Micro Raman characterizations of Pompei's mortars

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Micro Raman characterizations of Pompei's mortars

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Abstract.

The ancient town of Pompei offers a unique opportunity to study in details many aspects of the every day life during the Roman early imperial age. The application of micro-Raman spectroscopy can be of great help in performing a reasonably rapid comparative analysis of the mortars, quite useful to ascertain the degree of uniformity of the technical recipes among the various building firms and the eventual technical evolution in the time; moreover, the individuation of minerals of specific geographical origins can give useful information about the extension of commercial intercourses. An example of a micro-Raman investigation on building materials is reported in this work, concerning the analysis of the mortars coming from different points of the wall in the "*The House of the Wedding of Hercules*". Remarkable differences between ancient and modern mortars are found, allowing a discrimination that can be useful in case of historical building which underwent to several restoration works.

***Keywords*: micro-Raman spectroscopy / non-destructive analysis / Mortars / Minerals / Pompei**

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INTRODUCTION

In the last years, micro-Raman spectroscopy has been increasingly used as analytical techniques for investigations on historical and cultural artefacts[1]. Its success, first of all, derives from its non–destructive character, but this diagnostic technique results also very specific, sensitive, immune to interference, high spatially refined, and easy to apply, allowing to perform in-situ investigations when optical fiber accessories are employed[2]. It has been applied mainly to pigments detection on many different art objects: i.e. manuscripts, wall paintings, icons, sculpture, paints, papyri, ceramics, pottery and so on[1-16]. Of course it finds application also for the detection of mineral, resin, binding and many (if not all) components of the analysed art object[17-19] and also biomaterials coming from archaeological environments (human and animal tissues, skeletal remains and so on) [20-21].

Beside the importance for restores and conservators, the knowledge of the material used for realizing the artwork, can allows the historians, for instance, to know whether the artist followed the doctrine of the Academy, or, in contrast, the artist experimented with the most novel pigments available at its time[22-24].

Generally these studies were focused on a single art object. The present study will explore the chance to use the Raman spectroscopy as a rapid tool to estimate statistically the compositions of different mortars collected from the walls of "*The House of the Wedding of Hercules*" (*Regio VII, insula 9.47)* in the ancient roman city of Pompei. The information on the composition of the mortars can give useful hints about the social organization of the building work in that time. For instance it can ascertain whether the sands used in making the mortars were supplied by a unique sand seller or any small

building company provided of that on its own. Answers on such kind of problems will improve the knowledge of the social and economical life of the people in Pompei town. Moreover it will be interesting, especially for archaeologists, to explore the possibility to determine by a non-destructive scientific tool some variation of the sand composition and relate it with the different period of fabrication of the mortar. In the particular case of Pompei, archaeologists individuate different construction phases: an older one starting from sannitic age through the Roman Republic Age and a later phase of intensive city reconstruction after the earthquake of 62 A.D. and before the Vesuvius eruption of 79 A.D. In addition there is the important problem to discriminate between the real ancient roman mortars and those used during the modern restoration works performed in the last two centuries after the rediscovery of the city, in many cases without any associated report.

Of course, calcium carbonate ($CaCO_3$) is expected to be the ubiquitous basic component of all the investigated mortars. It comes by two routes: the well known carbonatation reaction between the CO_2 and the calcium hydroxide $Ca(OH)_2$ and from the marble powders recycled from the previously destroyed buildings, used to give some “marble like” translucency to the mortars. The sands, other basic component of the mortars, came from river ores, because the sea beach sands are not useful for building applications for their salt content.

It is reasonable to think that in the ancient time the sand ores should be very close to Pompei town. Of course the average compositions of these sands are representative of the geological composition of the South-West side of the Vesuvius volcano before the eruption of 79 A.D. Such composition was somewhat different from the present one, dominated by minerals coming from plinian explosive eruptions, based on acid lava.

The ancient geological landscape near Pompei was probably similar to the present one, on the Northern side near Somma Vesuviana, dominated by alkaline lava coming from effusive eruptions. All these considerations should provide a frame to classify the investigated mortars and to help in attributing the age of the fabrication.

EXPERIMENTAL

The study has been performed on thirteen specimens of mortars; the first 10 were collected from different parts of the walls of "*The House of the Wedding of Hercules*" (Fig. 1), while the last where painted pieces of mortars, collected in the ground inside the house. Before starting the Raman investigations, these samples have been catalogued and photographed.

The Raman investigation has been performed by using Jobin Yvon micro-Raman LABRAM instrument, with He-Ne (632.8 nm) laser source using a 50X Olympus objective with a focal length of 15 mm. The spectral resolution can be estimated at about 2 cm^{-1}, with some excess. The illuminated spot size is about 5 μm of diameter. Due to the small spot size of the laser many spectra for each sample have been collected in order to obtain a sampling statistically representative of the materials present on the samples.

RESULTS AND DISCUSSION

Most of the investigated samples shown Raman features typical of different minerals whose vibrational modes occur in the wavenumber range below 1150 cm^{-1}. The major contributes above such wavenumber are coming from carbon inclusions, revealed by the

typical D (1330 cm^{-1}) and G (1580 cm^{-1}) bands. For such reason the most representative Raman spectra collected on the different specimens are shown in figure 2 in the wavenumber range between 265 and 1150 cm^{-1}. In many cases the resulting Raman spectra is due to the presence of more substances. However, by selecting many spots on each sample was possible isolate spectral patterns of specific minerals.

The spectrum (a) shows a pattern assigned to minerals of the orthopyroxene group (281, 339, 385, 510, 532, 665, 772, 815, 825, 1000 and 1038 cm^{-1})[25,26]. The spectrum (b) is due to a superposition of materials: the Raman bands at about 289, 405, 493, 512 and 599 cm^{-1} can be assigned to the hematite, while the band at about 660 cm^{-1} is assigned to the presence of magnetite[27-32]. These two iron minerals are general associated in the investigated samples but in some cases the spectrum of isolated magnetite is obtained, as in spectrum (c). However, some authors assign[33] the band at 660 cm^{-1} to hematite, as due to a disorder effect and/or to the presence of nanocrystals of the iron oxide. In the studied samples it is not possible to discriminate the two cases; since there is evidence that magnetite (alone) is present (spectrum c), this band will be assigned to magnetite.

The spectrum (d), with its Raman features at about 495, 526 and 958 cm^{-1}, has been assigned to leucite[34-35]. The spectrum (e) shows a pattern, 325, 392, 495, 529, 665, 1011 and 1037 cm^{-1}, due to mixed leucite and pyroxene materials.

The spectrum (f) with its modes 299, 424, 600, 820, 851 and 958 cm^{-1} has been assigned to forsterite, a mineral of the olivine group, today known as typical of Somma Vesuviana area, on the northern slopes of the Vesuvius mountain; in addition, like in many other spectra, low intensity signal at about 1085 cm^{-1} reveals the presence of traces of chalk[26,36-37], because of its binder role.

The spectrum (g) is assigned to clinopyroxene with is Raman bands at about 323, 353, 390, 508, 530, 557, 663, 821, 862, 926, 1007 and 1038 cm^{-1} [25]. Clinopyroxene is still observed in the spectrum (h), showing a slightly different pattern. The spectrum (i) shows two broads bands at 484 and 676 cm^{-1}. The attribution of the broad bands has been quite difficult, because at first sight they could be due to the presence of ulvospinel[26], but the Raman pattern of such mineral shows a different intensity ratio of those bands. For these reason the spectrum (i) has been thought due to the contribution of two substances: the band at 676 cm^{-1}, has been assigned to the chromite mineral[26,29] while the band at 484 cm^{-1} assigned to some mineral of the feldspatoid group such as analcite[38-40]. The identification of analcite (*analcime*) is also based on the presence in the spectrum (i) of the bands at 299 and 390 cm^{-1}, visible in the figure, typical of that species. The spectrum (j) can be assigned to potassium sodium aluminum silicate like microcline $(K_{1-x}Na_x)AlSi_3O_8$ [40]; nevertheless the contribution of others similar feldspars cannot be completely excluded. The spectrum (k) shows common features to spectra (b) and (j), that means that it is due to: hematite, magnetite and microcline. The spectrum (l) [355, 369, 490, 526, 553, 602, 641, 673, 756, 820, 880, 936 and 983 cm^{-1}] can be due to calcium aluminum silicate like the grossular $(Ca_3Al_2Si_3O_{12})$[41]. The spectrum (m) represent the chalk (1085 cm^{-1})[30,42], the spectrum (n) the quartz 466 cm^{-1} [30,43], the spectrum (o) is due to gypsum, with modes at 415, 492 and 1006 cm^{-1} [30,42-43] associated to chalk, revealed by the mode at 1086 cm^{-1} [30, 42]. The spectra (p) and (q) 328, 349, 389, 429, 530, 586, 662, 815, 860, 1004, 1047 and 1082 cm^{-1} are due to clinopyroxene[25]. The band at about 960 (s) of the spectrum (q) is assigned to apatite [38]. Finally the spectrum (r) is assigned to a mixture of lead carbonate 1049 cm^{-1} [42] and quartz 461 cm^{-1} [30].

In Table 1 are listed the main modes observed on the representatives spectra (see Fig. 2), the substance whose such patterns have been associated and all the samples where the spectra have been collected. Reorganizing all the experimental findings it has been possible to list for any sample all the substances observed by micro-Raman spectroscopy and the results are shown in Table 2. Among all the individuate substances some are very common while others are very specific. As it was expected, in almost all the collected spectra the Raman spectrum of chalk ($CaCO_3$) appears, often as traces of the binder. In many spots the Raman spectrum of gypsum, $CaSO_4 \cdot 2H_2O$, appears, associated in smaller amount to chalk and in some sample zone, as pure or prevalent component. In the former case it is possible to explain the sulfate presence as due to transformations of chalk due to air pollution phenomena, catalyzed in some way by the action of lichens, bacteria and other microorganisms; even if Pompei is not close to great industrial areas, degradation phenomena of building and frescoes are however, well documented[44]. In some case of prevalent gypsum presence, it cannot be excluded an explanation in terms of wanted addition of such compound to the mortars, in the modern restoration works.

Other minerals very frequently detected in the investigated mortars are hematite and magnetite, generally associated together, and the minerals of pyroxene group. All these components are ubiquitously present in the soil of Pompei, and in general, of vesuvian area, and their presence cannot constitute a discrimination element for the origin of sands.

Others minerals seem to be more specific of single mortar sample or group. This is the case of forsterite which has been found in S1, S3-S4, S10 samples but never in the others samples. Forsterite, belonging to the olivine groups, is typically found in the

Monte Somma (Somma Vesuvius Complex, Naples province, Campania, Italy) which is an igneous, arc-shaped mountain representing the remnants of the older volcanic cone destroyed in the cataclysmic eruption of 79 A.D. [45], but it was more common in the ancient geological landscape of all vesuvian area before such eruption. On the basis of such elements it is reasonable that the sands used for making the ancient mortars contained a remarkable amount of forsterite; on the contrary the sands used for mortars in the modern restoration works, in the Pompei area after the eruption, should not contain an appreciable amount of such mineral. Therefore, that mineral can be proposed as marker to discriminate between authentic mortars and modern restoration. Taking into account the mortar samples on the wall of *"The House of the Wedding of Hercules*" it possible to classify as "authentic ancient Roman" the sample S1, S3, S4 and S10, while the others S2, S5-S9, S11-S13 could be assigned to modern mortars. Such classification match quite well the one derived by archaeological classification of the parts of the house, that assigns the mortar samples S1-S4 to ancient roman works and the others S5-S10 to modern restorations. The presence of others minoritarian components, like grossular, in the mortars classified as "modern", helps to reinforce this hypothesis of classification. In conclusion, the resulting evidences obtained by following two independent routes allow to classify the samples S1, S3 and S4 are ancient and S5-S9, S11-S13 as modern, while deeper investigations are required for the samples S2 and S10.

CONCLUSIONS

The micro- Raman investigation on several mortars collected mainly from the wall of the "*House of Hercules weddings*" in Pompei, allows to characterize an average composition of the sands employed in these mortars. The origin seem always local, but an appreciable difference in the forsterite content can be associated to the sure ancient origin of the mortars, against modern restoration works. Presence of calcium sulfate constitute an evidence of air pollution phenomena.

Further investigations and a more detailed statistical analysis are probably useful to improve the degree of certainty of the statements about the mortars. However, this experiment to apply micro-Raman analysis to such kind of research seems promising.

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Spectra	Main Raman Features (cm^{-1})	Assigned species	Sample
(a)	281(sh), 339(s), 385(sh), 510(m), 532(m), 665(s), 772(sm), 815(m), 825(m), 1000(s), 1038(sm)	Orthopyroxene	S1
(b)	289(s), 405(s), 493(sm), 512(m), 599(s), 660(s),	Hematite & Magnetite	S1, S2, S3, S4, S6, S7, S10, S11, S12
(c)	326(sm,br), 505(sm), 667(s), 996(sm), 1037(vsm),	Magnetite,	S1, S3, S4, S5, S6, S7
(d)	495(s), 526(s), 958(vsm)	Leucite	S1, S7, S12, S13
(e)	325(m), 392(m), 495(m), 529(m), 665(m), 1011(m), 1037(vsm)	Leucite and Pyroxene	S1, S12
(f)	299(sm), 410(sm), 424(sm), 600(m), 820(s), 851(s), 958(m), 1084(sm), 1136(vsm)	Forsterite, Chalk & Gypsum	S1, S3, S4, S10
(g)	323(m), 353(m), 390(m), 508(sm), 530(sm), 557(sm), 663(s), 821(sm), 862(vsm), 926(vsm), 1007(s), 1038(vsm)	Clinopyroxene	S3, S5, S6, S7, S8, S9, S10, S11
(h)	512(vsm), 663(m) 812(m), 825(sm), 964(vsm), 1004(m), 1037(vsm), 1081(vsm)	Clinopyroxene	S1
(i)	299(vsm), 390(sm,br), 484(s), 676(s, br), 1085(vsm)	Chromite & Analcite	S4
(j)	473(s), 514(s), 945(vsm), 1085(vsm)	Microcline $(K_{1-x}Na_x)AlSi_3O_8$ Potassium sodium aluminum silicate	S2, S5, S6, S7, S8, S9, S10, S11, S13
(k)	289(m), 405(sm), 476(m), 510(s), 665(s, br), 961(sm)	Hematite, Magnetite & Microcline $(K_{1-x}Na_x)AlSi_3O_8$.	S1, S2, S5, S7
(l)	355(sh), 369(s), 490(vsm), 526(m), 553(vsm), 602(vsm), 641(vsm), 673(vsm), 756(sm, br), 820(sm), 880(m), 936 (vsm), 983 (vsm)	Grossular $(Ca_3Al_2Si_3O_{12})$ Calcium aluminum silicate	S6
(m)	1085(s)	Calcite	S1, S2, S3, S7, S8, S9, S10, S11, S12, S13
(n)	466(s)	Quartz	S5, S6, S11
(o)	415(vsm), 492(m), 1006(s), 1086(sm)	Chalk & Gypsum,	S2, S6, S9, S10, S11, S13
(p)	327(sm), 355(sm), 391(m), 531(br), 663(s) 1007(m), 1038(vsm), 1082(vsm)	Clinopyroxene	S5, S6, S10
(q)	328(s), 349(sh), 389(m),429(vsm), 530(sm), 586(vsm), 662(s), 815(m), 860(sm), 960(s), 1004(s), 1047(sm), 1082 (vsm)	Clinopyroxene & apatite	S5, S9
(r)	461(s), 633(vsm), 1049(sm)	Lead carbonate & Quartz .	S2

Table 1. Raman Shift and relative intensity of the observed Raman bands and attribution to the relative specie. (vsm) very small, (sm) small, (m) medium, (s) strong, (vs) very strong, (vvs) very very strong, (sh) shoulder, (br) broad, (vbr) very broad.

Sample	Assigned species
S1	Chalk, Clinopyroxene [$(Ca,Mg,Fe,Al)_2(Si,Al)_20_6$], Forsterite [$Mg_2SiO_4$], Hematite, Leucite [$KAlSi_2O_6$], Magnetite, Microcline [$(K_{1-x}Na_x)AlSi_3O_8$], Orthopyroxene [$(Mg,Fe,Ca)(Mg,Fe,Al)(Si,Al)_2O$], Pyroxene.
S2	Chalk, Gypsum, Hematite, Lead carbonate, Magnetite, Microcline $(K_{1-x}Na_x)AlSi_3O_8$, Quartz .
S3	Chalk, Clinopyroxene, Forsterite [Mg_2SiO_4], Hematite, Magnetite
S4	Analcite, Chalk, Chromite, Forsterite [Mg_2SiO_4], Hematite, Magnetite
S5	Apatite, Clinopyroxene, Magnetite, Microcline [$(K_{1-x}Na_x)AlSi_3O_8$], Quartz
S6	Chalk, Clinopyroxene, Gypsum, Grossular [$(Ca_3Al_2Si_3O_{12})$], Hematite, Magnetite, Microcline [$(K_{1-x}Na_x)AlSi_3O_8$], Quartz.
S7	Chalk, Clinopyroxene, Hematite, Magnetite, Leucite [$KAlSi_2O_6$], Microcline [$(K_{1-x}Na_x)AlSi_3O_8$].
S8	Chalk, Clinopyroxene, Microcline [$(K_{1-x}Na_x)AlSi_3O_8$]
S9	Apatite, Chalk, Clinopyroxene, Gypsum, Microcline [$(K_{1-x}Na_x)AlSi_3O_8$]
S10	Chalk, Clinopyroxene, Forsterite [Mg_2SiO_4], Gypsum, Hematite, Magnetite, Microcline [$(K_{1-x}Na_x)AlSi_3O_8$].
S11	Chalk, Clinopyroxene, Gypsum, Hematite, Magnetite, Microcline $(K_{1-x}Na_x)AlSi_3O_8$, Quartz
S12	Chalk, Hematite, Magnetite, Leucite [$KAlSi_2O_6$] and Pyroxene
S13	Chalk, Gypsum, Leucite [$KAlSi_2O_6$], Microcline [$(K_{1-x}Na_x)AlSi_3O_8$]

Table 2. Composition of the samples obtained by the Raman investigation.

Figure captions

Figure 1. Photographs of the "*The House of the Wedding of Hercules*" (*Regio VII, insula 9.47)* in Pompei and of the different analyzed specimens.

Figure 2 Representative Raman spectra collected on the different samples. Fig. 2a: spectra (a-f). Fig. 2b: spectra (g-l). Fig. 2c: spectra (m-r). All the spectra are explained in the text.

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Figure 1

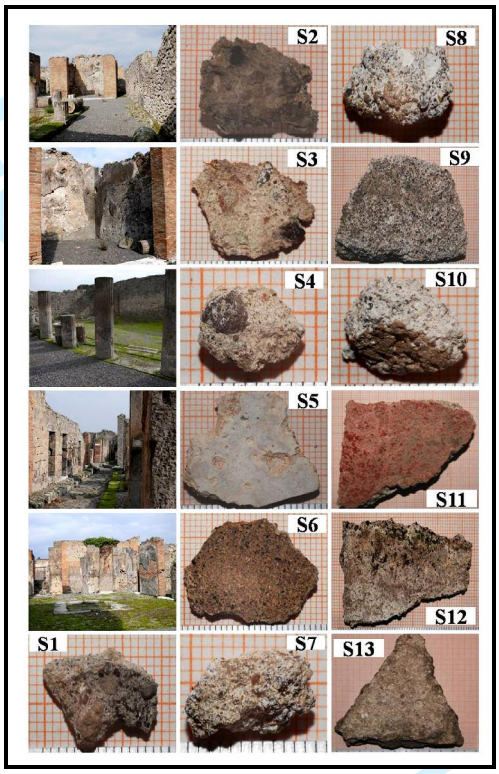

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Fig. 2a

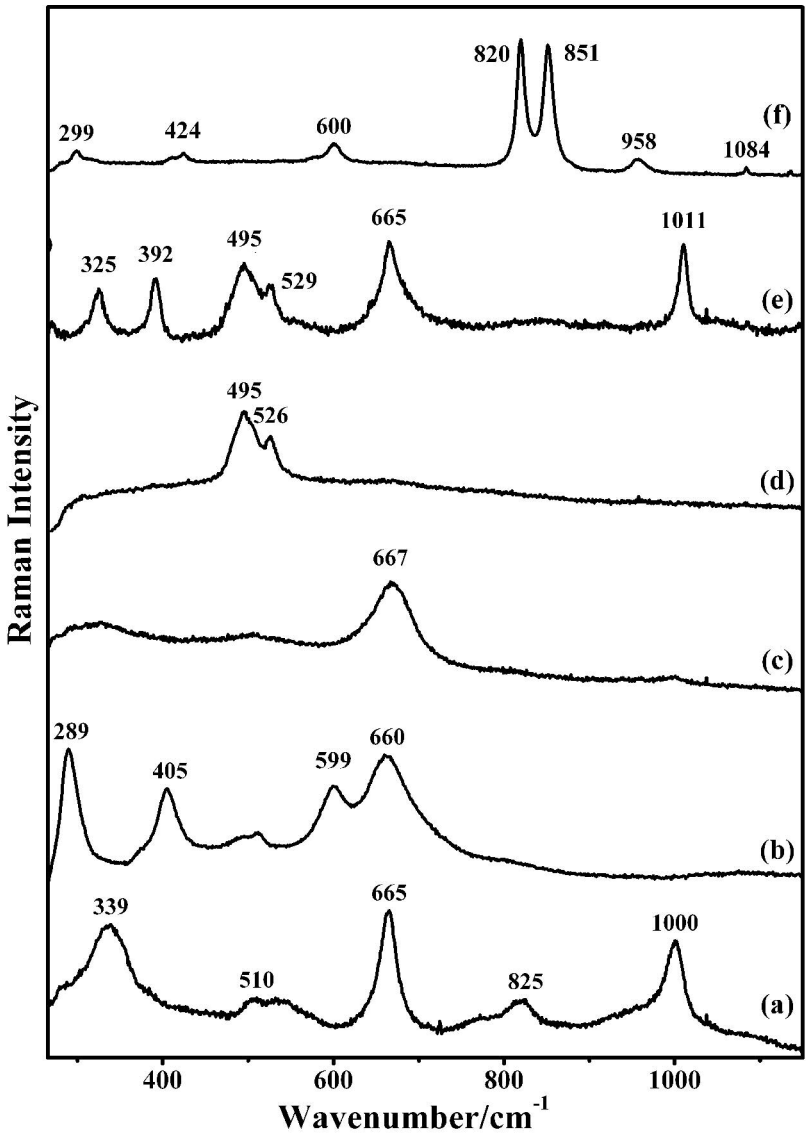

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Fig. 2b

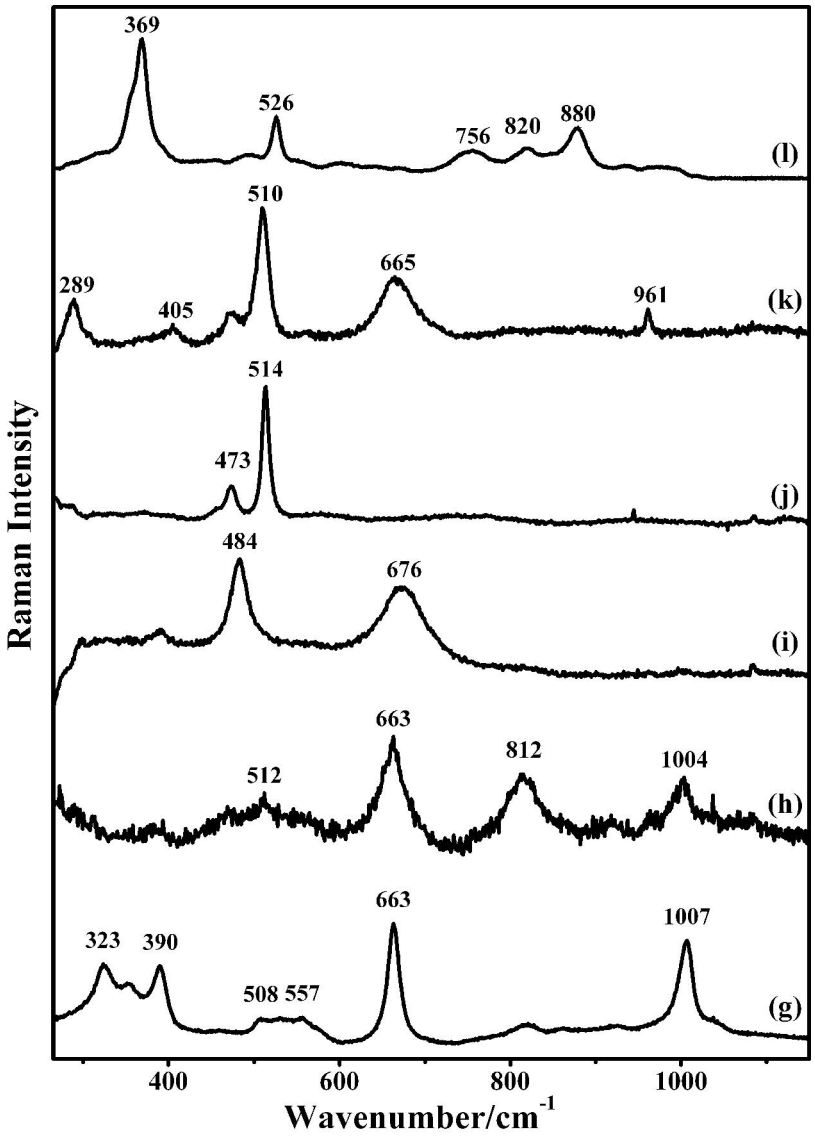

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Fig. 2c