VIII Congresso Nazionale di Archeometria
Scienze e Beni Culturali: stato dell'arte e prospettive
Bologna 5 - 7 Febbraio 2014

APPLICATION OF MICRO-RAMAN SPECTROSCOPY FOR GEMSTONES CHARACTERIZATION. THE CASE OF RUBIES.

G. Barone[1*], D. Bersani[2], P.P. Lottici[2], P. Mazzoleni[1], S. Raneri[1], U. Longobardo[3]

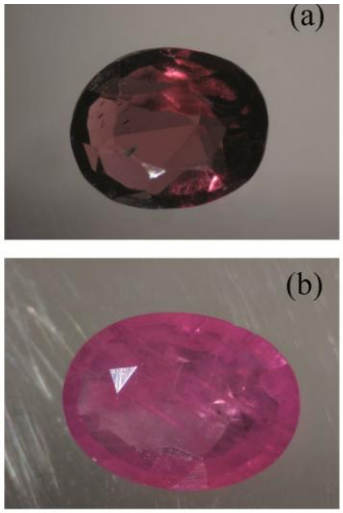
[1] Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Catania, Corso Italia 57, 95129 Catania, *gbarone@unict.it*
[2] Dipartimento di Fisica e Scienze della Terra, Università di Parma, Parco Area delle Scienze 7/a, 43124, Parma
[3] Jeweler, Catania

In the last decade Raman spectroscopy has been used in routine test for gems characterization [1-3]. In particular, as it is non-destructive and non-invasive, Raman spectroscopy is largely used in the evaluation of precious artistic and archaeological objects [4]. In fact, since ancient times natural precious gems were used to adorn precious objects and jewels; however, in view of their rarity, they are often replaced with simulant, synthetic or imitation gems. Fore these reasons, the certification of natural precious gems represents a relevant issue not only for gemological purpose but also in archaeometry.
Among the major commercial gems, ruby is considered one of the four most precious gemstones, together with sapphire, emerald and diamond. Ruby is the red transparent gem variety of corundum; the colors are intense red to pink due to traces of chromium^{3+} ions [5].
The goal of the present study is to identify rubies and their imitation gems. In order to obtain this result, micro-Raman analysis has been carried out on a selection of seven red gems ranging from 0.230 to 2.380 carats (ct). In Tab. 1 are summarized colour, weight and shape features for each gem while in Fig. 1 are shown two representative analysed samples.

Tab. 1. List of the investigated samples, together with some characteristics, such as colour, weight and shape.

Sample	*Colour*	*Weight (Carats)*	*Shape*
R1	Deep red	0.945	Oval
R2	Pink	0.655	Oval
R3	Light red	0.230	Trapezoidal
R4	Light red	0.575	Rectangular
R5	Light red	1.715	Oval chabochon
R6	Red	2.380	Octagonal
R7	Deep red	0.990	Drop

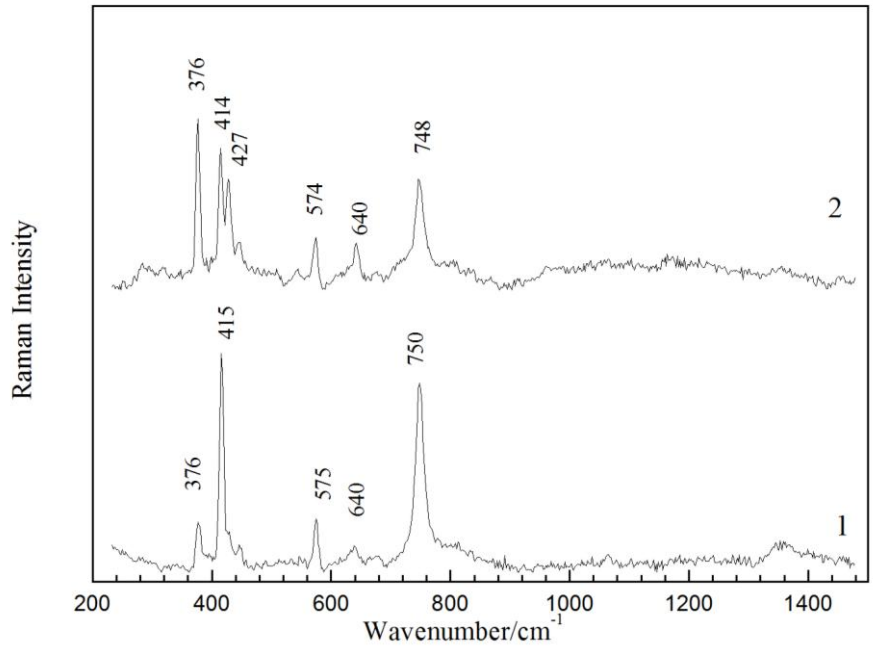
Fig. 1. Pictures of (a) R1 and (b) R2 samples.



Micro-Raman spectra were recorded using a Jobin-Yvon Horiba LabRam apparatus equipped with a confocal Olympus microscope; the 473 nm line of doubled solid-state Nd:YAG laser was used for excitation.

All the experimental Raman spectra were compared with data from various databases [6-8] and literature [9]. A large part of investigated gems (R2, R3, R4, R5, R6) exhibits the typical Raman peaks of corundum (Fig. 2; Tab. 2).

Fig. 2. Raman spectra collected by means of the micro-Raman equipment.
1, sample R3: ruby; 2, sample R6: ruby..

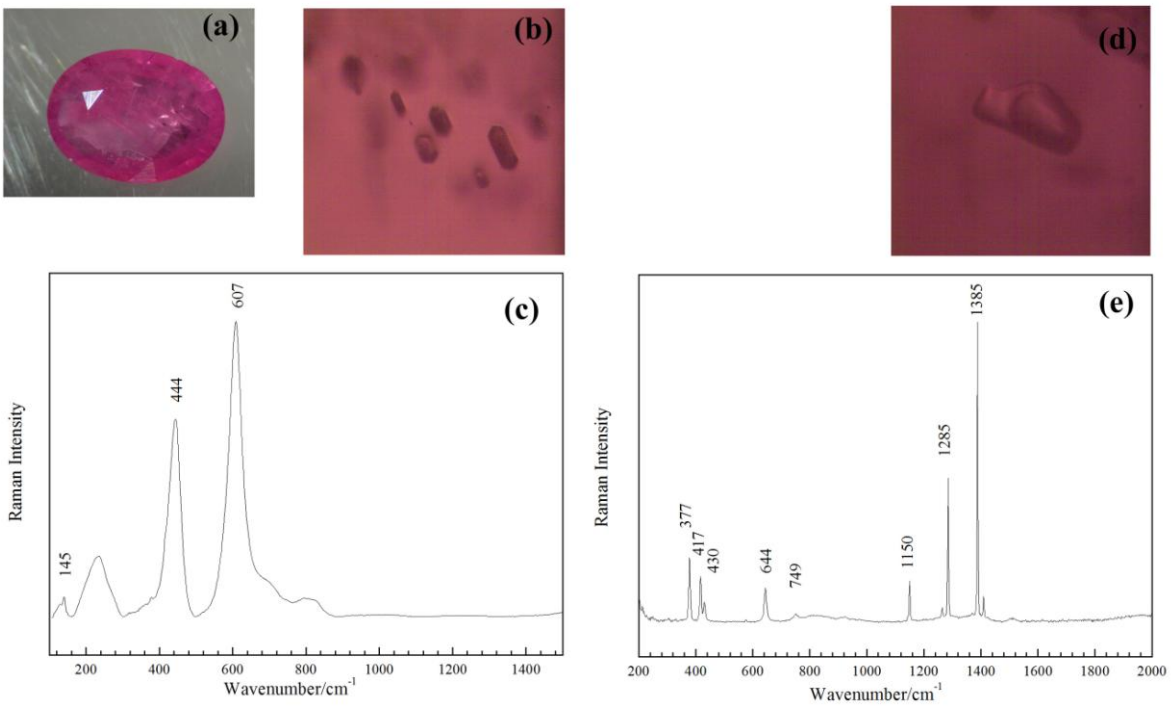


Tab. 2. Main features (in cm^{-1}) and their symmetry species [7] revealed in micro-Raman spectra.

Corundum						***Garnet***		
R2	**R3**	**R4**	**R5**	**R6**	*Symmetry species*	**R1**	**R7**	*Symmetry species*
377	376	375	367	376	E_g	340	344	A_{1g}
417	415	417	415	414	A_{1g}	376	370	E_g+F_{2g}
430	-	-	426	427	E_g	557	555	A_{1g}
-	575	-	575	574	E_g	863	865	E_g+F_{2g}
644	640	645	-	640	A_{1g}	920	916	A_{1g}
749	750	749	748	748	E_g	1052	1040	E_g+F_{2g}

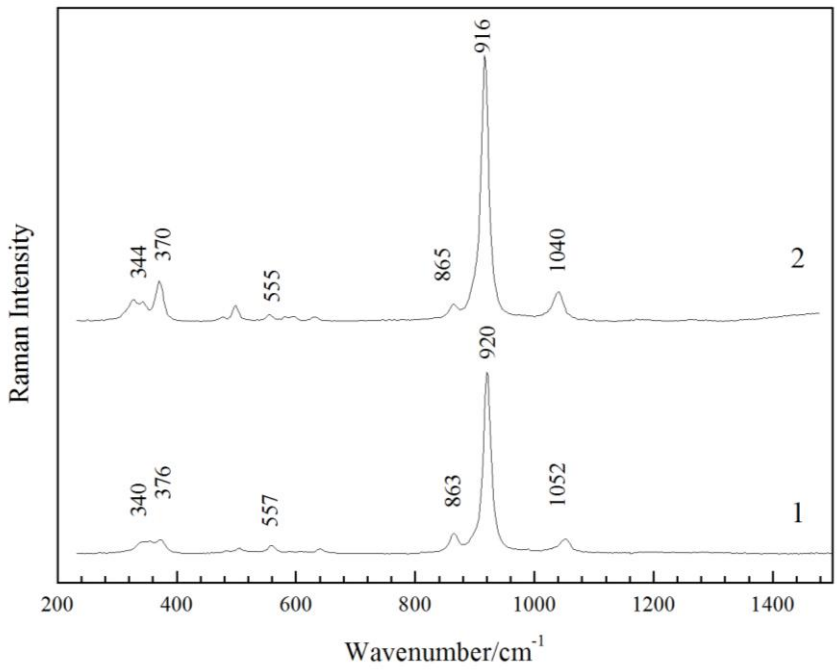
In order to obtain additional useful information, Raman spectra are collected on some inclusions. In particular, among studied gems, it is note worthy the presence in R2 (Fig. 3 (a)) of well shaped crystals (Fig. 3 (b)) and gas inclusions (Fig. 3 (d)); their identification is supported by the micro-Raman spectra. In detail, the micro-Raman spectrum on crystal inclusions reported in Fig. 3 (b) shows the typical peaks of rutile (444 cm^{-1}; 607 cm^{-1}), while the spectrum collected on the gas inclusion shows the characteristic Fermi doublet of CO_2 (modes at 1285 cm^{-1}; 1385 cm^{-1}) and SO_2 (mode at 1150 cm^{-1}) [10] (see Fig. 3 (e)).

Fig. 3. (a) Sample R2, (b) microphoto (100X) of the crystals of rutile (TiO_2) and (c) the associated micro-Raman spectrum; (d) microphoto (100X) of the gas inclusions (CO_2 and SO_2) and (e) the associated micro-Raman spectrum



Finally, micro-Raman analyses carried out on R1 and R7 samples allow to identify them as garnets. In order to distinguish the type of garnet, we used a routine based on a Matlab software called Miragem [11]. According to the obtained results, the investigated garnet consists of almandine and pyrope. In particular, the Raman spectra suggest a composition of R1 sample 52% Pyr and 48% Alm, while composition of R7 88% Alm and 12% Pyr (Fig. 4).

Fig. 2. Raman spectra of 1, sample R1: garnet; 2, sample R7: garnet.



In conclusion, this work presents a non destructive approach for the analysis of red gems using micro-Raman spectroscopy. Even if this work was made with a laboratory micro-Raman apparatus, it should be the basis for the identification of rubies made with portable Raman spectrometers directly in museums on gems mounted in precious and unmovable artworks. In order to go deeper in the study of these gems and recognize their origin and provenance, further red gems are scheduled for analyses in order to improve the existing databases on gems and support gemologists and researchers in studies of precious natural gemstones.

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