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APLICATION OF ADVANCED ANALYTICAL TECHNIQUES RAMAN AND FTIR-ATR FOR CHARACTERIZATION AND IDENTIFICATION OF SOME GEMSTONES

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ABSTRACT

The reliability of FT-Raman and FTIR-ATR analytical techniques is critical for gemstone authentication and reliability. As they are non-destructive techniques, FT-Raman and FTIR have become powerful tools for the characterization and differentiation of these gems. In order to certify their respective origins and assess their reliability, some samples such as: beryl, spodumene, topaz, quartz and tourmaline were analyzed. The results were compared to a reference database, consolidating these tools as reliable in identifying authenticity.

1. INTRODUCTION

Gemstone identification has always been a great challenge in both commercial and scientific fields. Even a well-trained and educated gemologist often struggles to determine whether a gemstone is natural, synthetic, enhanced (irradiated, for example), or to identify its origin [1] [2].

With the advent of techniques capable of synthesizing minerals with characteristics identical or very similar to natural gems, as well as the different possibilities for generating imitations of gems using similar materials, the challenges only increase every day. An even more complex scenario represents the fact that gem identification techniques still need to offer non-destructive or, at least, minimally invasive analysis capabilities. On the other hand, technical laboratory resources for identifying minerals and chemical substances in general have also progressed intensely [1] [2] [3]. The search for a reliable analysis of gemstones is obviously extremely important, as many of them may present counterfeit. Therefore, contributing with more advanced analyzes in the forensic and commercial areas promises to make them reliable, by proving their real authenticity. And two major technical advances that are very important for overcoming it is represented by FT-Raman and FTIR-ATR (Attenuated Total Reflection Infrared Spectroscopy). They are extremely important for mineral identification and thus become very relevant tools for more in-depth studies that often cannot be determined accurately with naked eye [4] [5].

FT-Raman is one of the vibrational techniques that allows molecular characterization of inorganic species by identifying specific types of chemical bonds through the production of an infrared absorption spectrum that acts as a molecular fingerprint. The technique involves measuring the inelastic scattering of monochromatic radiation by substances with covalent components. In this process, there is an energy exchange between the incident photon and the chemical bond, resulting in scattered photons with higher or lower energy than the incident photon [6] [7].

Likewise, FTIR-ATR is an analytical technique that uses internal reflection to analyze the interaction of infrared radiation with a sample. This method relies on the phenomenon of evanescent

waves that occur when infrared light is internally reflected within a high refractive index crystal in contact with the sample [5] [6] [7].

Both techniques require simple preparation and can produce well-defined spectra with very accurate results. The processes are not necessarily destructive, although FTIR-ATR might require minimal pulverization. It is always highly advisable to perform a comparative analysis of the spectra from both techniques, as they are complementary laboratory tools [4] [8].

Therefore, contributing advanced analyses in forensic and commercial fields promises to ensure considerable advances in gem identification [9].

FT-Raman, complementarily, due to its non-destructive nature in evaluating single crystals, can be used to differentiate between natural and irradiated or treated gemstones. The spectra are able to detect subtle changes in the chemical bond structures of gemstones caused by treatments such as irradiation. The only drawback of this technique is its high cost of acquiring [9] [10].

This article addresses the possibility of using these two spectroscopies as possible substitutes for traditional gemological procedures.

2. METHODOLOGY

This study involved samples of Tourmaline, synthetic gemstone, Topaz, Beryl, Quartz, and Spodumene, which were provided by a dealer from the Belo Horizonte region (Minas Gerais State, in Brazil). The sample information is presented in the Tab. 1

Table 1. Samples available for analysis on FT-Raman and/or FTIR equipment

Gem	Mineral Class	Mineral	Color	Procedure
G1	Tourmaline	Tourmaline	Yellow-green	Minas Gerais
G2	Synthetic Gem	Synthetic Gem	Green	Teófilo Otoni/MG
G3	Topaz	Imperial Topaz	Orange	Ouro Preto/MG
G4	Beryl	Aquamarine	Blue-green	Santa Maria de Itabira/MG
G5	Beryl	Goshenite	Colorless	Santa Maria de Itabira/MG
G6	Beryl	Morganite	Pink	Sao Jose de Safira/MG
G7	Quartz	Prasiolite	Green	Rio Grande do Sul
G8	Spodumene	Kunzite	Colorless	Governador Valadares/MG

The samples were analyzed by means of FT-Raman and FTIR-ATR analytical techniques. FT-Raman spectra was performed on single crystals using a laser with a wavelength of 1064 nm. For FTIR-ATR, a pulverization in the microgram range was in this case necessary, with the amount needed only to cover the analyzer's crystal (1 mm in diameter). It is important to note that the records available in the RRUFF database [11] for the FT-Raman technique were at 532 and/or 785 nm. RRUFF is a free and online spectral database that provides detailed information about minerals and gemstones, including their physical and chemical properties and crystallographic data. It is important to note that Raman equipment can operate at various wavelengths, both in the visible range and in the NIR. Experimentally, a wavelength of 1064 nm was used, which is not the one employed in the RRUFF database. However, the Raman results do not show significant differences based on the choice of a specific wavelength. The only significant differences occur in the intensities of the bands, not in their positions.

The FT-Raman RAM II module coupled with the Vertex 70V spectrometer was controlled by OPUS software and met performance test standards. The power used for each single crystal sample was $500\,\mathrm{mW}$, which represents the maximum power of the equipment. The FTIR-ATR Vertex 70V spectrometer, equipped with the "Platinum ATR, Multiple Crystals CRY" diamond accessory, was also controlled by OPUS software [1] [10]. The spectra were scanned with a $4\,\mathrm{cm}^{-1}$ resolution and with 128 scans (one minute).

The spectra for each gemstone studied were plotted on Spectragryph software and presented allways in absorbance for suitable standardization, and compared with spectra from the RRUFF reference database [11].

3. RESULTS

The sample G2, represented in Fig. 1 was provided as a synthetic gem, showed quartz characteristics when comparing the spectra with the RRUFF database [11]. As it is a green sample it was classified as Prasiolite.
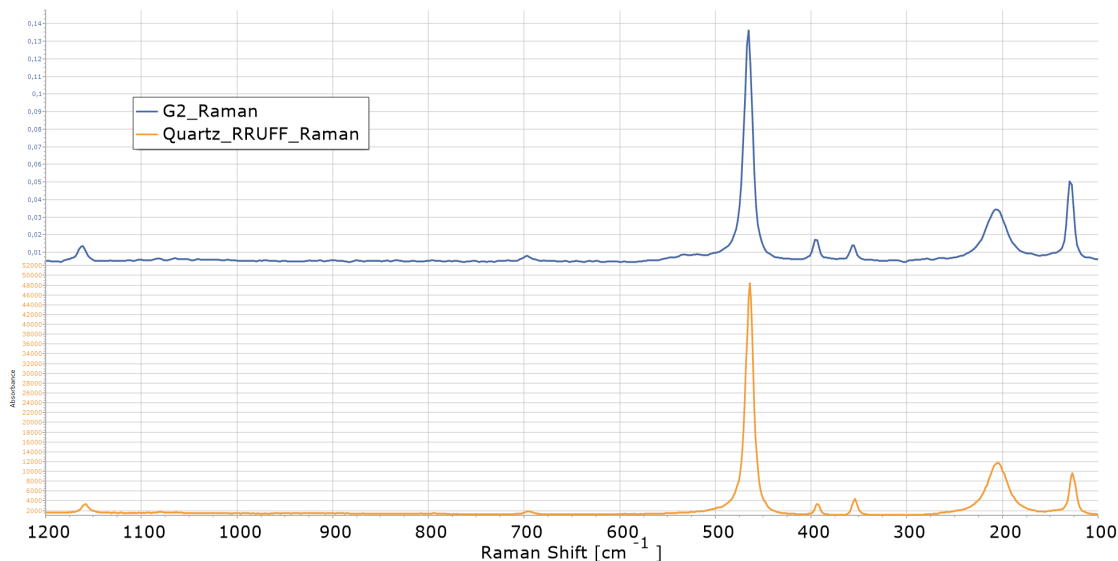
Figure 1. Received as Synthetic Gem and identified as Quartz

In Fig. 2 Fig. 3 Fig. 4 Fig. 5 are the spectra the G3, G4, G5 e G7 samples which were received as Imperial Topaz, Aquamarine, Non identified, and Prasiolite, respectively. All the gemstones were analyzed using both analytical techniques and mostly exhibited the same spectroscopic pattern as the RRUFF database [11]. In the case of the G5 gem, colorless Beryl (Goshenite) was identified once both analytical techniques have confirmed a match with a reference spectra in the database.

The spectrum shown in Fig. 6 (G6) represents the sample that was received as Morganite (pink beryl), but was actually Kunzite (pink spodumene). This is confirmed when compared with the spectra from the RRUFF database as well [11]. For this gem, no representatives bands were shown by the FTIR technique. However, just using the FT-Raman technique, it was possible to identify and confirm to be Spodumene.
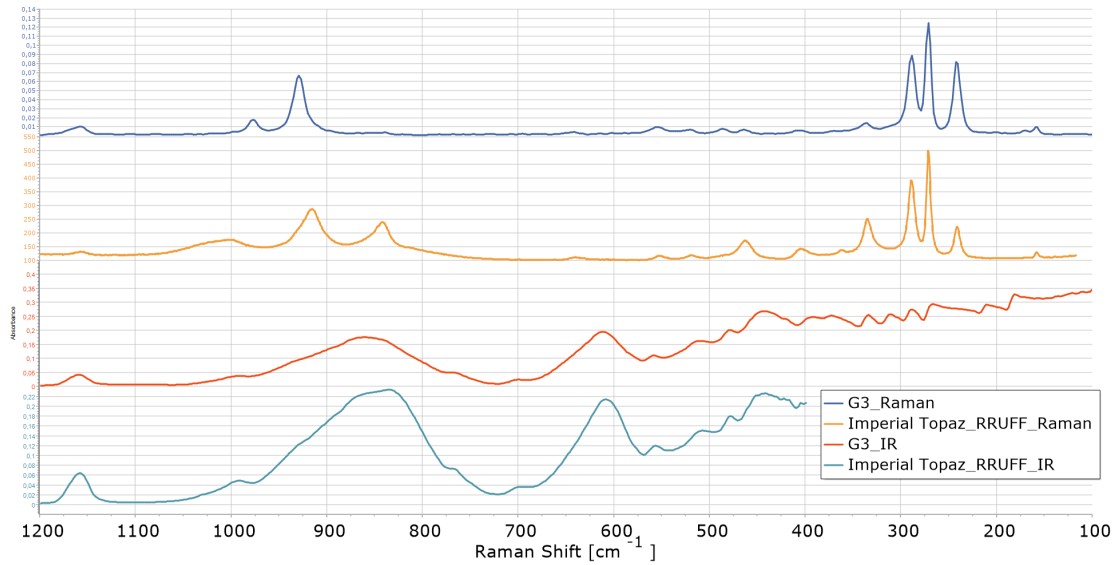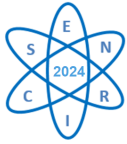
Figure 2. Mineral received and identified as Imperial Topaz
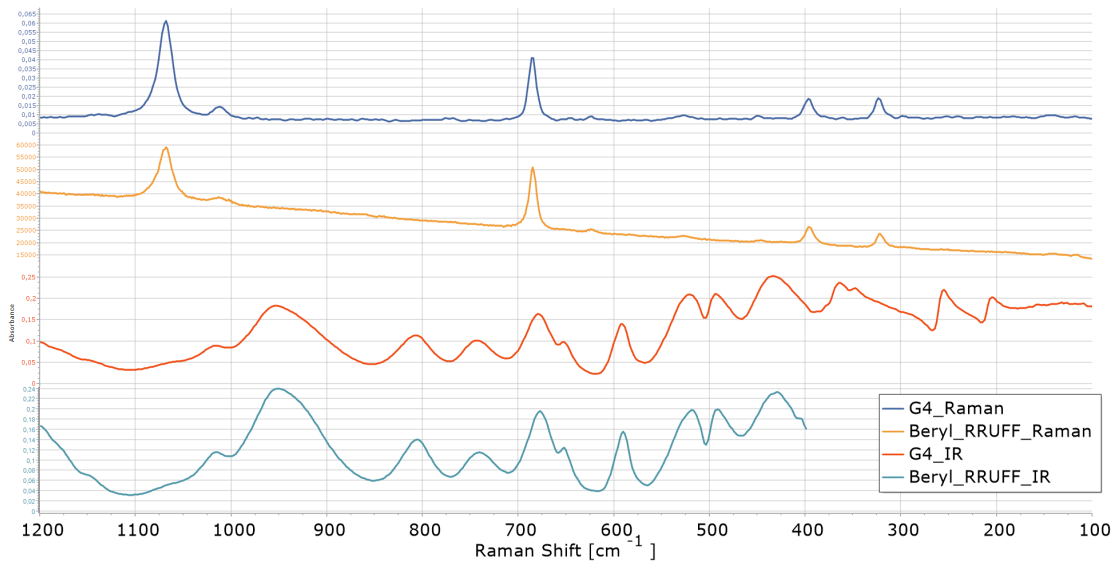

Figure 3. Mineral received and identified as Aquamarine

In Fig. 7 (G8) the mineral was provided as Spodumene (colorless). However, upon analyzing the spectra with both techniques, it was found to be Goshenite (colorless beryl).

The spectra Fig. 8 of sample G1 did not result in such conclusive scenario. The FTIR spectrum, for example, showed a practically inert spectroscopic pattern (no representative peaks for silicates or any other chemical bond with any percentage of covalent component), suggesting to be a sample with high percentages of ionic bonding. Considering that this sample shows gemological quality,
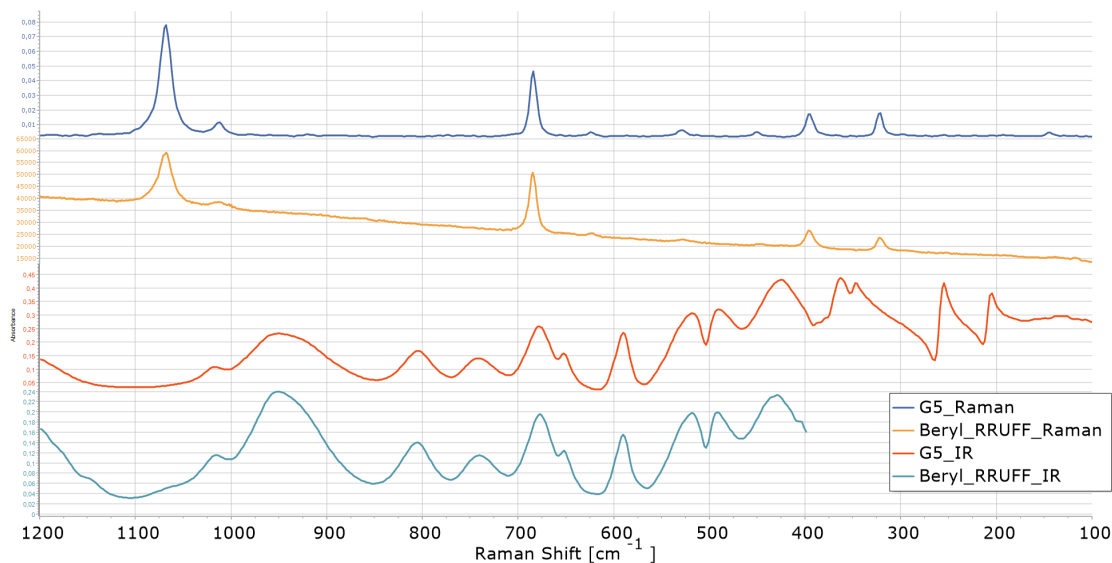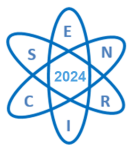
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Figure 4. Mineral received without identification and confirmed to be Goshenite
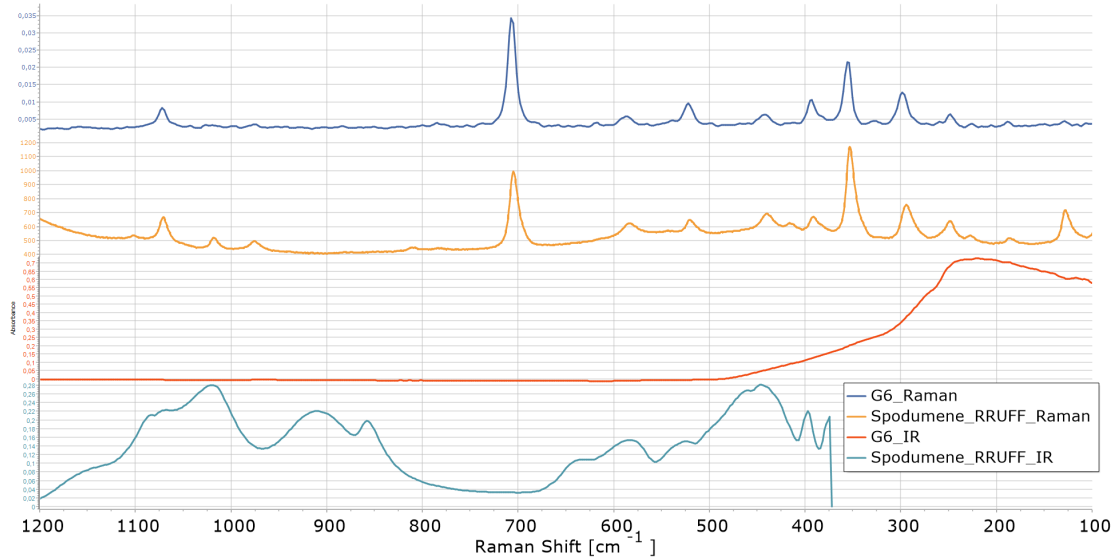

Figure 5. Mineral received and identified as Prasiolite

one might conclude to be an oxide. According to the RRUFF database, only the spectrum of Zincite would therefore fit a candidate for a gemological oxide. However, this was not confirmed when compared with the respective Raman spectrum of Zincite.
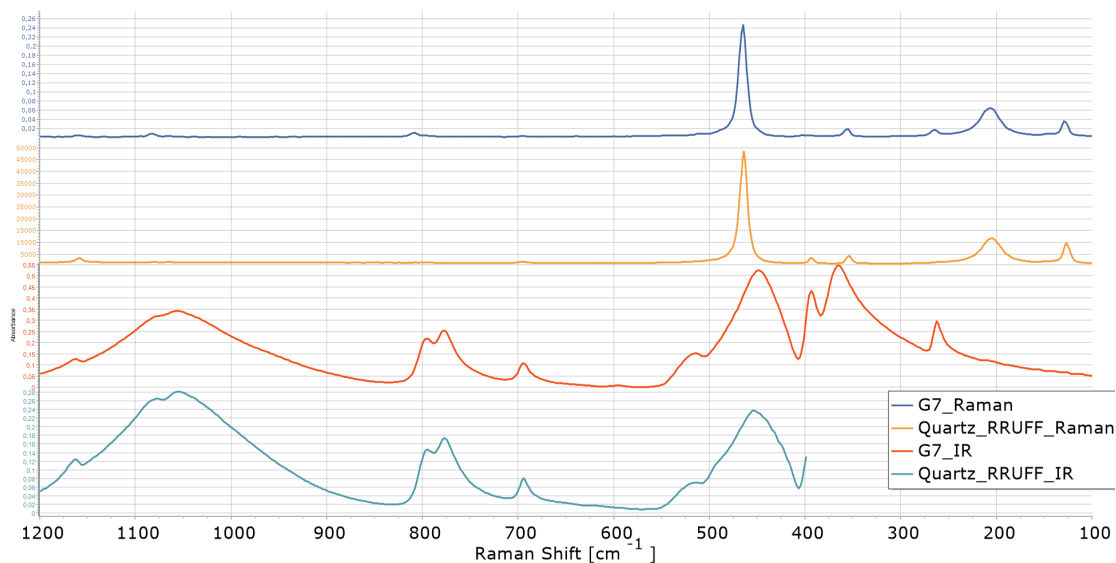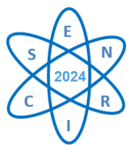
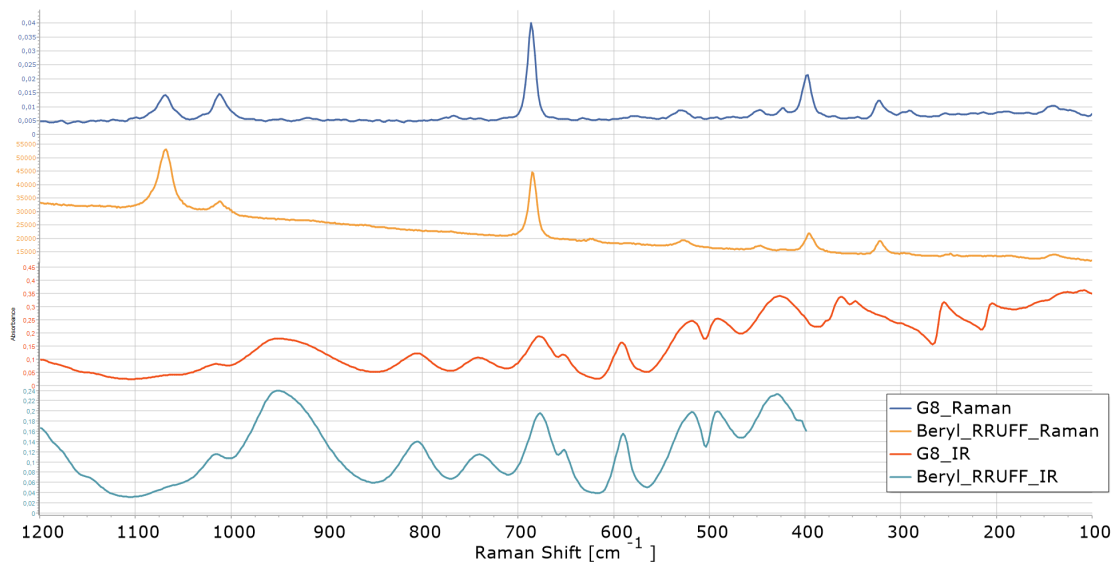Figure 6. Mineral received as Morganite and identified as Kunzite

Figure 7. Mineral received as Spodumenium and identified as Goshenite

4. CONCLUSION

Although the 1064 nm wavelength laser has not been used yet in the RRUFF database it surprisingly yielded results similar to, if not identical to, those obtained with the 532 nm and 785 nm wavelengths. It can be concluded that comparing spectra obtained at different wavelengths, the 1064 nm wavelength in these cases produced better spectral quality. This might be due to the germanium
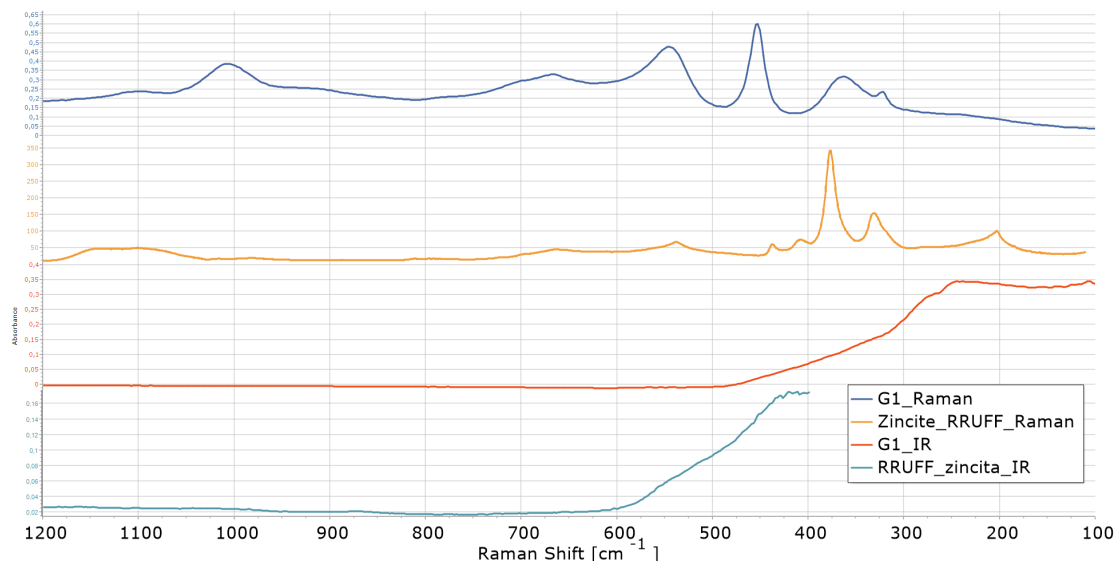
Figure 8. Mineral received as Tourmaline and not identified

detector, which is cooled with liquid nitrogen, making it more sensitive. The signal-to-noise ratio therefore improves significantly, generating better spectral results compared to a conventional Raman spectrometer

The application of FT-Raman and FTIR-ATR techniques in gemstone characterization and identification keeps being very promising, as it allows for precise identification of gemstones without needing to know the mineral type in advance, as demonstrated by the G5 sample. These techniques not only help determine which gemstone is truly valuable but also detect potential counterfeits or incorrect information. In addition to improving the understanding of the chemical and physical properties of gemstones, these techniques can also offer a non-destructive analysis that does not compromise the authenticity and value of gemstones in the market.

However, the total dependence on spectral databases and robust search algorithms is still a challenge that will force researchers to keep their knowledge of traditional gemological laboratory techniques very active.

ACKNOWLEDGEMENTS

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