World Academy of Science, Engineering and Technology
International Journal of Chemical and Materials Engineering
Vol:17, No:1, 2023

Investigation and Identification of a Number of Precious and Semi-Precious Stones Related to Bam Historical Citadel Using Micro Raman Spectroscopy and Scanning Electron Microscopy

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***Abstract*—**The use of gems and ornaments has been common in Iran since the beginning of history. The prosperity of the country, the wealth, and the interest of the people of this land in a luxurious and glorious life, combined with beauty, have always attracted the attention of Iranian people to gems and jewelry. Iranians are famous in the world for having a long history of collecting and recognizing precious stones. In this case, we can use the unique treasure of national jewelry. Raman spectroscopy method is one of the oscillating spectroscopy methods that is classified in the group of nondestructive study methods, and like other methods, in addition to several advantages, it also has disadvantages and problems. Micro Raman spectroscopy is one of the different types of Raman spectroscopy in which an optical microscope is combined with a Raman device to provide more capabilities and advantages than its original method. In this way, with the help of Raman spectroscopy and a light microscope, while observing more details from different parts of the historical sample, natural or artificial pigments can be identified in a small part of it. The EDX (Energy Dispersive X ray) electron microscope also functions as the basis for the interaction of the electron beam with the matter. The beams emitted from this interaction can be used to examine samples. In this article, in addition to introducing the micro-Raman spectroscopy method, studies have been conducted on the structure of three samples of existing stones in the historic citadel of Bam. Using this method of study on precious and semi-precious stones, in addition to requiring a short time, can provide us with complete information about the structure and theme of these samples. The results of experiments and gemology of the stones showed that the selected beads are agate and jasper, and they can be placed in the chalcedony group.

***Keywords*—**Bam citadel, precious stones, semi-precious stones, Raman spectroscopy, scanning electron microscope.

I. Introduction

THE golden leaves that have been obtained from the historical sites of Iran for thousands of years show a clear sign of the taste, intelligence and art of the people of this land, so that with scientific, historical, technical knowledge, form, decoration, etc., there can be found unique works that can have a special place in the culture and art of the world as a precious memory. Unfortunately, nowadays, people pay more attention to the gender of this precious material, while their form, composition, decoration, technique, etc., can keep the attention of the eyes and heart throughout the years and even for many centuries [1].

Considering that many art objects left from distant centuries are considered valuable in every way and we also have to consider these objects non-renewable, it is very important to use nondestructive methods when studying them. In recent years, various destructive and nondestructive methods have been used to study the works, among them X-ray radiation methods (PIXE, XRF and XRD), Inductively Coupled Plasma Spectroscopy (ICP), Atomic Absorption Spectroscopy (AAS) , Scanning Electron Microscope (SEM), optical spectroscopy and vibrational spectroscopy (IR and Raman) can be considered as the most important of them [2].

The strategic importance of the Kerman region and especially the region we are discussing, Bam, in prehistoric times is on the great roads that connect the civilizations of the Indus Valley and Mesopotamia to the extent that the evidence shows that the oldest trade exchanges and technological and cultural in the continent of Asia, obsidian stone is from this region [9]. The city of Bam was registered as the first city in Iran in 2004 in the list of UNESCO World Heritage Sites with number 1204. (Fig. 1), and in this respect, it is unique and a source of pride [10]. Based on this, all works with historical and cultural values within the scope of this world heritage work, whether natural or artificial, tangible or intangible, are subject to protection.

Introducing samples

As explained earlier, in this article, we intend to use a Raman microscope to obtain Raman spectra from samples of exploratory precious stones from Bam citadel, and then extract information about the structure of these materials by examining these spectra. SEM and gemological studies have also been used to complete and correct the information. (There is no information about where the samples were obtained.) The studies conducted in this research were conducted on three different samples, whose pictures can be seen below: Sample A1 is shown in Fig. 2, Sample A2 is shown in Fig. 3, and Sample A3 is shown in Fig. 4.

Sample A1 belongs to a three-faceted beaded stone (BEAD) weighing 7.41 carats, size about 21 * 7 mm, semi-matte red-

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brown color, with dark streaks and a visible hole on one side, that is possible is formed during stone cutting (Fig. 2 (a)). Inclusions of iron oxide (hematite) are visible on it.

Sample A2 belongs to a BEAD weighing 19.7 carats, size about 8 * 20 mm, semi-matte green-brown color, with dark and light streaks on all its sides and a stain. Ocher is visible on both sides. The stone is generally dark and light.

Sample A3 belongs to a BEAD weighing 12.18 carats, size about 19 * 7 mm, dark green semi-matte color. In some parts of it, there are tiny red spots of hematite. On all its faces, there are small irregularities similar to erosion, which may be due to the separation of square grains of less than one millimeter of hematite, or caused by wear and tear of a stone equivalent to the hardness of this stone.

Fig. 1 A view of the historical citadel of Bam

(a) (b)

Fig. 2 Image of sample A1 by gemological microscope; there is a small hole on the surface of the bead

Fig. 3 Image of sample A2 by gemological microscope

According to the relevant historical documents, the type of stone cutting can be attributed to the third millennium AD. Microscopic images were taken with an Olympios gemological microscope at 40X magnification.

Fig. 4 Image of sample A3 by gemological microscope

II. Test Method

A. Raman Spectroscopy and Scanning Electron Microscope (SEM)

Raman Spectroscopy

Currently, archaeologists have focused a large part of their studies on the objects and artworks left from historical era in order to know how people lived in the distant years [3].

Micro-Raman spectroscopy is one of the types of Raman spectroscopy in which an optical microscope is combined with a Raman device to provide more capabilities and advantages than the original method. In this way, with the help of Raman spectroscopy method and an optical microscope, while observing more details from different parts of the historical sample, natural or artificial pigments can also be identified in a small point of it [4]. An Apos model Raman microscope of Teksan company was used to perform the experiments in this research. This microscope is equipped with a green laser with a wavelength of 532 nm, and objective lenses were used to focus the beam on different points of the sample.

Spectroscopy of Sample A1

The obtained spectrum from sample A1 (Fig. 5) is very similar to the reference spectrum of quartz on the website *RRUFF* [8]. Comparing this obtained spectrum with the spectrum introduced for Quartz stone shows that there is SIO2 in the existing stone structure. We have Raman spectrum in the range of 465 cm^{-1}, 199 cm^{-1} and 502 cm^{-1}; that the intensity of the spectrum is high in the range of 465 cm^{-1}, it is considered the main spectrum.

Spectroscopy of Sample A2

The spectrum obtained from sample A2 (Fig. 6) is also very similar to the reference spectrum of quartz (there is SIO2 in the existing rock structure), and for this reason, there is no tangible difference between the spectrum obtained from this sample and the reference spectrum witnessed. We have a Raman spectrum in the range of 465cm^{-1} and 199 cm^{-1}; that the intensity of the spectrum is high in the range of 465 cm^{-1}, it is considered the main spectrum.

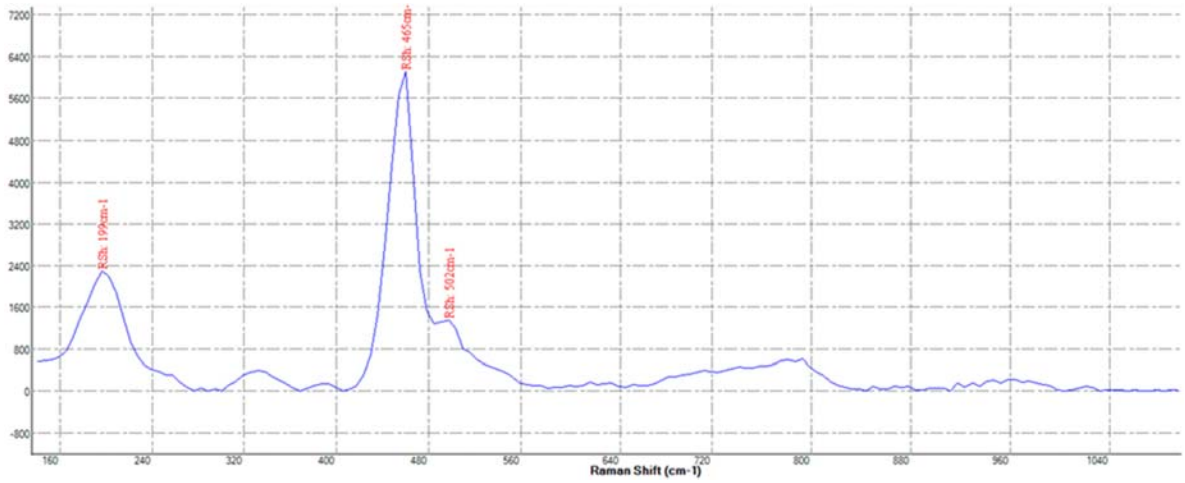

Fig. 5 Normalized Raman spectrum of sample A1

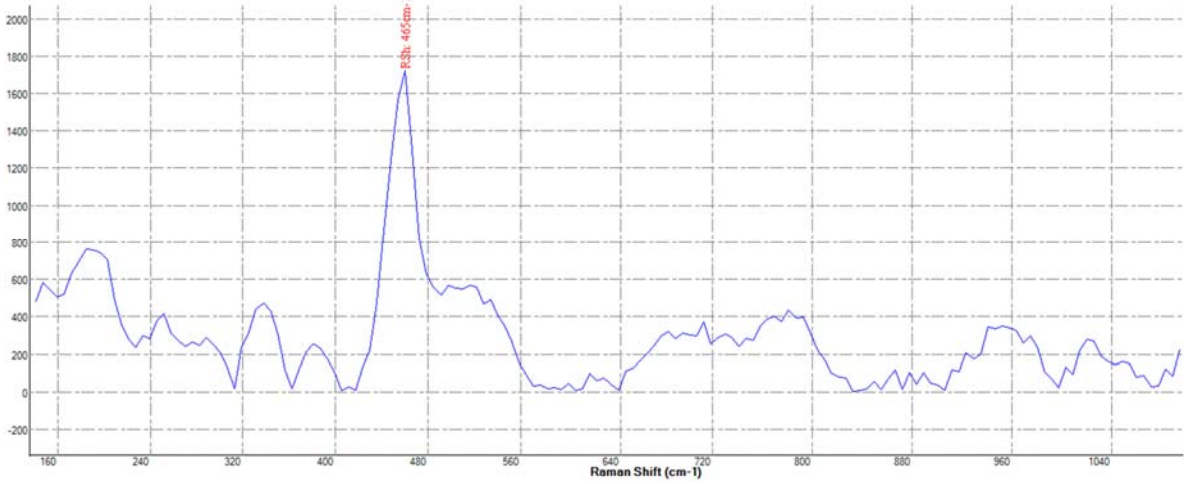

Fig. 6 Normalized Raman spectrum of sample A2

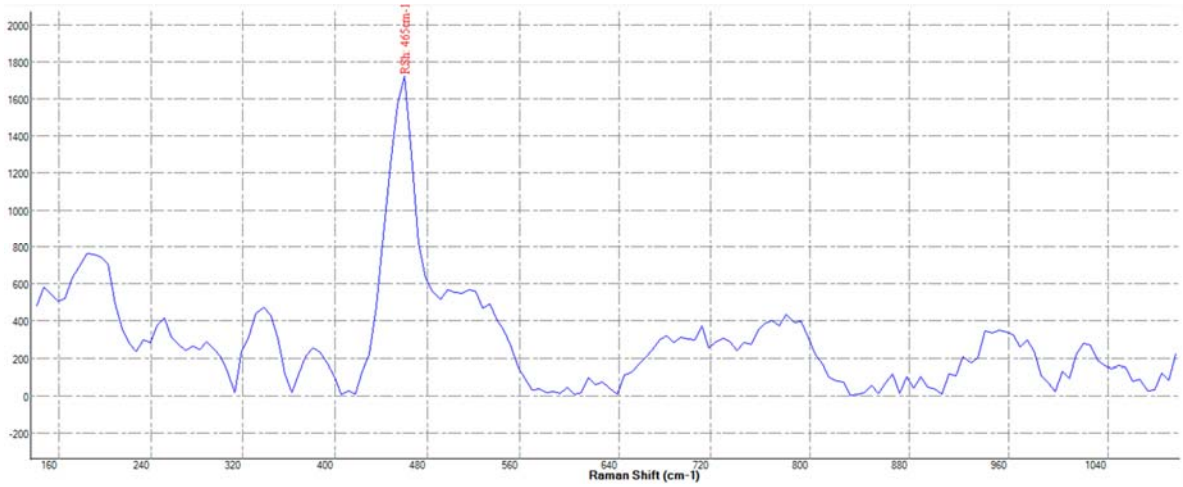

Fig. 7 Normalized Raman spectrum of sample A3

Spectroscopy of Sample A3

The obtained spectrum from sample A3 (Fig. 7) is related to the spectrum of quartz as in the previous samples. In the range of 465 cm^{-1} we have Raman spectrum, which is considered the main spectrum.

Scanning Electron Microscope (SEM)

SEM is one of the most famous types of electron

microscopes, which has found many applications especially in nanotechnology.

The construction of SEM allowed researchers to study samples more easily and clearly. Bombarding the sample with an electron beam causes electrons and photons to be released from the sample and towards the detectors, where they are converted into signals. The movement of the beam on the sample provides a set of signals, on the basis of which the microscope can display the reciprocal image of the sample surface on the screen moment by moment. Therefore, the working mechanism of SEM is completely different from optical microscopes.

At first, the main advantage of the SEM device was the preparation of microscopic images directly from solid samples with better clarity, resolution and focus compared to optical microscopes. But later, the executive and operational power of the device was developed and it was equipped with analytical methods, such as X-rays to determine the chemical composition and electron channeling to detect the crystalline state [5]. Figs. 7-9, which are accompanied by the table, show the elements in samples A1, A2, and A3, respectively.

Sample A1: With a high percentage of silica and oxygen in its composition, it is quite distinct and belongs to the chalcedony family.

The high percentage of silica and oxygen in the composition of sample A2 is quite clear that this item belongs to the chalcedony family.

Sample A3 has the same composition as chalcedony (agate) and is usually cryptocrystalline and appears opaque or cloudy. In this sample, the high percentage of silica and oxygen is quite clear.

ElementA1 C	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. [at.-%]
Oxygen	K series	49.97	51.35	66.00
Magnesium	K series	0.78	0.80	0.67
Aluminium	K series	1.79	1.84	1.40
Silicon	K series	37.04	38.06	27.87
Chlorine	K series	3.52	3.62	2.10
Potassium	K series	0.72	0.74	0.39
Calcium	K series	1.63	1.67	0.86
Iron	K series	1.88	1.93	0.71

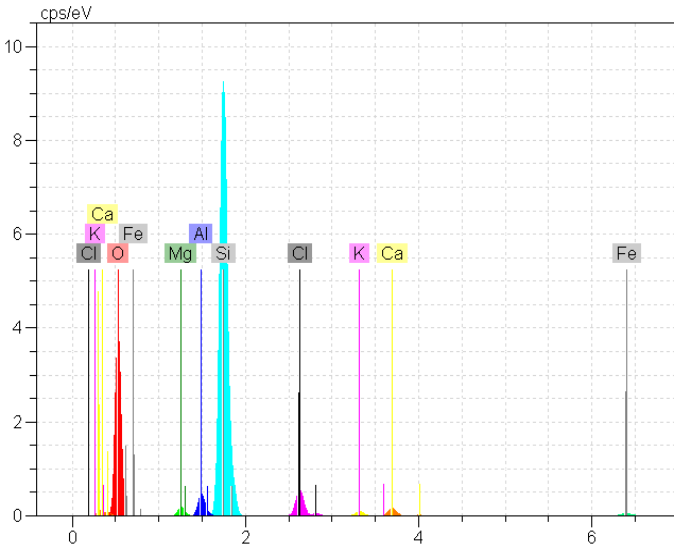

Fig. 8 SEM graph and table, sample A1

Element **A2**	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	50.42	50.72	65.20
Sodium	K series	2.46	2.21	1.98
Magnesium	K series	1.57	1.41	1.20
Aluminium	K series	4.15	5.53	4.22
Silicon	K series	31.53	31.94	23.39
Sulfur	K series	0.88	0.79	0.51
Chlorine	K series	0.78	0.70	0.41
Potassium	K series	2.83	2.55	1.34
Calcium	K series	1.83	1.64	0.84
Iron	K series	2.79	2.50	0.92

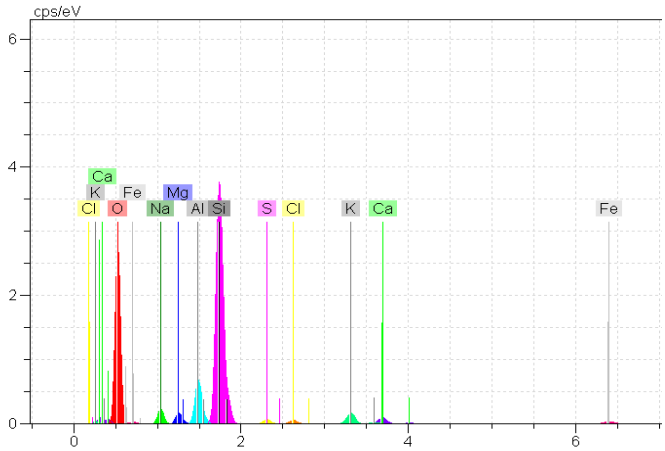

Fig. 9 SEM graph and table, sample A2

Element **A3**	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	50.90	51.01	65.43
Magnesium	K series	0.56	0.56	0.47
Aluminium	K series	1.41	1.42	1.08
Silicon	K series	41.29	41.38	30.24
Chlorine	K series	2.28	2.29	1.32
Potassium	K series	0.45	0.45	0.24
Calcium	K series	1.05	1.05	0.54
Iron	K series	1.84	1.84	0.68
Total:	99.8 %			

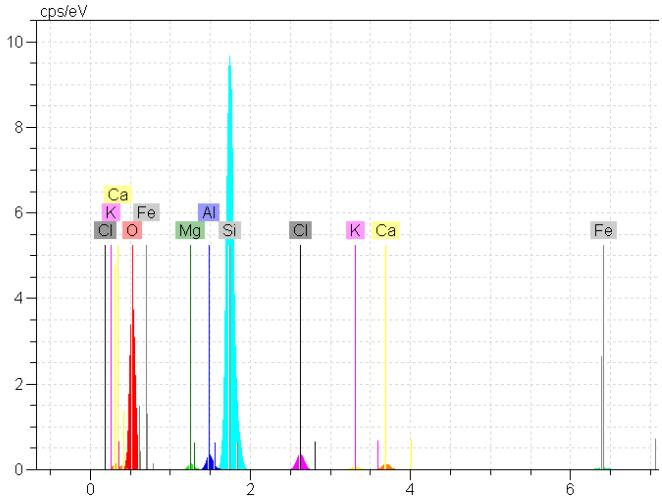

Fig. 10 SEM graph and table, sample A3

III. Conclusion

According to the information obtained by the gem identification tests conducted in the gemology department, the Raman spectroscopy tests as well as the SEM, the following results can be cited:

Examining the Raman spectra taken from the samples with an index peak of 465 cm^{-1} and also because it is not possible to see a tangible difference between the spectrum obtained from the existing samples and the reference spectrum on the RRUFF site, it can be concluded that the existing stones are from Chalcedony group. Of course, in order to complete the information, we added other nondestructive tests such as SEM to the identification of these stone samples, and the results of SEM/EDAX also led to high accuracy of the information.

Finally, gem tests analysis showed that sample A1 is red opal, sample A2 is brown ocher opal, and sample A3 is jasper, all three of which belong to the chalcedony family. As previously mentioned, Raman spectroscopy is an ideal method for examining precious stones due to the lack of sample preparation and the nondestructive nature of Raman analysis.

Today, rapid identification of precious stones and minerals is possible using multiple and cost-effective Raman spectroscopy systems. In general, the polished surfaces of the gemstones produce good Raman scattering that have a high percentage of agreement with the RRUFF and IRUG databases.

In the science of gemology, the use of methods that do not destroy the sample is very important. Classic methods in gemology include determining the specific weight of stones, analyzing them under a microscope and examining their absorption spectrum. Tests that are common in mineralogy, such as measuring hardness, etching stones with acid, and preparing thin sheets for examination with a microscope, are not applicable to precious stones and jewelry. With the ease of access to analytical methods and after the advent of spectroscopic methods that were developed in different areas of the electromagnetic spectrum, gemologists were able to examine precious stones in more detail. Today, various devices are used in advanced gemology laboratories, including Vis-UV spectrophotometers, Fourier transform infrared spectrometers, and fluorescence spectrometers (ray-x to a lesser extent). These methods are used to detect the nature of single crystals, but all of them are macro methods that only give information about the whole stone or its surface [6]. In particular, Raman devices mounted on a microscope allow to analyze a small point of the sample. Therefore, the Raman method is considered a very suitable method for validating, determining the authenticity and originality of gems and precious stones. Most of the materials that gemologists and mineralogists deal with have a specific Raman peak, which is called a "fingerprint" and characteristic of that material. Alloys and metals are a large subset of materials that have their own characteristic peaks that arise from their bonding properties [7].

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