologists and mineralogists, but for the general worldwide public. Therefore, a website for the RRUFF database (http://rruff.info) was built to provide free access to all the collected data, allowing users to view and download X-ray diffraction patterns, Raman and infrared spectra, electron microprobe data, references, photographs, and acquisition data of well characterized mineral samples. The RRUFF database is constantly reviewed and updated, following strict protocols to ensure the quality and durability of the data. It currently receives ~80000 hits per week. Its success, together with the interest of Michael Scott in mineralogy and Raman spectroscopy, has led him to also fund a similar free-access database, called WURM (http://www.wurm.info/), which contains the results of ab initio Raman spectra calculations [12].

It was also important in the early days of the RRUFF project to obtain a list of the known mineral species. With the help of the International Mineralogical Association (IMA) and its nomenclature commission, an outreach committee of the IMA was formed to develop and maintain an interactive and searchable list of the IMA-approved minerals. This list, referred in this paper as the IMA-List, is found at: http://rruff.info/ima/ (Fig. 1.1) and provides our preferred interface to the data of RRUFF as well as the Handbook of Mineralogy [13] maintained by the Mineralogical Society of America, the American Mineralogist Crystal Structure Database (AMCSD) for structural data [14–16], a reference library of publications and in some cases their pdf's, a Mineral Evolution database for mineral localities and their ages, and links to other databases that search on mineral names. In addition, and in order to promote private use of the IMA-List of minerals, the site includes an option to create additional links to any other website that will accept queries based on mineral names. For example, we have a link to our mineral museum database. The site also offers a downloadable spell check dictionary file containing the mineral names from the IMA-List which can be added to a user's computer dictionary.

Fig. 1.1: The IMA-List homepage layout (http://rruff.info/ima/). At the top left is the interactive list of IMA-approved minerals, which is searchable by mineral name (e.g. quartz) or by chemistry through the available periodic table. At the top right is the list of provided links to other mineral database, including our customized link to the University of Arizona Mineral Museum (UAMM).

1.3 The RRUFF database

As of this moment, 3527 of the 4985 known mineral species have been incorporated into the RRUFF sample collection. As data from a sample is collected, it is posted into the database with password restricted access, referred to as non-public access. After a review process, if the data appears to be representative of the sample, then the password restriction is removed and the data becomes publicly accessible. As a consequence, measurements from only 2128 mineral species are currently publicly accessible. When possible, data from at least two samples of each species, ideally from different localities, are included in the database. Having multiple samples provides a means to confirm data and capture the chemical variability frequently observed in minerals. For instance, the database currently contains 42 records on the important olivine forsterite-fayalite series, with associated Mg-Fe chemical variations. In total, data from 3791 samples are publicly accessible through the RRUFF database.

1.3.1 Sample collection and characterization

Mineral samples for the database were initially obtained from the University of Arizona Mineral Museum (UAMM) and from the purchase of the Cureton reference collection of 6500 specimens by Michael Scott. Currently, new mineral specimens are mostly obtained from donations by collectors, dealers, and museums around the world. In 2013 alone, the RRUFF project received over 10000 samples through donations, including two major ones: Mr. Rock Currier (~8000) and Dr. Robert Lavinsky (~2000).

We insert the samples of interest into the database by giving them a unique RRUFF ID (e.g. R070563) and we scan and post the original labels, if they exist. We also record important acquisition data, such as source and locality, according to the label. After the record has been created, the next step is to confirm the identity of the sample. We have found that more than 25 % of all the samples that we have studied have been previously incorrectly identified on their labels. This failure rate illustrates the difficulty in determining the identity of a mineral, even for experts. Until the identification is confirmed, users should carefully suspect the correctness of the mineral name. The *Status* line in the top portion of each sample record reports the degree of the certainty in the identification and the techniques used. Even though our goal is to have all samples characterized by means of X-ray diffraction and chemical analysis, due to limited resources and the cost of chemical analysis, we try to identify them first by X-ray diffraction because this equipment is in our laboratory. However, some minerals can be difficult to be unambiguously identified by X-ray diffraction. For example, different mineral species belonging to the garnet or amphibole groups may have similar cell parameters and because they are isostructural, their diffraction patterns will be similar. In these cases, chemical composition is required. When using RRUFF data, it

is always important to review the *Status* field in order to know the degree of certainty with which the minerals has been identified.

Most specimens in the RRUFF project are also documented with a *macro* photograph of the entire sample, intended to show host material, and a *micro* photograph to illustrate the quality of the mineral specimen under examination. Examples of both *macro* and *micro* photos are shown in Fig. 1.2.
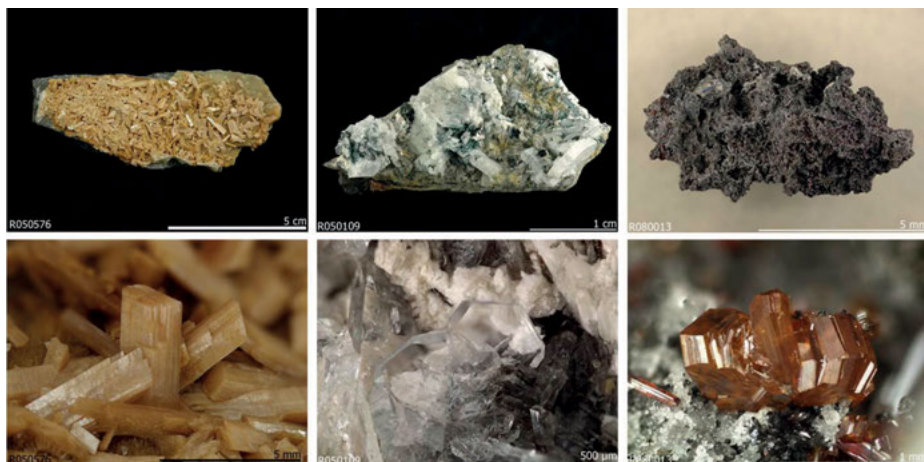
Fig. 1.2: Photos *macro* (top) and photos *micro* (bottom) of some RRUFF samples. From left to right: sigloite (R050576), bobdownsite (R050109), and xanthoconite (R080013).

1.3.1.1 Chemical analysis

The chemical composition is mainly determined with electron-microprobe analysis (EPMA) complemented, when necessary, with inductively coupled plasma massspectrometry (ICP-MS) analysis for the measurement of light elements (lighter than oxygen, such as B, Be, and Li).

Electron-microprobe analyses are conducted at the University of Arizona Electron Microprobe Laboratory at the Lunar and Planetary Laboratory (LPL) on a fully automated CAMECA SX50 or SX100 Ultra instrument. A detailed description of microprobe analysis applied to geology and mineralogy can be found in Reed [17] and the calculations to determine the empirical chemical formula are explained in detail in Deer et al. [18]. The determination of light-elements (H, Li, Be, B) is done by inductively coupled plasma mass-spectrometry (ICP-MS) on a Thermo Scientific X-SERIES 2 Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q-ICPMS).

The chemical analysis for each mineral is posted to the RRUFF website along with a photo of the image of the polished fragment used in the probe. An Excel file con-

CHEMISTRY

RRUFF ID: R140428.2
Sample Description: Microprobe Fragment
Measured Chemistry: $(Fe_{1.51}Mn_{0.39}Mg_{0.06}Ca_{0.03})_{\Sigma=1.99}Al_{1.99}(Be_{1.02}Li_{0.08})(P_{0.99}O_4)_2(OH)_6$; The BeO and Li2O were determined by ICP-MS.
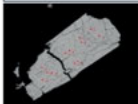**Microprobe Data File:** [Download Excel File]

Fig. 1.3: Chemistry section of lefontite (R140428) showing the measured chemistry, photo of SEM image (link to a larger high-resolution image), and the access to the Excel spreadsheet.

taining all the probe data is also provided and it can be downloaded and manipulated by anyone who is interested in the results or to use as a template for other analyses (Fig. 1.3).

The IMA-List provides an interactive interface to search for minerals based on their ideal chemistry using a periodic table (Fig. 1.4). With this tool, the search can be done not only by elemental composition but also by valence state (i.e. Fe^{3+}) and strings (i.e. H_2O, OH), which results in a single selected mineral, or a set of minerals.

Fig. 1.4: Periodic table interface in the IMA-List. The example illustrates a searching based on minerals that contain the elements Mn, P, O and Ca, the strings Fe^{3+} and H_2O, and exclude Mg. The system retrieves seven minerals meeting these conditions: bederite, jahnsite–(CaMnFe), jahnsite–(CaMnMn), keckite, wicksite, wilhelmvierlingite, and zodacite.

1.3.1.2 X-ray diffraction

All the RRUFF samples are examined by either powder or single-crystal X-ray diffraction. When there is sufficient sample then powder X-ray diffraction is the method of choice because it produces a pattern that matches the established gold standard format for identifying minerals. The reader can refer to Lavina et al. [19] for an extended

description on the modern X-ray diffraction methods in mineralogy and geosciences. For powder X-ray diffraction analysis, the RRUFF project uses a Bruker D8 Advance where a powdered sample is examined from 5° to 90° 2-theta at 2.0 seconds per 0.010° step with Cu radiation.

The diffraction patterns are compared against the ICDD using the EVA search/ match module provided by Bruker. Each measured diffraction pattern is then indexed and cell parameters are refined with CrystalSleuth [20] using $h\,k\,l$ values from AM-CSD, as computed by the module XPOW [21] included in the XtalDraw software [22]. The cell parameter refinement in CrystalSleuth is based upon determining the positions of isolated diffraction peak $K\alpha1$ and $K\alpha2$ doublets and fitting the set of positions with a non-linear least-squares algorithm [20, 22] (Fig. 1.5). The peaks are fit using a χ^2 minimization routine known as the Levenberg-Marquardt Method similar to that described in Press et al. [23].

On the RRUFF website, the diffraction pattern is displayed and the profiles are posted as XY-ASCII files, along with the refined crystallographic parameters.
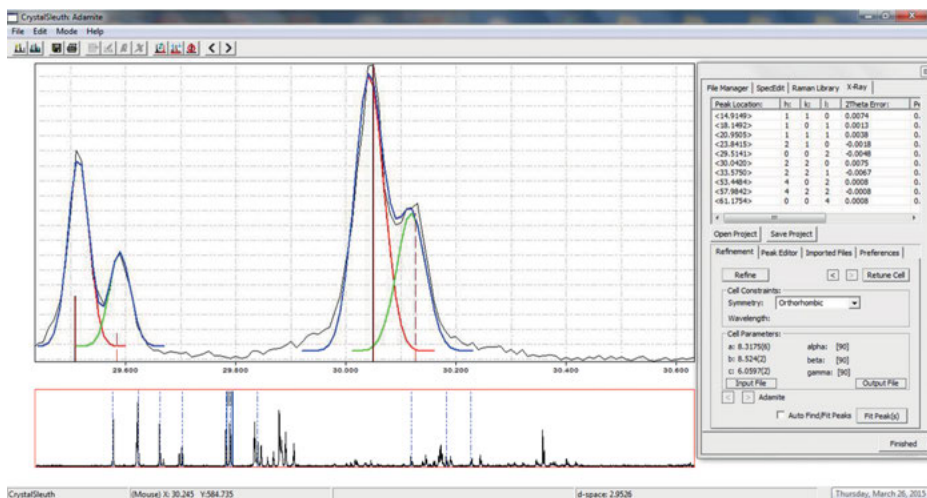
Fig. 1.5: CrystalSleuth interface showing an example of fit and index processes of an experimental powder X-ray diffraction pattern of an adamite sample.

If the identification or refinement by powder X-ray diffraction is ambiguous due to, for instance, extreme peak overlap, or the amount of sample is too small for powder work, then single-crystal X-ray diffraction is the preferred technique. The analyses are conducted using a state-of-the-art Bruker X8 diffractometer with Apex2 CCD detector and Mo radiation.

In this case, the mineral is identified on the basis of its cell parameters and search/match is performed using the IMA-List, which offers a routine for search-

Fig. 1.6: Cell parameter search control interface in the IMA-List.

ing cell parameter extracted from the literature and from the RRUFF and AMCSD databases. It also provides a tolerance of 1 %, 10 %, or any value chosen by the user to the cell parameters to enable a search within a range of values (Fig. 1.6).

With single-crystal diffraction data, a theoretical powder diffraction pattern is computed using XPOW (Fig. 1.7) and it is posted in the database along with its associated XY-ASCII file.

Fig. 1.7: Theoretical powder X-ray diffraction pattern of iranite [24] generated by XPOW.

1.3.1.3 Raman spectroscopy

Raman spectroscopy is based upon the inelastic scattering of light due to its interaction with the vibrational modes of the target sample [25, 26]. During the analysis, the transfer of energy of the incident photons (gain or loss) results in a spectrum of energy shifts characteristic of the chemistry and structure of the compound, and therefore, may provide a fingerprint that can be used in the identification of most minerals.

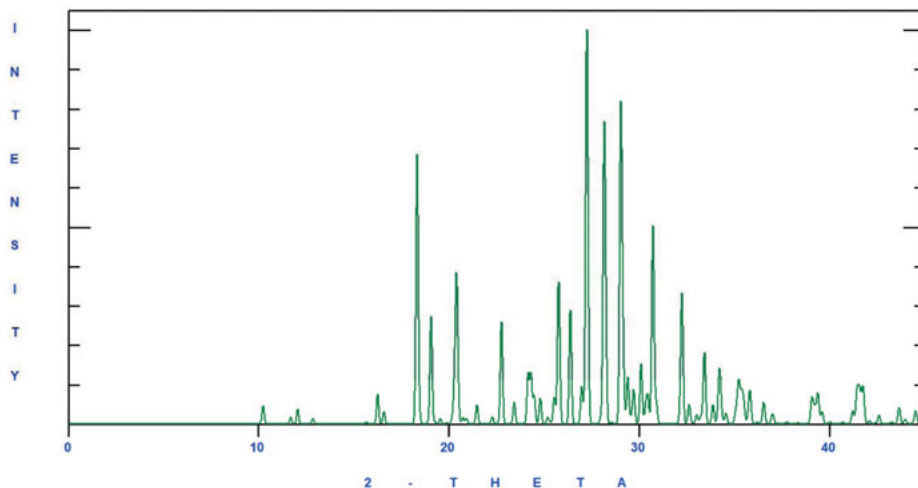Interestingly, Griffith [27] studied the Raman spectra of the major rock-forming minerals in order to understand the effects of SiO_4 condensation, and claimed that Raman is "unlikely to be useful for the identification of silicate minerals". Nevertheless, the RRUFF project has shown that 80 % of the samples examined can be correctly identified by their Raman spectra.

In general, four Raman spectra are collected from unoriented samples with 532 (green) and 785/780 (red) nm lasers in a Thermo-Almega micro Raman system. The instrument is equipped with an Olympus BX microscope with 10X, 50X, and 100X objective lenses. Whenever possible, the measurements are collected using 50X. The lasers are partially polarized with 4 cm^{-1} of maximum resolution and a spot size < 1 μm. High-resolution narrow scans, usually from 70–1400 cm^{-1}, and low-resolution wide scans usually from 70–4000 or 70–6500 cm^{-1} are collected with the 532 and 785/780 nm lasers from exactly the same spot in the sample and until the signal to noise ratio is optimal.

The high-resolution narrow scans are used as reference spectra in the search/match library installed with CrystalSleuth (Fig. 1.8), because the strongest main Raman peaks representative of a sample usually fall within this region. The CrystalSleuth search/match routine treats the background-removed pattern as a multi-dimensional vector (of norm 10) where an interpolated intensity (y-axis) at every two wavenumbers (x-axis) is treated as the coordinate value. We intentionally view the pattern and each of the spectra within our search-library as defined within the same vector-space. A dot product reveals the spectra that are most similar. Because of the normalization, a perfect match returns a value of 100. This process is repeated for the top matches; then, for greater resolution, the intensities are interpolated at every integral wavenumber. An ordered list of matching results with a confidence value (0 to 100) is listed left of each result. The confidence is the calculated result of the dot products discussed above, which indicates the coincidence between each pattern in the search/match library and the spectrum of interest. As this software produces the closest matches to samples in the installed RRUFF library, it is important to remember that even with a high confidence, this does not necessary imply a match, just the best match within the database. In some cases, it is possible that the right reference is not even in the library.

The low-resolution wide scans are performed with both 532 and 785 nm lasers in order to record other Raman peaks, such as the O-H stretching modes, and other spectral artifacts. With our instrument, only the spectra collected with the 532 nm laser reveal the presence of O-H bands that are often located in the 2700–3700 cm^{-1} region, as
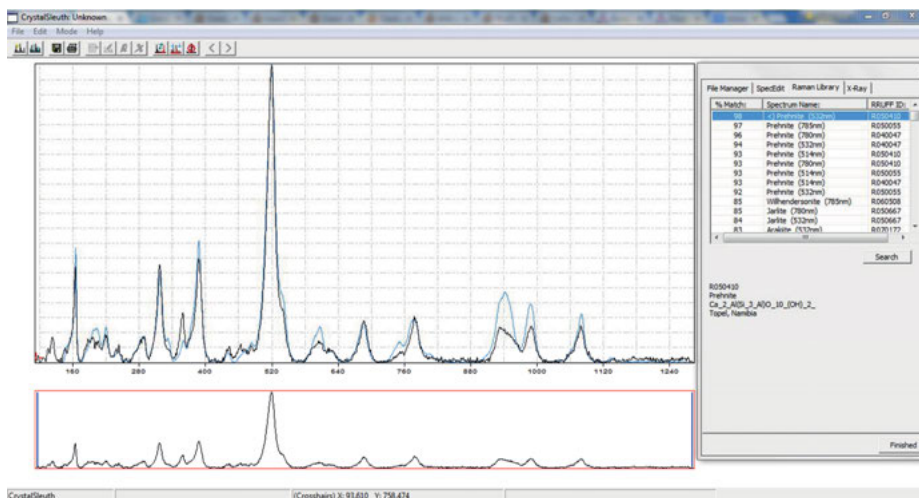
Fig. 1.8: CrystalSleuth interface showing an experimental unknown Raman spectra (in black), which matches the spectrum of the RRUFF record for prehnite R050410 (in blue).

shown in Fig. 1.9. The sensitivity of the silicon detector in the 785 nm laser is quite poor at higher wavenumbers which makes it useless for the detection of the O-H modes.

CrystalSleuth is used to correct the spectral baseline, using a subroutine from the Razor library (http://www.spectrumsquare.com) by Spectrum Square Associates, to remove cosmic rays events from patterns [28], to trim edges, to reverse X-axis display, and to visualize and compare multiple spectra. Both raw and processed data are included on RRUFF as XY-ASCII files.

The intensities of certain Raman peaks of a mineral may vary appreciably as a function of sample orientation, depending upon its symmetry and the origin of the Raman modes (Fig. 1.10).

Such variations in intensity can significantly affect the success of the search/ match routines. Thus, in certain cases, especially for rock-forming minerals, Raman spectra collected in additional different orientations with respect to the polarization direction of the incident laser are collected. The analyses are conducted with an IRIS Raman instrument built by Alex Goncharov and Victor Struzhkin of the Geophysical Laboratory at the Carnegie Institution of Washington. It uses a tunable 100 mW Ar-ion laser (usually at 514.532 nm) and a Jobin Yvon Spex HR 460 spectrometer equipped with a liquid nitrogen cooled Princeton Instruments 1152×256 pixel CCD detector. We use a 1200 groves mm^{-1} grating centered at 530.4 nm and collect data with Roper Instruments Winspec/32 software. Samples can be oriented onto a goniometer stage and rotated precisely into position, or spun at speeds up to 720 degrees per sec.

Some mineral records also provide a pdf file with the description of the Raman active modes corresponding to the mineral species (e.g. beryl, R040002). The analysis
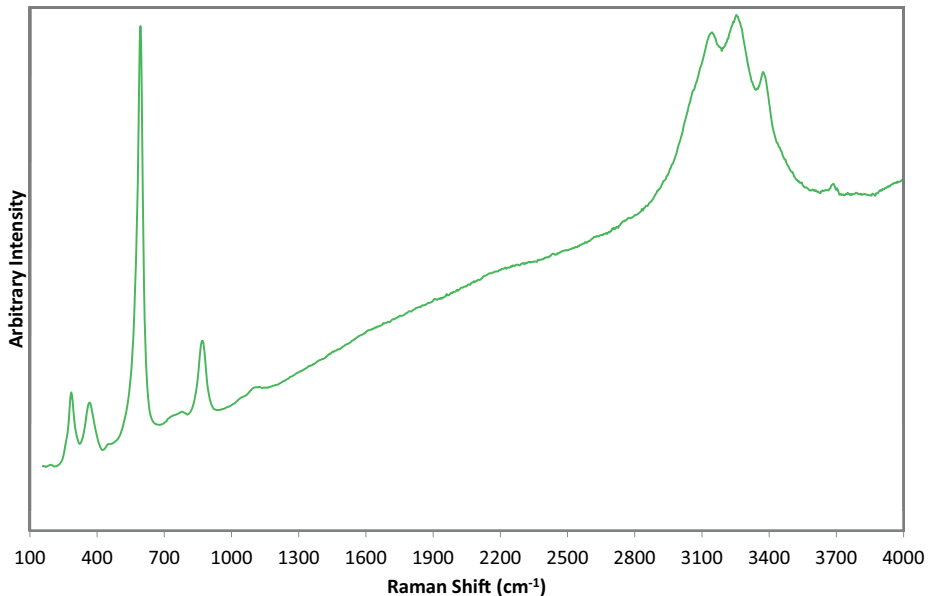
Fig. 1.9: Low-resolution Raman spectrum of tetrawickmanite, $Mn^{2+}Sn^{4+}(OH)_6$ (R100003), collected with the 532 nm laser, illustrating the O-H stretching vibrations Raman bands between 2700 and 3700 cm^{-1}.

is done by using the crystal structure data from AMCSD and the SAM routine at the Bilbao Crystallographic server (http://www.cryst.ehu.es) [29].

1.3.1.4 Infrared spectroscopy

Similarly to Raman spectroscopy, the infrared spectrum can provide additional information and a quick way to identify a mineral, assuming that a database is available for comparison. The two techniques are complementary because while Raman scattering requires a change in polarizability with vibration, infrared requires a change in dipole moment. Therefore, in molecules with different elements of symmetry, certain bands may be infrared active, Raman active, both or neither. When sufficient powder sample exists, the infrared absorption spectra are collected at the California Institute of Technology (Caltech) in Dr. George Rossman's lab. The analyses are performed using a SensIR Durascope on a Thermo Nicolet Magna 860 FTIR (wavelength 4000–375 nm). The collected data is included as XY-ASCII file. The RRUFF project does not include a search/match routine for identification of minerals by infrared spectroscopy. Additional details can be found at George Rossman's website at Caltech. The user can access the Mineral Spectrosocopy Server (http://minerals.gps.caltech.edu/) where visible, near-infrared, and infrared absorption spectra are available for a number of min-
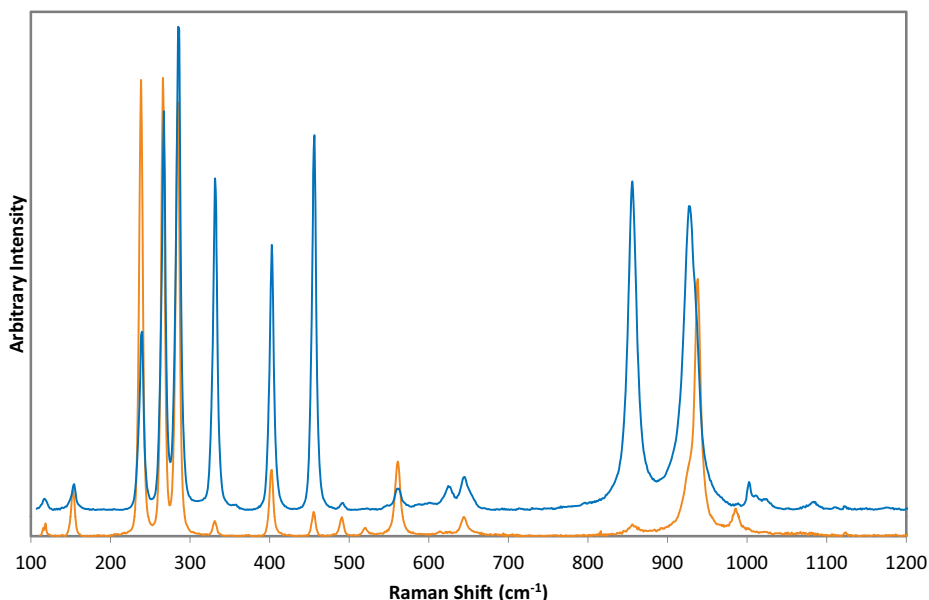
Fig. 1.10: Raman spectra of topaz (R040121) in two different orientations. The lower spectrum (orange) was recorded with the laser parallel to the *b*-axis, polarized parallel to *c*, while in the upper spectrum (blue) the laser is parallel to the *c*-axis, polarized parallel to *b*.

erals, including rock-forming minerals, gem minerals, and other minerals of particular interest.

1.3.1.5 Data from external sources

Some rare minerals are very difficult to obtain by the RRUFF project. However, if the Raman and infrared spectra are available in the literature, we contact the authors and invite them to share their data through the RRUFF database. Microprobe analysis and crystal structure information, if available from the manuscript, are also included in the record. We thank all the authors for sharing their data with the RRUFF project. The list of minerals needed to complete the project can be found at http://rruff.info/about/minerals_needed.php. If you have Raman or infrared spectra of minerals that are not currently represented in the database, we encourage you to contact us.

1.3.2 Reference library

The RRUFF project includes an extensive reference library of publications directly linked to their associated minerals. For the most part, these articles are focused on spectroscopy, structure, and chemistry of minerals. The complete list of collaborators can be found at: http://rruff.info/about/about_publishers.php. Only when the publi-

cation has permission for free viewing, its pdf can be freely downloaded. In addition, with funding from the National Science Foundation (The American Mineralogist Crystal Structure Database, 2006–2009, National Science Foundation EAR-0622371), the RRUFF project scanned and made public the older pre-digital journals of a number of societies including USA, Canada, Great Britain, France, Italy, Russia, and Japan. For those minerals with reported structure, the reference list also provides a link to their AMCSD record. The access to the references is facilitated either through the sample record itself, which provides a list of related publications, or through the webpage interface for Search References (http://rruff.info/rruff_1.0/reference_search.php).

1.3.3 Search and access to mineral records

Each record in the RRUFF database can be accessed by different pathways. Through the database homepage, an interactive search procedure provides a series of text fields for searching by mineral name, chemistry, or keywords. It also includes a periodic table interface to search by chemical composition (*lookup* button), which is done by selecting elements included in the chemistry (click element once), or elements that needs to be excluded from the chemistry (click element twice). For example, all silicate minerals can be obtained by selecting only Si and O. To obtain the SiO_2 polymorphs, the rest of elements in the periodic table needs to be excluded. The *Exclude all non-selected* button excludes all of them automatically. The search hits can be sorted and displayed in different formats that can be set as default.

The mineral records can be also accessed by typing the name of the mineral or the RRUFF ID in the website URL in the format: http://rruff.info/[*mineral name or RRUFF ID*]. For example, rruff.info/quartz returns a page listing all the public quartz samples that have been analyzed by the RRUFF project, while rruff.info/R040031 displays all the data collected for one of the specific samples of quartz. This type of access also facilitates a way for other websites or software to independently access data from the RRUFF webpages. The IMA-List uses the URL method to provide a link to the mineral records in RRUFF. This link will be only active (black font) when the RRUFF database contains at least a record of the selected mineral.

1.3.4 Software design and server infrastructure

The RRUFF database is built using the open-source database-management software MySQL, which runs on all platforms. MySQL is combined with the PHP scripting language to create the database structure, to populate and maintain the database, and to support data retrieval. PHP not only securely supports the MySQL database but also it is the link between the database and the Web page.

The Web search interface is dynamically created with PHP using the *Select* commands to access the criterion tables in the MySQL database. We use an Apache Web server running on a Linux platform, which is well suited for PHP and MySQL. The searchable fields in the user interface include interactive HTML elements such as text boxes, drop-down list boxes, radio buttons, push buttons, etc., which are created with PHP. The results of the queries populate the search criteria fields in the HTML form.

The RRUFF project spends considerable time and resources to ensure the availability of the RRUFF database at all times. As the database is used worldwide, it is a priority for the project to provide users with a reliable tool that can be used at any time and whose data last over time. Server infrastructure used for the RRUFF database uses RAID (Redundant Array of Inexpensive Disks) for local storage to ensure data integrity within the local archive. This ensures that a single or double disk failure in the system will not result in loss of data. This hardware is regularly maintained and upgraded to ensure performance and availability.

1.4 Experimental observations during collection of Raman spectra

An outcome of building the RRUFF database is the opportunity to examine hundreds of minerals by Raman spectroscopy and to observe diverse factors that may affect the collection of the data [30]. We summarize some of these factors in this section.

1.4.1 Thermal effects of laser power

During the collection of a Raman spectrum, the incident laser beam may heat the illuminated portion of the sample, which, in some cases, can cause phase transitions, loss of hydration water, or partial or total decomposition of the sample. The increase of the temperature depends upon experimental conditions, such as excitation wavelength, laser power, and exposure time, as well as mineral properties, including size, chemistry, and color. When heating effects are suspected, we typically lower laser power, modify exposure time, or defocus the laser beam. The downside of reducing the laser power to its minimum value is that it also implies lowering the intensity of the Raman signal and worsening the signal to noise ratio, therefore providing a lesser quality Raman spectra.

Usually small or thin isolated crystals tend to burn more easily because they are not able to dissipate much of the heat. When we collect Raman data from the same single crystal used for X-ray diffraction analysis, the power of the laser is usually reduced to its lowest value. Minerals with weak bonds, such as many of the sulfides or highly hydrated minerals, also tend to burn more easily even under the lowest laser intensity setting. Cinnabar (HgS) provides an example where the high intensity 514 nm laser produces the spectrum of sulphur (S). Opaque phases, such as iron oxides, ab-

sorb more of the incident radiation making them also more susceptible to burning. Interestingly, even though the 532 nm laser is higher energy than the 785 nm laser, we have found cases where a mineral burns under 785 nm but not under 532 nm (i.e. para-montroseite, VO_2). Visual evidence such as dark brown to black craters of the size of the beam spot or discoloration of the mineral surface are usually indicative of burning and dehydration, respectively.

Another not so often effect related to the heating of the sample by the incident laser is that while the spectra remains essentially the same, the peak positions shift to lower wavenumbers with increasing the energy of the laser. We detect this phenomenon when we compare the spectra from the 532 and 785 nm lasers and correct the lower wavenumber spectrum by lowering the intensity of the laser.

1.4.2 Effects of the incident laser wavelength

While the position of the peaks in the Raman spectrum remains mostly constant under different excitation wavelengths, their intensities can vary. As we have seen, we collect Raman scans using two different laser excitations from the same spot on the sample and in the same orientation. Therefore, the high-resolution narrow scans provide a
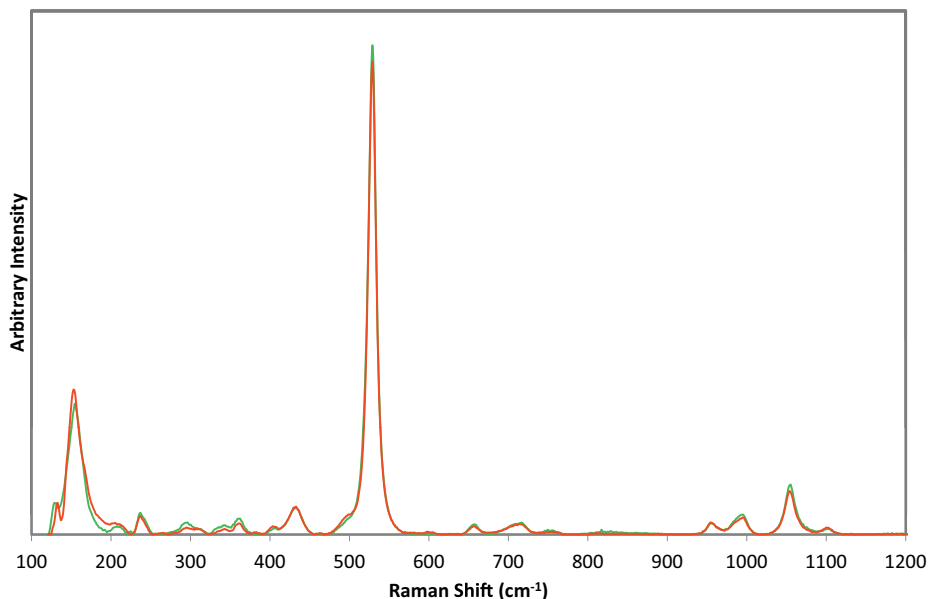

Fig. 1.11: High-resolution Raman spectra of the zeolite edingtonite (R040003), collected with both 532 (green line) and 785 (red line) nm lasers, illustrating an example of spectra whose patterns are essentially identical for both incident lasers. The sample was in identical position for both data collections, which eliminates the variation in intensities caused by orientation effects.

Fig. 1.12: High-resolution Raman spectra of enstatite (R040093), collected with both 532 (green line) and 785 (red line) nm lasers, illustrating an example of spectra whose patterns differ for both lasers. The sample was in identical position for both data collections, which eliminates the variation in intensities caused by orientation effects.
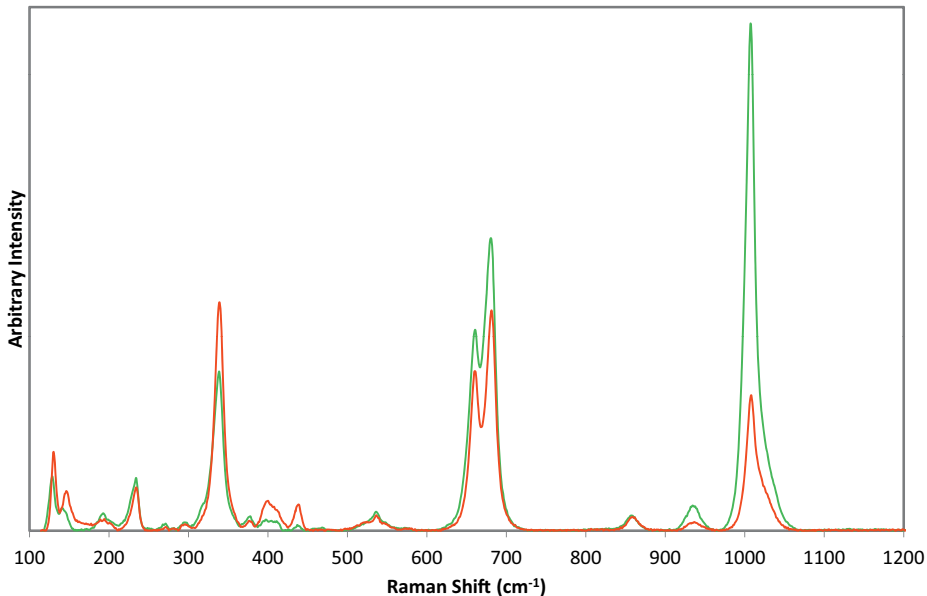
measure of how the spectra change with incident wavelength. We have seen that for some of the minerals, these two spectra may be the same or very alike, as in Fig. 1.11, but for others the intensities of identical modes can be different, as in Fig. 1.12.

1.4.3 Fluorescence

It has been found that about 16 % of the samples examined in the RRUFF project produced spectra that cannot be used for their identification, mostly due to the presence of broadband fluorescence or luminescence peaks dominating the Raman spectrum. Of these, half of them cannot be identified with either of the two lasers (532 and 785 nm) (Fig. 1.13), while the other half can be identified only with one of the lasers (Fig. 1.14).

   Usually, moving to longer wavelengths of excitation can significantly reduce fluorescence [31] with the tradeoff of reducing the Raman signal because of the relation $I_{Raman} \sim 1/\lambda^4$ [25]. However, we have observed that some minerals fluoresce under 785 nm but not under 532 nm, as shown in Fig. 1.14.

Fig. 1.13: High-resolution Raman spectra of loparite-Ce (R070251), collected with both 532 (green line) and 785 (red line) nm lasers, illustrating an example of spectra where both incident wavelengths are dominated by fluorescence.
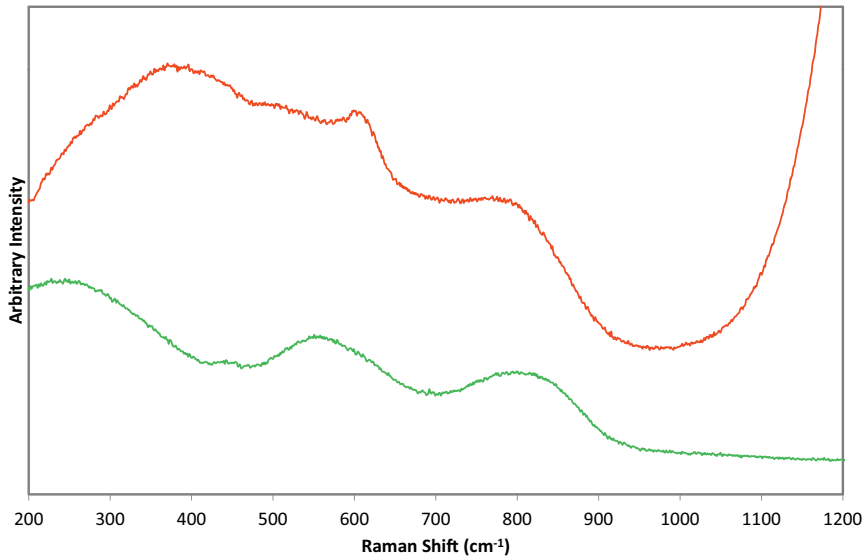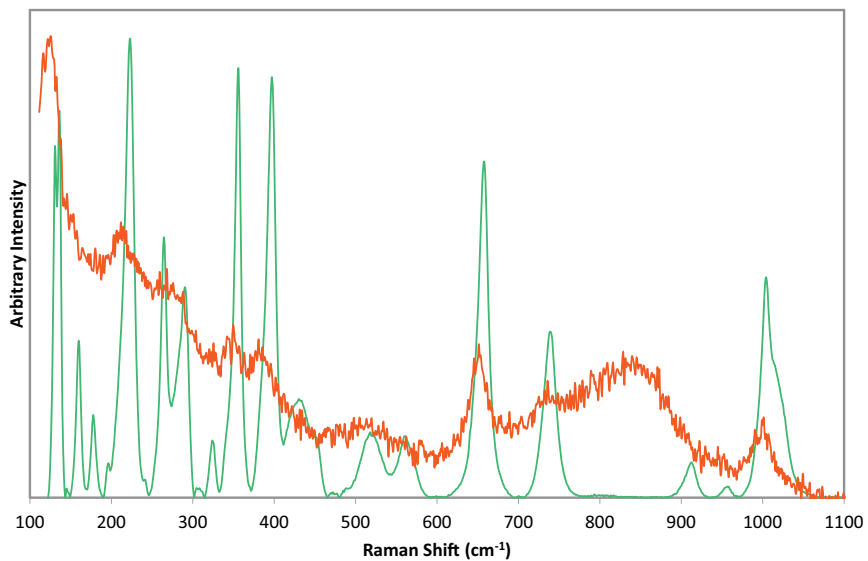

Fig. 1.14: High-resolution Raman spectra of dioptase (R040028), collected with both 532 (green line) and 785 (red line) nm lasers, illustrating an example of spectra where one of the incident wavelengths (780 nm laser) is associated with a poor pattern dominated by fluorescence.
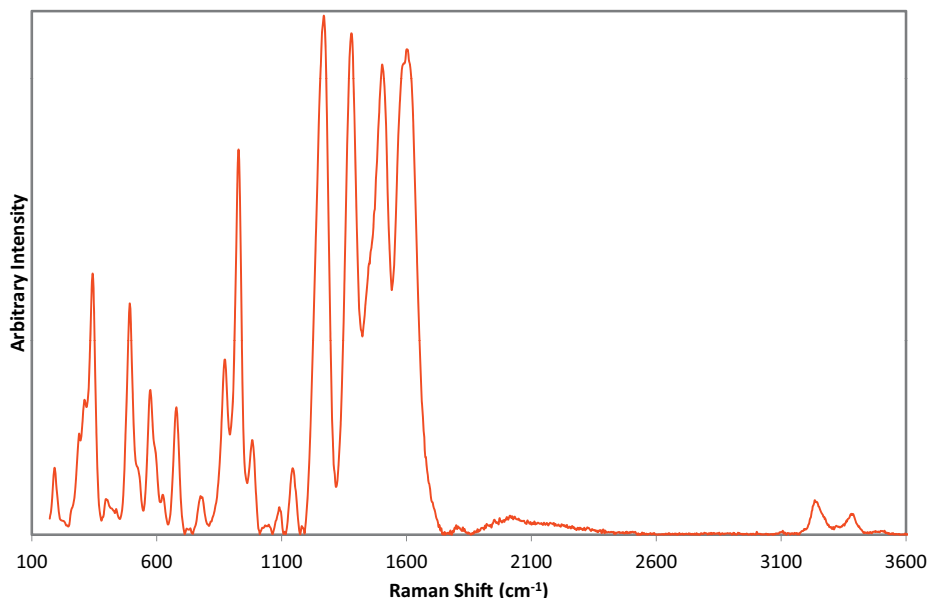
Fig. 1.15: Low-resolution Raman spectrum of zoisite (R060567), collected with the 785 nm laser, illustrating the significant luminescence features between 1200–1700 cm^{-1}. Such features were observed in the spectra of all the Ca-containing minerals from the deposits in Umba Valley, Tanzania [30]. The study proposes that these features are due to Nd^{3+} luminescence centers.

Some minerals may exhibit obvious luminescence peaks, as in Fig. 1.15, often due to the presence of transition metal or rare-earth ion centers [32], which in some situations, it can be used as a signature for the locality of the sample [30].

If the luminescence features are very intense, as in Fig. 1.16, they can obscure the Raman peaks of the particular mineral.

1.4.4 Presence of inversion center

Of the 4967 known mineral species, twenty-seven of them cannot produce a Raman signal because every atom is positioned on an inversion center. These include minerals that crystallize with the rocksalt (16) or copper (11) structures. In minerals containing an inversion center, the change in polarization of the atoms due to the incident beam is negated because the distortion of the electron cloud in one direction is equal to the distortion of the cloud in another direction. As a result, the Raman spectrum has intensity equal to zero. We have nevertheless collected the spectra for theses minerals and included them in the database (Fig. 1.17) because the absence of Raman activity also reveals important information about the sample. It is possible that some of these twenty-seven minerals may show weak Raman peaks. We interpret this as indicating
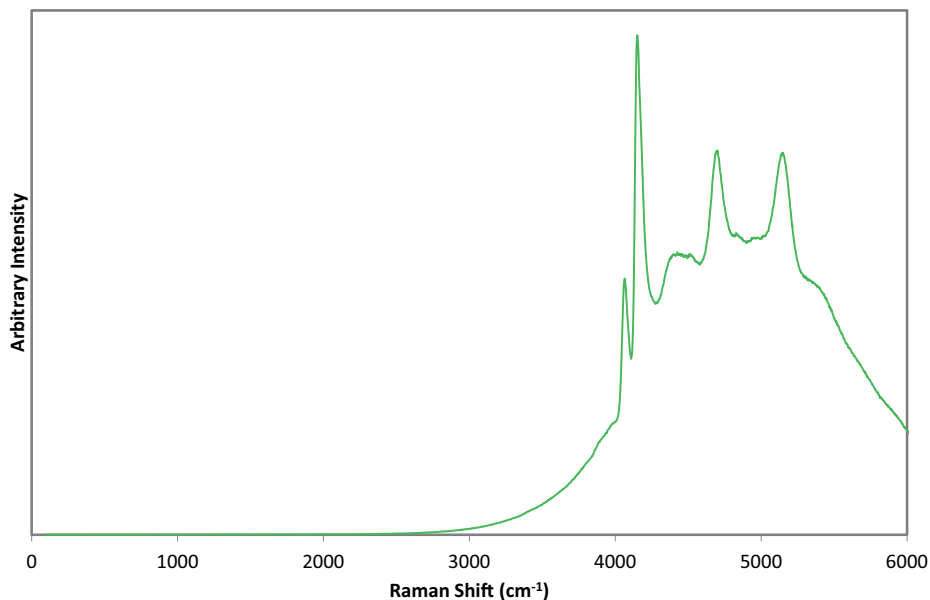
Fig. 1.16: Low-resolution Raman spectrum of unoriented topaz (R060024), collected with the 532 nm laser, illustrating intense luminescence features (4000–5200 cm^{-1}) that mask the Raman peaks under 1200 cm^{-1} (Fig. 1.10 shows the Raman bands of topaz in that specific region).

surface alteration. For instance, the oxidized surface of galena (PbS, rocksalt structure) may show weak peaks corresponding to minium (Pb$_3$O$_4$).

1.4.5 Metamict minerals

Metamict minerals are materials that were initially crystalline, but that have lost their crystallinity, partial or total, due to radioactive decay [33, 34]. Zircon [35], allanite [36], and titanite [37] are some examples of minerals that may exhibit metamictization. By annealing an unidentified metamict mineral at the appropriate temperature, its crystallinity can usually be restored and the sample identified by X-ray analysis. The RRUFF project studied eight metamict samples before and after heating to explore the effects on their Raman spectra. For example, the metamict gadolinite-(Y) (R060856) was identified and its Raman obtained after heating the sample at 1000ºC during 23 h [38].

Radiation damage produces change in the chemical and structural properties of minerals, and therefore, it can have dramatic effects on the Raman spectrum of a sample including loss of peak intensity, increase in peak width, and shifts in peak frequencies. For example, Nasdala et al. [39] calibrated the degree of metamictization in natural zircon crystals (ZrSiO$_4$) by measuring the broadening and shift towards lower
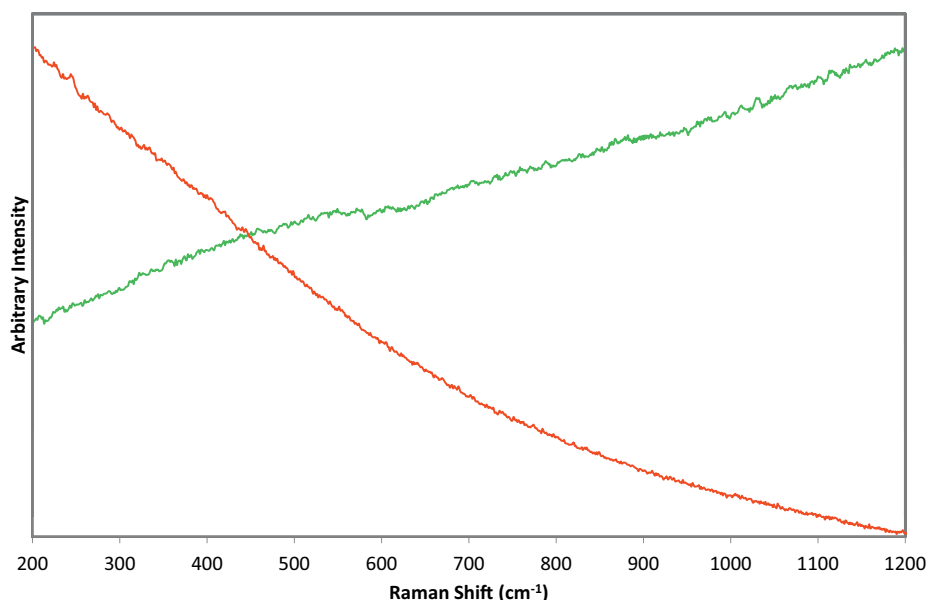
Fig. 1.17: High-resolution Raman spectra of halite (R070534), collected with both 532 (green line) and 785 (red line) nm lasers, illustrating the absence of Raman activity in minerals with every atom positioned on an inversion center.

wavenumbers of the Raman band at ~ $1008\,\mathrm{cm}^{-1}$ ($v_3\mathrm{SiO}_4$). Fig. 1.18 shows the variability in the position and width of the $v_3\mathrm{SiO}_4$ band in the Raman spectra of six zircon samples collected for the RRUFF project.

1.5 Applications of the RRUFF project

The power of the RRUFF project lies in its capability to aid in mineral identification and characterization. Records of well-characterized minerals can be used as a reliable Raman reference, and the ancillary software, including CrystalSleuth, XtalDraw, and XPOW, provides visualization and manipulation of data. Equally important to the RRUFF project is that its database should also provide the capability for inspiring other research efforts. For instance, a search on March 2015 of the Science Direct website (http://www.sciencedirect.com) retrieved a listing of 339 manuscripts that use data from the RRUFF project. These publications come from a broad variety of disciplines, including mineralogy, crystallography, geology, archeology, planetary science, art, medicine, material science, physics, chemistry, environmental, biology, and forensics.

The abundant and diverse collection of Raman spectra, X-ray diffraction patterns, and chemical analysis permit the systematic examination and analysis of mineral groups, chemical variations, phase transitions, etc. For example, using chemical anal-
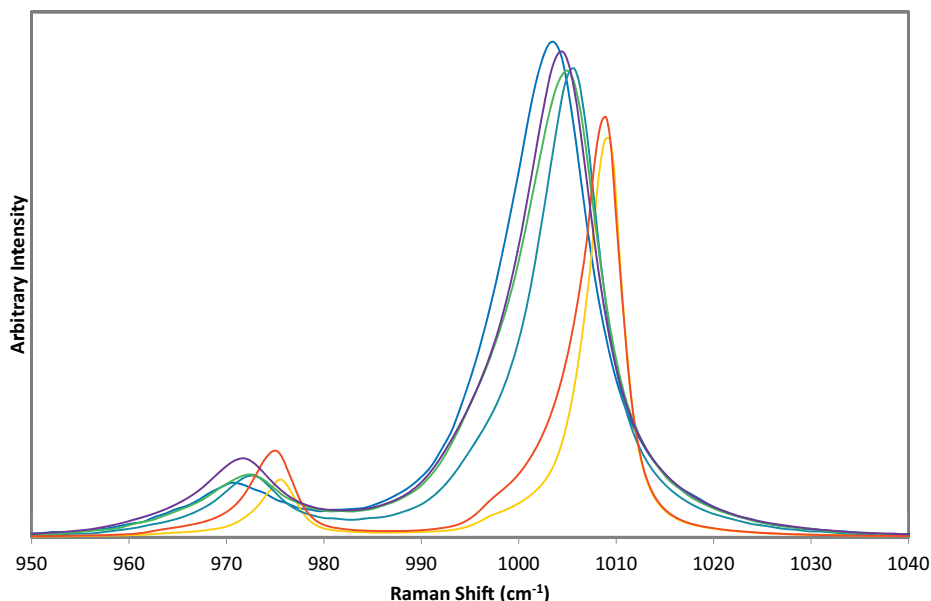
Fig. 1.18: Raman spectra in the 950–1040 cm^{-1} region of six unoriented zircons from the RRUFF database collected with 532 nm laser, showing the shift and broadening of the v_3 SiO4 mode: R050034 (blue), R100144 (purple), R050488 (green), R050286 (aquamarine), R100128 (red), and R050203 (orange).

yses of 40 various garnets from the RRUFF project, Henderson and Downs [40] shows that the Raman spectra of silicate garnets are correlated to their empirical chemical compositions and can be used to estimate the compositions of unknown garnets to within 3 % atoms per formula unit, based on measurements of sixteen cations.

The collection of Raman spectra in the RRUFF database has had a profound impact on the gemology community. The inexpensive and non-destructive nature of Raman spectroscopy makes it a suitable technique for its use in this field, especially given the perfection of gemstones. The Raman spectrum of gemstones is not only used for their identification but also to determine their provenance (Fig. 1.15), as well as natural or synthetic origin and possible treatments applied to them [41]. For example, Lowry et al. [42] acquire Raman spectra from 96 semi-precious gemstones with the aim of classifying them with reference spectra from the RRUFF database. The RRUFF database and CrystalSleuth are used by Kuehn [43] to study the application of Raman spectroscopy for the identification of gemstones. The work by Jasinevicius [30] characterizes the vibrational and electronic features in the Raman spectra of many gemstones in the RRUFF database. The Raman instruments developed by M&A Gemological Instruments (MAGI) include the GemmoRaman software (http://www.gemmoraman.com/GemmoRaman-532.aspx) which provides a plugin

for the automatic export of collected spectra into CrystalSleuth for their identification.

The variability in the RRUFF Raman spectra collection, reflected in chemical composition, laser wavelength, fluorescence, symmetry, site occupancy, and orientation, makes it suitable to use for building and testing mathematical models to automatically identify mineral phases from their Raman spectra. In Hermosilla Rodriguez et al. [44] they use one hundred randomly selected spectra from the RRUFF library to test an algorithm to identify mineral phases by Raman spectroscopy. In a recent publication, Cochrane and Blacksberg [45] develop a method to identify individual Raman features in mineral mixtures by using 11572 Raman spectra downloaded from the RRUFF project. The development of these models is of special importance for planetary science as they will be necessary in the analysis of the data coming from the Raman instruments planned for future space missions (see for example [46, 47]). A Raman spectrometer has been chosen as a part of the science instrument payload of the European Space Agency 2018 ExoMars mission to target mineralogical and astrobiological investigations on the surface and subsurface of Mars [48, 49] and NASA has just announced that its 2020 Mars Rover payload [50] will carry two Raman spectrometers to determine fine-scale mineralogy and detect organic compounds.

The identification and characterization of mineral specimens for the RRUFF project requires considerable research, mostly when something does not match with the available data. The lack of a match may occur because it is a new mineral, because its data was previously reported wrong, or because we do not have it yet in our database. So far, the IMA nomenclature commission has approved 21 new minerals discovered and described by our group (e.g. [51–54]) with other 50 or so anomalous specimens that require more careful examinations and currently remain non-public in the database.

We also study crystal structures of minerals with previously unreported structures (e.g. [55–58]), or minerals with problems on their previously reported structural data (e.g. [59, 60]). In our experience, the greatest problem with previously reported cell parameters from the older literature is found where twinning or subcell/supercell relations were not recognized, especially for data collected with point detectors. In some cases, the redefinition of the structure leads to a new ideal chemical formula for that mineral. For instance, esperite was first defined by Moore and Ribbe [61] as monoclinic with a well-developed "superlattice". However, Tait et al. [62] demonstrated that the so-called "superlattice" reflections were due to the presence of triple twins probably resulting from a high-to-low temperature phase transformation, which led them to the redefinition of the ideal chemical formula from $PbCa_3(ZnSiO_4)_4$ to $PbCa_2(ZnSiO_4)_3$. In the case of the redefinition of the vladimirite, the work by Yang et al. [63] demonstrates that while the ideal chemical formula of this mineral was correctly reported by Nefedov [64] as $Ca_4(AsO_4)_2(AsO_3OH)\cdot4H_2O$, it had been modified incorrectly as $Ca_5H_2(AsO_4)_4\cdot5H_2O$ by subsequent studies [65].

1.5.1 Crystal-chemistry analysis of Mars samples

The RRUFF project is playing an important role in the study of the chemical composition of the mineral phases analyzed by the CheMin X-ray diffractometer [66] on the Mars Science laboratory rover Curiosity in Gale crater, Mars. Using the refined unit-cell parameters of samples analyzed at the sand dune, Rocknest [67, 68], Morrison et al. [69] estimates the empirical chemical formulas of the most abundant phases identified, including Mg-Fe-olivine, Mg-Fe-Ca-pyroxene and Na-Ca-K-feldspar. For the study, a large dataset of unit-cell parameters in combination with their associated chemical compositions were collected from the RRUFF project and the literature for each of these major phases. Moreover, by determining the chemical composition of the individual crystalline phases they were also able to estimate the bulk composition of the crystalline materials as well as the amorphous component. This methodology will be applied to each of the analysis performed by the CheMin instrument in the surface of Mars.

1.5.2 The Mineral Evolution database

The Mineral Evolution project [70] aims to understand how the episodes of planetary accretion and differentiation, plate tectonics, and origin of life lead to a selective evolution of mineral species through changes in temperature, pressure, and composition. In order to investigate questions related to these mineralogical changes through time and geological settings, the Mineral Evolution database [71] was created in partnership with the RRUFF project and Mindat.org (http://www.mindat.org). The goal of the database is to correlate the diversity of mineral species with their ages, localities, and other measurable properties. The RRUFF project serves as a platform to store and display the data accessed through the IMA-List. Mindat.org supplies the database with mineral localities and their associated mineral species.

1.6 Future directions

The RRUFF database was designed to include measurements restricted to microprobe analysis, Raman and infrared spectra, and X-ray diffraction patterns of minerals. This rigid structure prevents the addition of new measurements, such as Mössbauer, LIBS, or UV spectroscopy, without extensive and costly modification of the current software platform. The custom programmed solution used by RRUFF also makes it impracticable for other researchers to use with their data.

These limitations have led to the development of the Open Data Repository [72], an open-access platform for data publication funded by the Mars Science Laboratory CheMin team and NASA-Ames; developed by the University of Arizona's Department

of Geosciences, and the Open Data Repository non-profit organization. The platform aims to provide researchers with a simple tool to publish any or all data related to their research on material properties. The data publication system makes it possible to share data publicly, to invite collaborators, and ensure research integrity.

With this system, users can create their own data repositories in their local server for their diverse data sets. Creating a data repository is a drag-and-drop procedure facilitated through a web-based forms designer. No direct interaction with the under-lying database is required. The user can select and add different field types to their data sets and modify the design at any time to include new fields or file storage ar-eas. The user can then start creating data records that describe individual pieces of data. A plugin system allows data sets containing XY data to be graphed and plotted to HTML output. Plug-ins for rendering chemical formulas and for displaying images in galleries are also bundled with the system.

The platform has been in development for over two years and is undergoing beta testing by a number of research groups. NASA's CheMin data from the Mars Science Laboratory is being published on the system as a proof of concept. Many new fea-tures and sharing tools will be developed under a new, 5-year contract with funding from NASA's SERA initiative and the Astrobiology Habitable Environments Database (AHED) [73] which will host data from a number of researchers in the astrobiology community.

In the long term, the migration of the RRUFF database into this new platform will make it possible to complement the current characterization of the mineral specimens with other techniques.

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