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Temperature-controlled portable Raman spectroscopy of photothermally sensitive pigments

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Abstract

In this work, an innovative NIR Raman device (excitation wavelength at 1064 nm) was developed in order to avoid thermal stress and consequent chemical alterations of the materials analyzed. In particular, we devised and tested for the first time a sensed Raman probe allowing for temperature-controlled measurements based on a thermoelectric sensor providing the feedback signal for suitably modulating the output power of the laser source and then limiting undesired heating effects within the irradiated volume. The experimentation was carried out on cinnabar, lead white and indigo pigments frequently used during the past centuries, which presents pronounced photothermal instability. The results achieved in a set of instrumental and analytical tests using different measurement control parameters allowed demonstrating the effectiveness and reliability of the present approach for preventing thermal alterations effects during Raman spectroscopy and speeding the measurements, as well as for monitoring spectral variations associated with the crystals anharmonicity over large temperature ranges. These features along with the portability of the novel device can make in situ Raman characterisation of valuable painted surfaces including photosensitive materials very safe and efficient.

Keywords: portable Raman, thermopile, cinnabar, archaeometry, reflectance, thermoelectric sensor

1. INTRODUCTION

Raman spectroscopy is routinely employed in various fields of applications and in particular those where high spatial and spectral resolution of the molecular components along with the non-destructiveness are required. Moreover, thanks to its intrinsic features, the technique has also been widely exploited in order to study dynamic systems such as those for investigating catalysis processes [1], photochemical reactions [2], chemically or thermally induced phase-transitions [3], and oxidation mechanisms [4]. In all these cases the direct heating of the irradiated volume due to the laser excitation should be controlled in order to avoid undesired phase changes contributions, as well as intensity variation peak broadening and shift due to the increase of the anharmonic components [5]. Thus for example, a shift of about 120 cm^{-1} was observed for the OH-stretching overtone under temperature changes between 20-95 °C [6],

while for polymers and biological systems phase transitions are observed at relatively low temperatures, which produce significant spectral variations [7-10]

Laser heating represents a crucial feature whenever analyzing materials with a relatively high optical absorption at the excitation wavelength. This is a common situation when investigating pigments and polymeric materials with a pigment load using the typical laser wavelengths between 454-1064 nm. Undesired phase changes and discolorations induced by the laser excitation assume a peculiar relevance when considering the archaeometrical applications of the Raman spectroscopy, which are experiencing a significant growing along the last years also thank to the availability of portable devices. The non-destructiveness, which is achieved by properly selecting the irradiation parameters, represents the *conditio sine qua non* whenever investigating important painted artefacts (celebrated masterpieces and unique historical objects). However, in general the achievement of safe measurement conditions can be rather difficult because of the high photothermal sensitivity of some pigment mixtures, and of natural and synthetized binders, which can then easily undergo discolorations, reduction, phase changes, and combustion with unacceptable visible effects on the painted surface understudy [11-15] and spectral [alterations](#). This risk represents a severe obstacle to the practicability and meaningfulness of the Raman compositional mapping of painted surfaces. Spot diameters of several hundred microns would be preferable in order to collect more representative spectra and speed up the measurement but the mentioned variability of the pictorial materials and the unpredictability of their photothermal properties make such an approach to the compositional mapping very harmful unless an accurate control of the laser induced temperature rise is achieved.

In the present work, a novel portable Raman device (excitation wavelength at 1064 nm) including an online temperature control has been developed and tested on [cinnabar, lead white and indigo dye, which are](#) notoriously photothermally sensitive [pigments](#).

The temperature control has been achieved using a thermal sensor, which provided the feedback for suitably modulating the output power of the laser source and then limiting [undesired photothermal](#) effects within the irradiated volume. The experimentation carried out on samples of the mentioned [pigments](#) allowed showing the effectiveness and reliability of the present approach for preventing [alterations](#) during Raman spectroscopy and speeding up the [molecular](#) identification.

2. INSTRUMENTATION AND METHOD DEVELOPMENT

A portable Raman device (3.7 kg total weight) has been built by assembling a OEM spectrometer and Nd:YAG laser source (case sizes: 35×25×15cm), which was coupled to the homemade compact probe sketched in Fig. 1 (6×8×10cm) through two optical fibers. The former (BaySpec Inc., CA, USA) was equipped with a 512-pixel deep-cooled (-60°C) InGaAs array detector and a monochromator covering the spectral range between 165-1825 cm⁻¹ with a resolution of 8 cm⁻¹. The exciting source was a ultra-narrow linewidth diode pumped CW Nd:YAG(1064 nm) laser with a maximum output power of 500mW and a beam diameter of 700 μm (Innovative Photonic Solutions, NJ, USA). This laser system allows the external modulation of the output power, P(t), by means of a proportional signal 0 V <V(t)<1 V.

A thermal sensing line was conveniently designed, implemented and tested in order to collect temperature controlled Raman spectra of cinnabar, lead white, and indigo dye powders (Zecchi, Florence, Italy) flattened in small cells. They are deep red inorganic, white inorganic, and bluish organic pigments, respectively, commonly used in painting since ancient times. All of them exhibit high photothermal instability, which is cause of possible alterations during Raman characterization of paintings.

As shown in the schematic view of the probe of Fig. 1. The fiber-coupled Nd:YAG laser beam, collimated by the lens L₁, passes through a band-pass filter (BP, @ 1064 nm, FWHM 10nm) and a dichroic mirror (DM), and is focused onto the target by the lens L₂. The Raman-scattered light, collected and collimated by the lens L₂, reflected by DM and M mirrors, filtered by means of a notch filter (N) in order to cut-off the elastic scattering contribution, is then focused by L₃ into a 200 μm core diameter optical fiber leading to the spectrometer. The ZnSe lens, L_{IR}, collects and focuses onto the thermopile the IR radiation emitted by the irradiated area. The thermal sensor is equipped with a field diaphragm, D, in order to restrict the area imaged by the lens to the laser spot, and with a long pass filter (band 5.5-14 μm), F_{IR}, in order to shield the laser and ambient light.

A thermopile sensor with active area of about 750×750 μm², angle of view of about 10°, response time of $t_R=1.3$ s and an absolute accuracy at 25 °C of 0.5 °C was employed for thermal monitoring during Raman spectroscopy. The sensor was calibrated in order to provide the blackbody temperature, T_s , corresponding to the IR radiation collected and then used for estimating the temperature, T , of the laser heated spot. To this goal, the area of the material under laser excitation was imaged (1:1) on the active area of the sensor through the lens, L_{IR}, the IR filter (5.5-14 μm spectral band), F_{IR}, and the narrow field diaphragm, D (with a diameter of 1 mm) and the temperature was calculated by the following formula (in K) derived from Stefan-Boltzmann black body law:

$$T = \sqrt[4]{\frac{T_s^4 - (1-\epsilon)R_A T_a^4 \theta - (1-R_A)T_a^4}{\epsilon R_A \theta}} \quad (1)$$

where ϵ is the emissivity of the sample under analysis, T_a the ambient temperature, R_A =laser spot area/sensor area (about 0.64 in the present condition) and θ the lens transmissivity (0.98 in the present setup). Equation 1 is an adaptation to the present configuration of the correction formula for taking into account the reflected radiation [17]. In particular, it takes also into account the effect of the partial illumination of the active area of the sensor (R_A parameter).

The emissivity of the samples were achieved by heating them at a known temperature (as measured with a thermocouple) with an electrical resistance, imaging the heated surface using a thermocamera (PI 450, Optris), and eventually adjusting the emissivity in order to match the temperature measured by the latter with the known value.

In this way the sensor has been calibrated in order to measure an estimation of the real surface temperature at the target within the laser spot. However, in the present conditions, T still represents the average surface temperature within the imaged area, an underestimation of the real maximum temperature experienced by the material because of the inhomogeneous thermal distribution. Anyway, T is a usefully exploitable parameter in order to avoid undesired overheating and optimise the laser intensity release to the target.

The following time-dependent scaling law was assumed for suitably regulating the laser power:

$$P(t) = f(x) = \begin{cases} B[T_{exp} - T(t)]^{\frac{1}{4}} \tanh\left(\frac{t}{\tau}\right), & T_{exp} - T(t) > 0 \\ P_{min}, & T_{exp} - T(t) \leq 0 \end{cases} \quad (2)$$

where B and τ are adjustable parameters, T_{exp} is the expected temperature set while $T(t)$ is the actual temperature measured by the sensor, and P_{min} was set to 20 mW (a reasonable low value in order to avoid to switch-off the laser). Equation 2 represents a typical proportional control where the 4th root-dependence was preferred to the linear one in order to smooth the power variations associated to large temperature differences, $T_{exp}-T(t)$, while the factor $\tanh(t/\tau)$ favours its gradual increase during the onset phase, being $\tanh(t/\tau) \sim 1$ for $t/\tau > 2$.

In practical applications, B has to be suitably selected in order to achieve the rapid convergence of the control process and, at the same time, to avoid strong power and temperature modulations. As better described in the following, when operating at T_{exp} close to a critical temperature the selection of B can become in turn rather critical.

The whole system, thermal calculation, and power control was automated by developing dedicated LabView® driver and applicative code. The software allows setting T_{exp} , the total laser excitation exposure (J/cm^2) at the sample surface, the phenomenological parameters B and τ and to plot $T(t)$ and $P(t)$.

2.1 Application results and discussion

The novel thermal control system for Raman spectroscopy described above provides various advantages in terms of background control and prevention of sample alterations. Here, such an accessory was included in a portable device but, in principle, it can be implemented in any Raman spectroscopy setup.

2.1.1 Optimisation of the thermal control

The first optimisation step concerned the selection of the parameter B in Eq. 2. Let us consider the case of cinnabar and assume a given operative temperature $T_{exp}=200$ °C and a fixed $\tau=1$ s. As shown in Fig. 2a, B values between 0.20-0.21 $W/K^{1/4}$ (see green and yellow curves) allowed to approach T_{exp} after several seconds (190 °C after 5 s) with a corresponding smooth power control, after the initial relatively rapid rise. These measurements did not induce any evident alteration of the sample. On the contrary, the feedback of the thermal sensor for $B=0.22$ produced oscillations of the excitation power and consequent strong temperature modulations. In this situation, the temperature peaks overcame T_{exp} up to about 280 °C and at the end of the measurement a permanent alteration of the irradiated area was observed. The irradiated area was darkened and in some zones had a metallic appearance. Furthermore a slight ablation was observed at the middle (see inset in Fig. 2b). According to the literature [18], such darkening and metal appearance have to be reasonably attributed to a photothermal reduction effect, which ablation have to be ascribed to an uncontrolled temperature rise above the vaporization of mercury (357 °C). Such a spatial and temporal peak of the temperature cannot be detected by the sample because of the present temporal resolution limit (t_R) and because laser ablation corresponds to a sudden surface cooling. This phenomenology allows to state that, in the present experimental conditions, a critical temperature between 200-280 °C corresponding to the photothermal reduction of cinnabar can be defined. It is also

worth noting that at the mentioned temperature a sort of nucleation of the damage from microscopic areas within the laser spot was observed which make very difficult a more precise definition of the critical temperature. Thus, in practical measurements of the present pigment involving laser heating around 200 °C significant attention should be paid to the selection of B.

Of course, in real paint layers including cinnabar such critical temperature and laser intensity are expected to be much lower than the present ones because of the thermal sensitivity of the binder, but the conceptual approach remain the same: a preliminary temperature-based optimization can prevent the alteration.

In the current practice of Raman characterisation of paintings, preliminary tests are carried out at rising laser power (intensities) in order to achieve a satisfactory spectrum without visible alterations. However, the preliminary determination of a suitable power in a given site does not guarantee the repeatability of the result in other sites, where a given photothermally sensitive pigment could be for example mixed with a strongly absorbing pigment (ex. black carbon), which drastically rises the laser energy coupling and then the surface temperature. Thus, any preliminary phenomenological optimisation based on empirical power selection cannot be extended from one site to another. Conversely, if an interaction parameter such as the surface temperature is monitored, the repeatability and the safety of the Raman characterization of paint layers can be enormously improved. This is the basic idea of the present work.

Figure 2b displays the spectra of cinnabar corresponding to the different values of B considered in Fig. 2a where the behavior of the two intense bands of cinnabar can be observed at 253 cm^{-1} and 345 cm^{-1} . As shown, the visible permanent darkening corresponded to a strong reduction of the signal to background ratio of the associate Raman spectrum since only the early irradiation phase contributed to the signal.

Similar investigations were carried out also for lead white and indigo dye in order to show the general valence of the present approach. In the former case, the alteration (critical) temperature was about 165 °C, which determined the surface transformation of the white cerussite (lead white) in yellow massicot. A relatively precise determination of the critical temperature was possible for this pigment since it corresponded to the appearance of the a massicot and litharge bands at 285 cm^{-1} and 335 cm^{-1} , in the spectrum (Fig. 3b). Figure 3a shows as the suitable selection of B can allow maximizing the signal/background ratio (S/N) of the lead white spectra and avoid the mentioned phase transformation.

A test was carried out by mixing lead white with 1 wt% of black carbon, beside the general reduction of the Raman signal, we found that the mentioned critical temperature for massicot formation was reached using just 70 mW instead of 500 mW needed for the alteration of the pure pigment.

For indigo dye the alteration was detected around 195 °C and appeared as a depigmentation. In Fig. 4a the Raman spectrum at this threshold and another one at much lower temperature (60 °C) are shown. In the latter the bands at 1700, 1468, 1373, 1310, 1229, 1074 and 549 cm^{-1} are clearly observable (black spectrum), whereas they are completely lost in the spectrum at 195 °C. This is made more evident after the subtraction of the background (Fig. 4b). As was done for lead white, for the present organic pigment as well the developed device allowed to detect the critical temperature through the spectral changes observed and to define safe operative conditions.

For sake of completeness, let us also discuss the general selection criterion for the parameter τ . As mentioned above, the suitable selection of the parameter τ in Eq. 2 allows optimizing the slope of the power release. Thus for example, for $T_{exp}=60$ °C and $B = 0.12 \text{ W/K}^{1/4}$, τ values between 1-4000 ms generate the profiles $T(t)$ and $P(t)$ displayed in Fig. 5. As shown, increasing values of τ increase the rise time of the temperature and laser power and slightly delays (1-5 s) the achievement of the equilibrium temperature T_{exp} . Such a refinement of the control represents a further caution in view of future application on unique painted masterpieces where no mistakes are allowed. In these cases it will be important to set $\tau > 2$ s since the present reading time of the sensor is 1.3 s. A larger τ could be selected in order to provide more time to the operator for stopping the acquisition in case of any perceptible undesired effects. The polymateric complexity, which could include unexpected photothermally sensitive components, and the need to avoid any visible damage to the artwork makes preliminary irradiation tests difficult, unreliable, and often unacceptable. On the other hand, too long power leading edge could be unsuitable in some situations such as those of fast scanning applications using the present or any portable Raman device.

The set of conditions used in order to collect Raman spectra of cinnabar reported in the following are displayed in Fig. 6, where T_{exp} and B were varied between 45-115 °C and 0.08-0.2 $\text{W/K}^{1/4}$, respectively, (at $\tau = 1$ s) while the total excitation exposure was set at 1300 J/cm^2 in all the cases shown. As observable, after the initial rapid rise, the temperature approached quite smoothly the values of T_{exp} set and remained below the values set, up to 30 s (the duration of the energy release to the target depends on the selection of T_{exp}).

2.1.2 Raman spectra at different temperatures below the alteration threshold

Figure 7 shows the Raman spectra of cinnabar sample collected at different temperatures using the control setting just described (Fig. 6). An increase of the background with the temperature is clearly observable, which has been attributed to the blackbody emission at the actual temperature [19]. The latter predominates on the fluorescence when using Nd:YAG(1064 nm) laser excitation since its photons are not enough energetic in order to excite molecular electronic transitions. The thermal background presents characteristic modulations, which can lead to band shapes distortion and errors in band positions therefore its reduction becomes crucial in order increase the signal/noise ratio. Various algorithms [19, 20] and laser modulation techniques [21] were proposed for reducing the thermal background in Raman spectra. As shown in Fig. 7, using the present portable device, significant reductions were achieved by decreasing T_{exp} , with a consequent increase of the S/N ratio.

Moreover, despite the low spectral resolution available, the device was also able to reveal the trends of the band broadening and shift associated with the temperature increase.

Fig. 8a shows the major Raman bands of cinnabar at 252, 283 and 345 cm^{-1} commonly assigned to Hg-S stretching modes [22]. An evident broadening of the bands can be noticed in the spectra at increasing temperatures, which is reasonably attributable to the to the anharmonic component associated with the thermal expansion [16]. Fig. 8b shows the trend of FWHM vs the measured temperature, T , for the mentioned bands of cinnabar: significant broadening was observed in the all the three Raman bands. FWHM was achieved through Gaussian multi-peak fitting process available in OriginPro-2015 software. Moreover, an initial reduction of the Raman shift of 4 cm^{-1} was also observed in both the bands at 252 and 345 cm^{-1} when T_{exp} was increased from 95 to 115 °C (Fig. 8a), which provide a further evidence of anharmonicity.

In order to show the analytical potential of the novel device developed, its validation in in situ (in the workshop of a private restoration company) on a real painting was carried out. To this goal a wooden panel painting of fifteen century by anonymous from private collection was selected and analysed. For the present purposes, the most meaningful spectra at different temperatures were achieved on the red tunic of a religious figure. As shown in Fig. 10, the cinnabar (*) bands were relatively weak at $T_{exp}=30$ °C (black colour), whereas they rise up to a very good S/N level at $T_{exp}=90$ °C (blue colour), which did not produce any surface alteration. Furthermore, only at the latter temperature Raman bands of gypsum (°) and calcium carbonate (+) were clearly readable.

The same setting was used on both saturated red and shaded zones without overcoming the mentioned thermal limit thank to the proper controlled smoothing of the energy release ($T_{\text{exp}}=90\text{ }^{\circ}\text{C}$, $B=0.30$, $\tau=1.3$) smoothing properly the laser power emission. When working with real art objects, the main concern is to use a proper laser power providing a satisfactory Raman signal without overheating the paint layers under analysis. However, as mentioned above preliminary phenomenological optimisation based on local power selection does not ensure any repeatability because of the large variety of material mixing and deterioration phenomena usually encountered. The procedure must be hence repeated in each measurement site with consequent time lose, difficulty to automate the acquisition process in scanning operations, and the permanent risk of overheating. On the contrary, enabling the temperature control through Eq. 2 and the parameters B and τ , which suitably smooth the laser energy release to the target, the optimization of experimental conditions is more immediate and the acquisition became safer. The present T-controlled Raman approach can indeed make the difference. Furthermore, if for valuable masterpieces the punctual definition of the operative power will be preferred, undoubtedly that also in these cases the online temperature control developed in this work can provide the objective assessment of the thermal stress involved in Raman spectroscopy.

3. CONCLUSIONS

The novel portable NIR Raman spectroscopy (exc. 1064 nm) device equipped with the thermal control system developed in the present work can provide various benefits for the molecular characterization of paintings and of other objects presenting photothermally sensitive materials. The thermal control includes a compact thermopile and software routines that can be integrated in any Raman instrument.

The temporal profile of the temperature and its maximal value can be carefully defined by suitably setting shape and peak parameters, thus allowing preventing alteration effects of highly optically absorbing materials. This is the main feature in view of the extensive application of the present device in the analytical characterization of valuable paintings. Furthermore, the present work proves the possibility to conveniently limit the thermal background by [adjusting the](#) temperature set thus avoiding consequent band shapes distortion and errors in band positions. In particular, under the temperature setting of $90\text{ }^{\circ}\text{C}$, Raman spectra of cinnabar pigment with a moderate and substantially flat thermal background have been acquired [on both pure pigment samples and real paint layers](#). Conversely,

photoreduction and microvaporisation spot was observed on the pure pigment above 200 °C, a temperature which should be decidedly avoided when investigating real paintings.

Despite the relatively low resolution of the present spectrometer, in optimized conditions the trends of band broadenings and shifts were also pointed out. In general, the present approach can be very useful for investigating the thermal behavior of absorbing materials where the heating contribution of the laser excitation cannot be neglected.

The device was also tested on lead white and indigo dye, which allowed to identify their critical temperatures for massicot (°C) formation and depigmentation (°C), respectively. Online phase changes were detected in these cases directly on the Raman spectra, which can effortlessly avoided in real operative conditions using the thermal control here proposed.

Forthcoming works will be dedicated to the improvement of the automation features of the portable Raman device developed.

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Figure captions

Fig. 1 Schematic view of the Raman probe setup employed for photothermal Raman measurements: L=lens; M=mirror; DM=dichroic mirror; N=notch filter; BP= band-pass filter; D=diaphragm; FIR= IR filter; LIR=ZnSe lens.

Fig. 2 Influence of the parameter B (fixed $\tau = 1$ s) on the characterization of cinnabar: a) temperature and laser power as a function of time for different values of $B=0.20-0.22$; b) corresponding Raman spectra.

Fig. 3 Influence of the parameter B (fixed $\tau = 1$ s) on the characterization of lead white: a) temperature and laser power as a function of time for different values of $B=0.58-0.66$; b) corresponding Raman spectra.

Fig. 4 Spectra of indigo dye at two different T_{exp} set without (a) and with baseline subtraction (b).

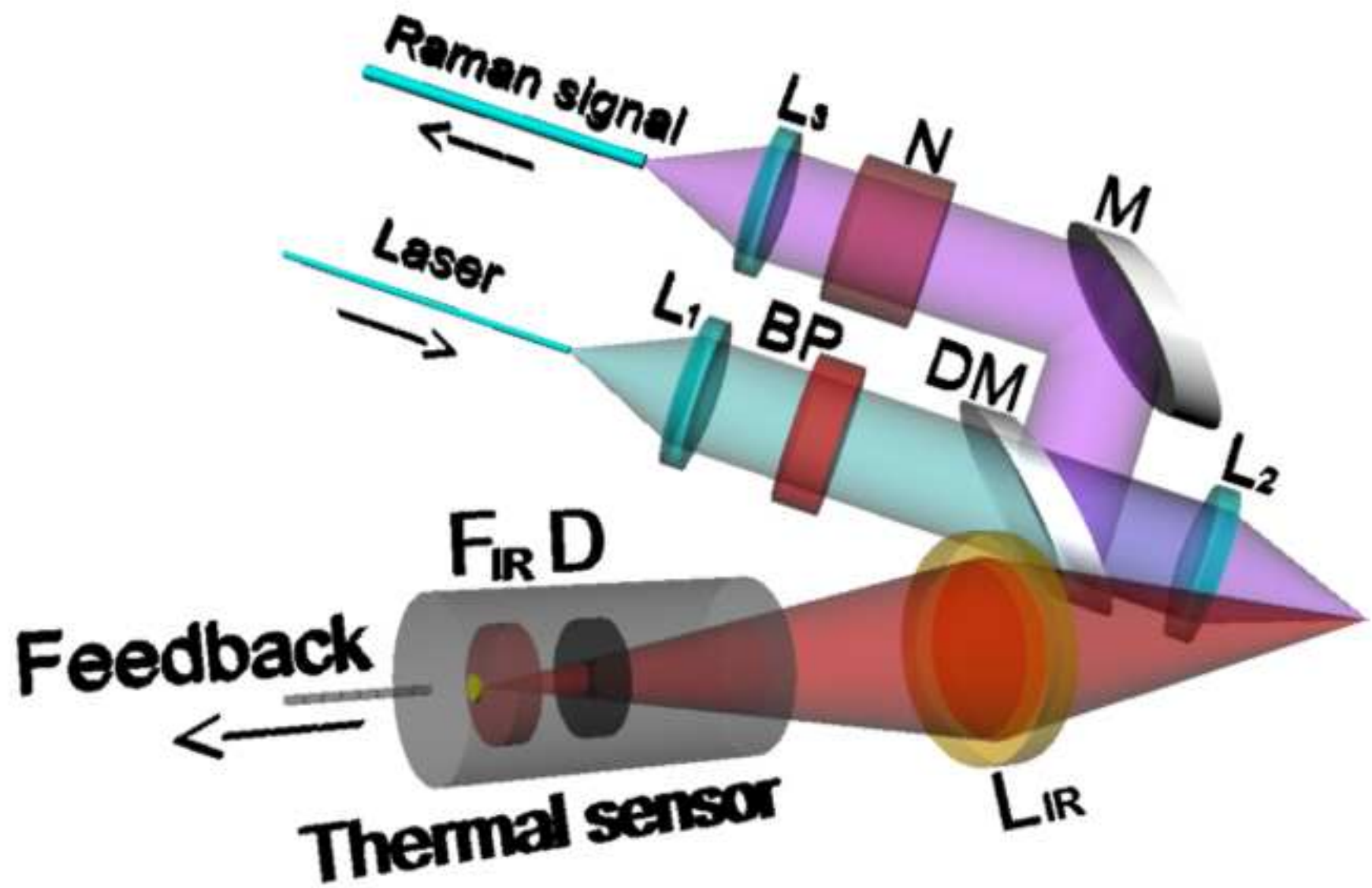
Fig. 5 Influence of the parameter τ on the thermal control (fixed $B = 0.12 \text{ W/K}^{1/4}$) for cinnabar: temperature (a) and laser power (b) as a function of time for different values of τ , from 1 to 4000 ms

Fig. 6 Behaviors of the thermal control with optimised B and $\tau= 1$ s for different T_{exp} sets: a) temperatures b) laser power

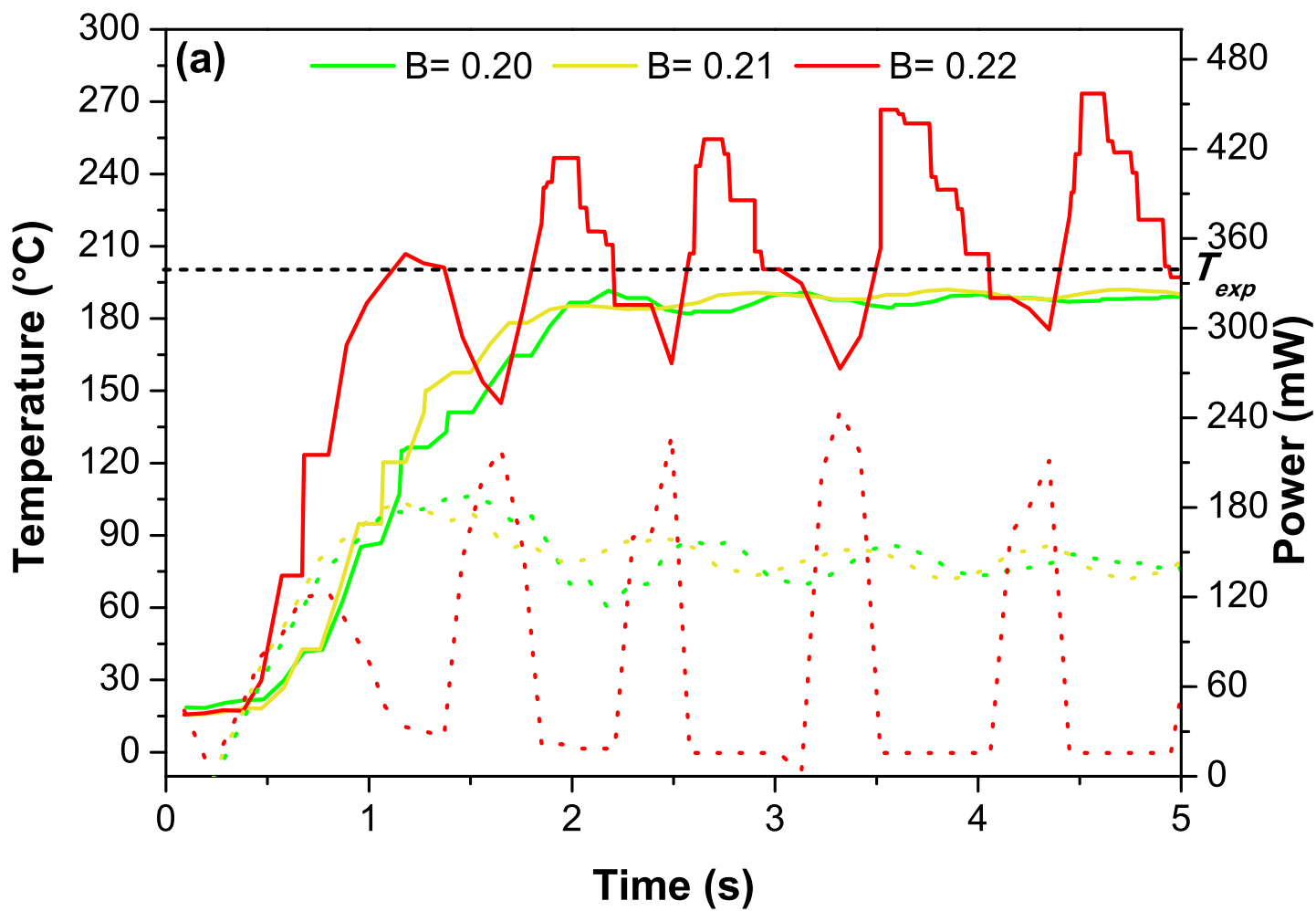
Fig. 7 Raman spectra of cinnabar pigment acquired at T_{exp} between 45 and 115 °C: the increase of the background with the operating temperature is clearly observable.

Fig. 8 Raman spectra of cinnabar at increasing values of T_{exp} evidencing band shift effects (a) and corresponding broadening trend (b).

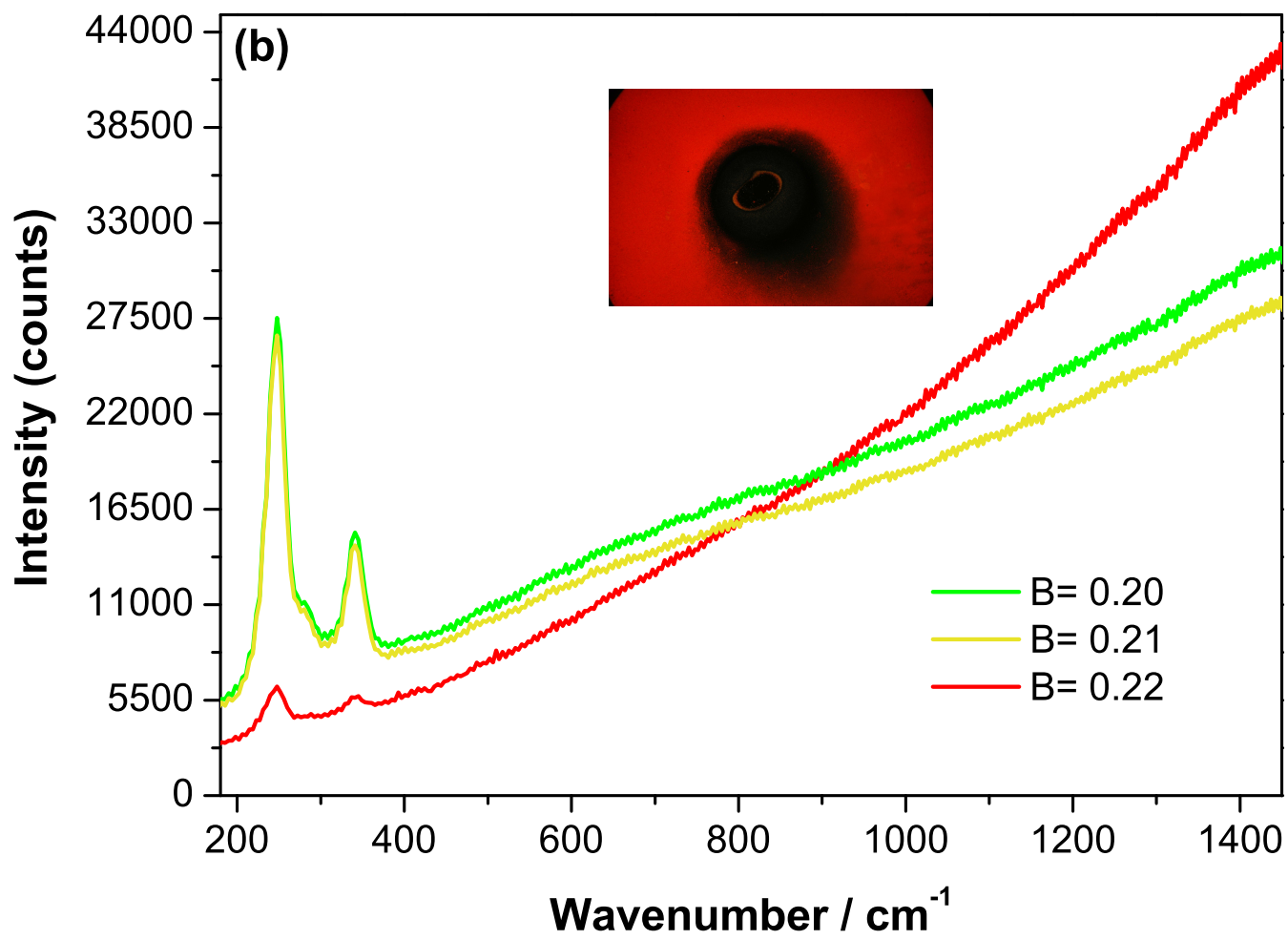
Fig. 9. T- controlled Raman measurements carried out on a wooden panel painting of the fifteen century (see the text).



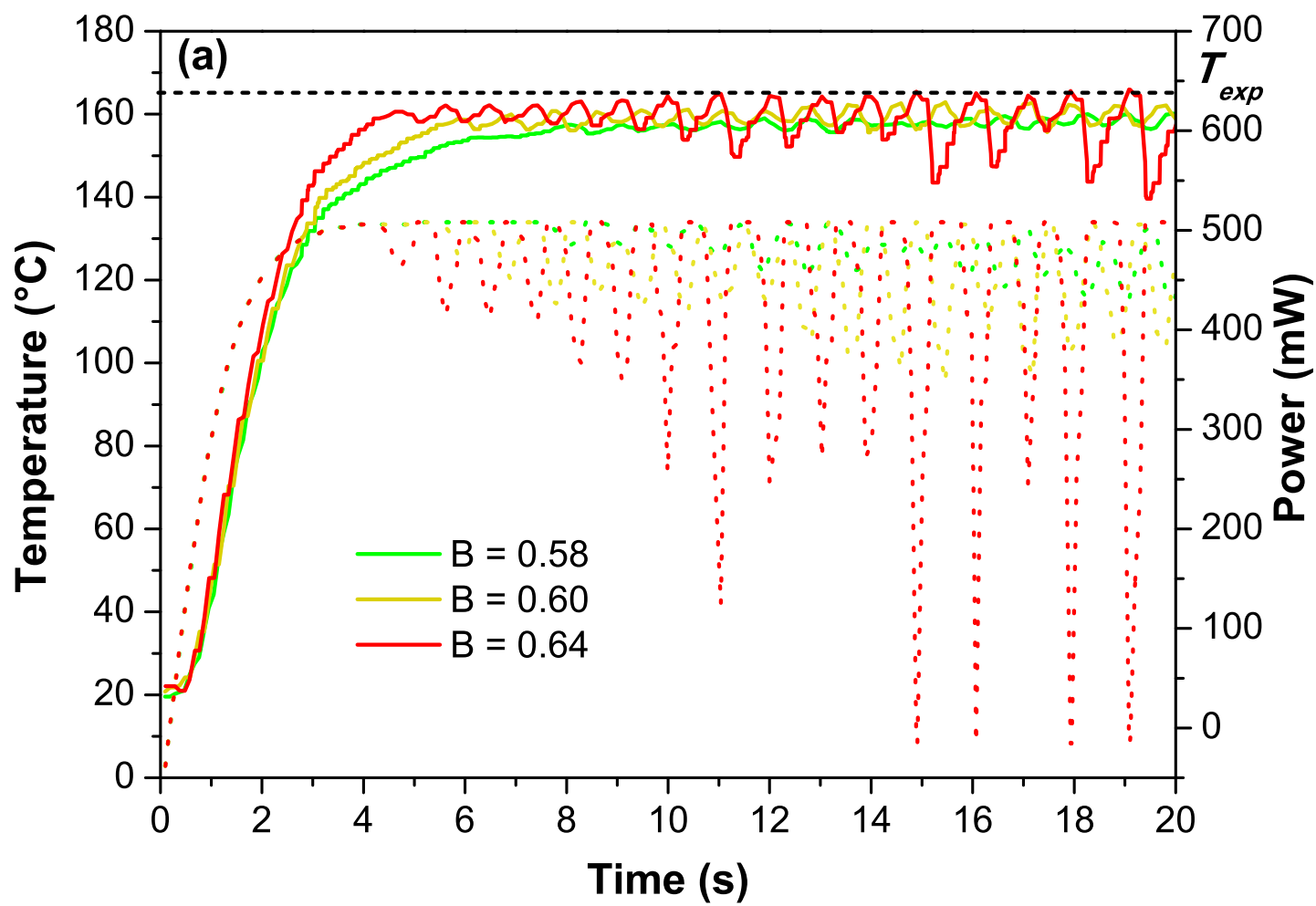
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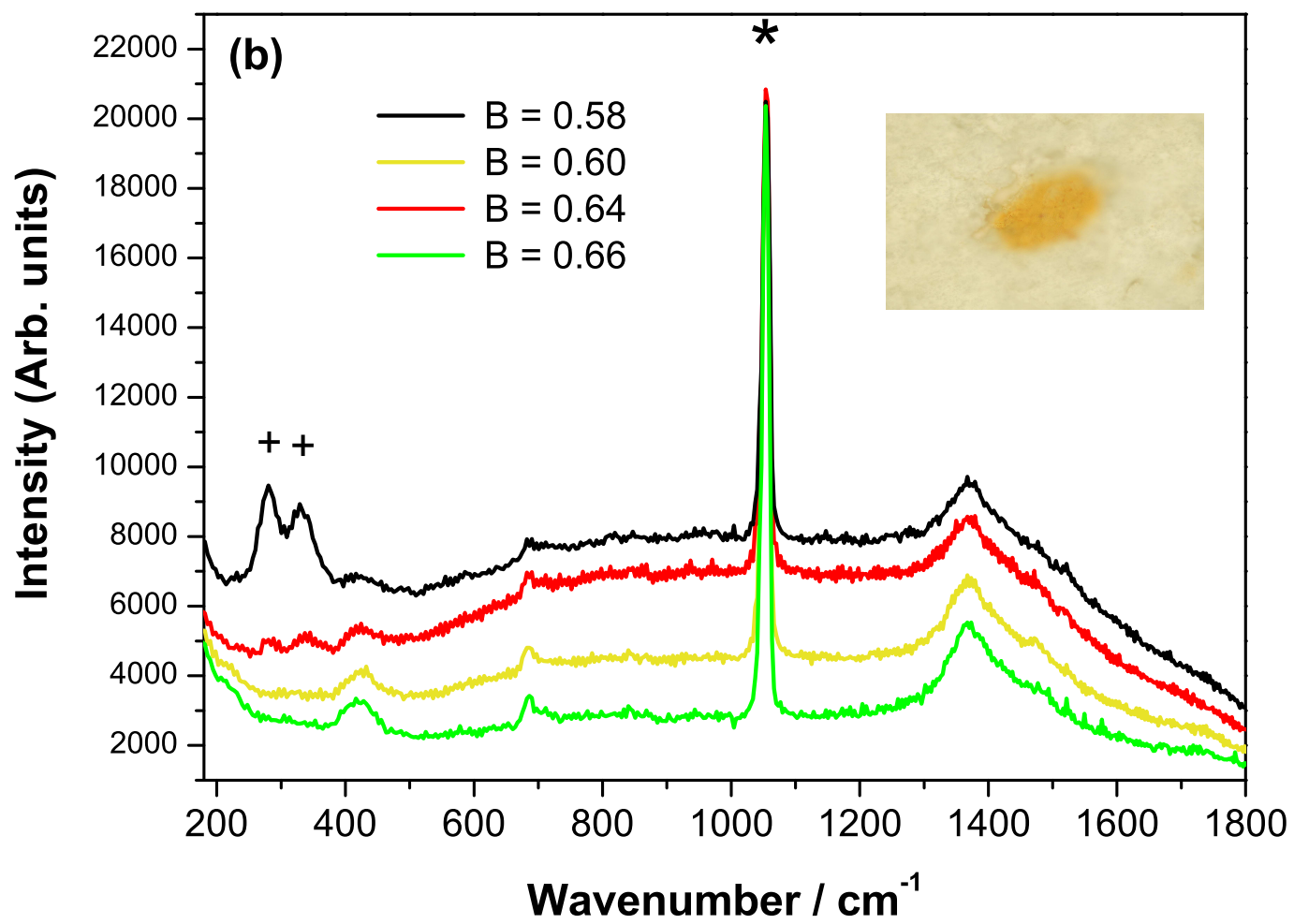
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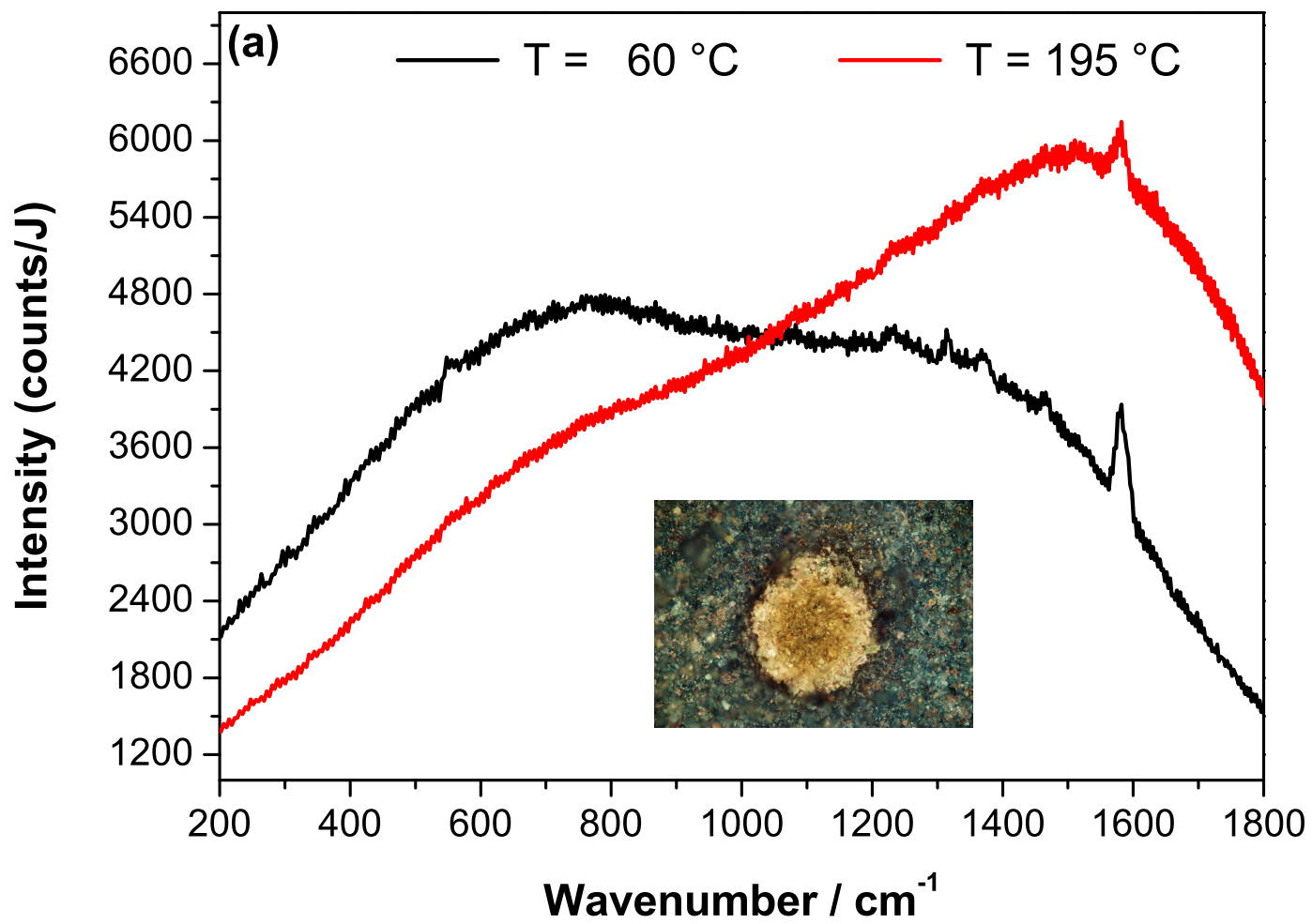
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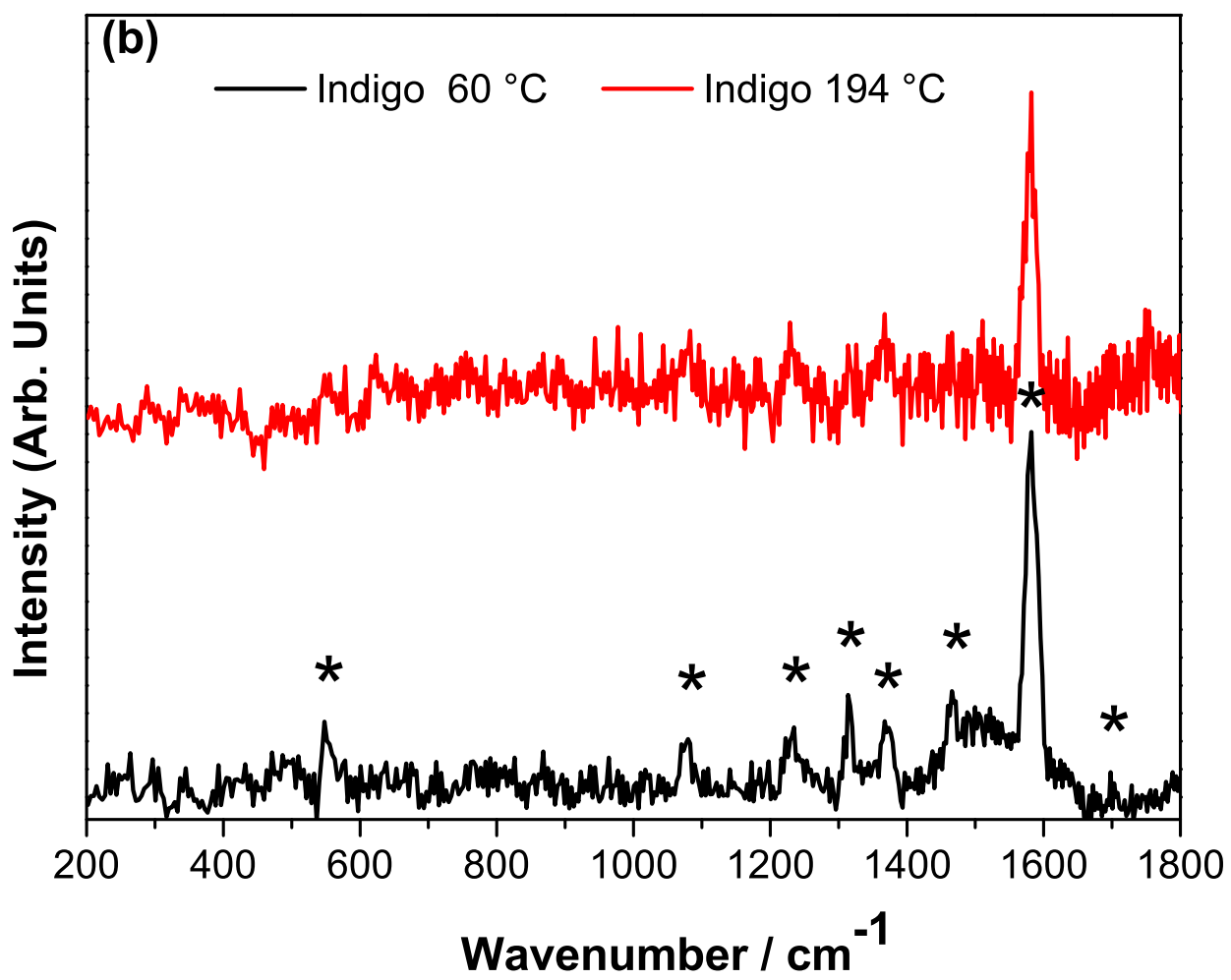


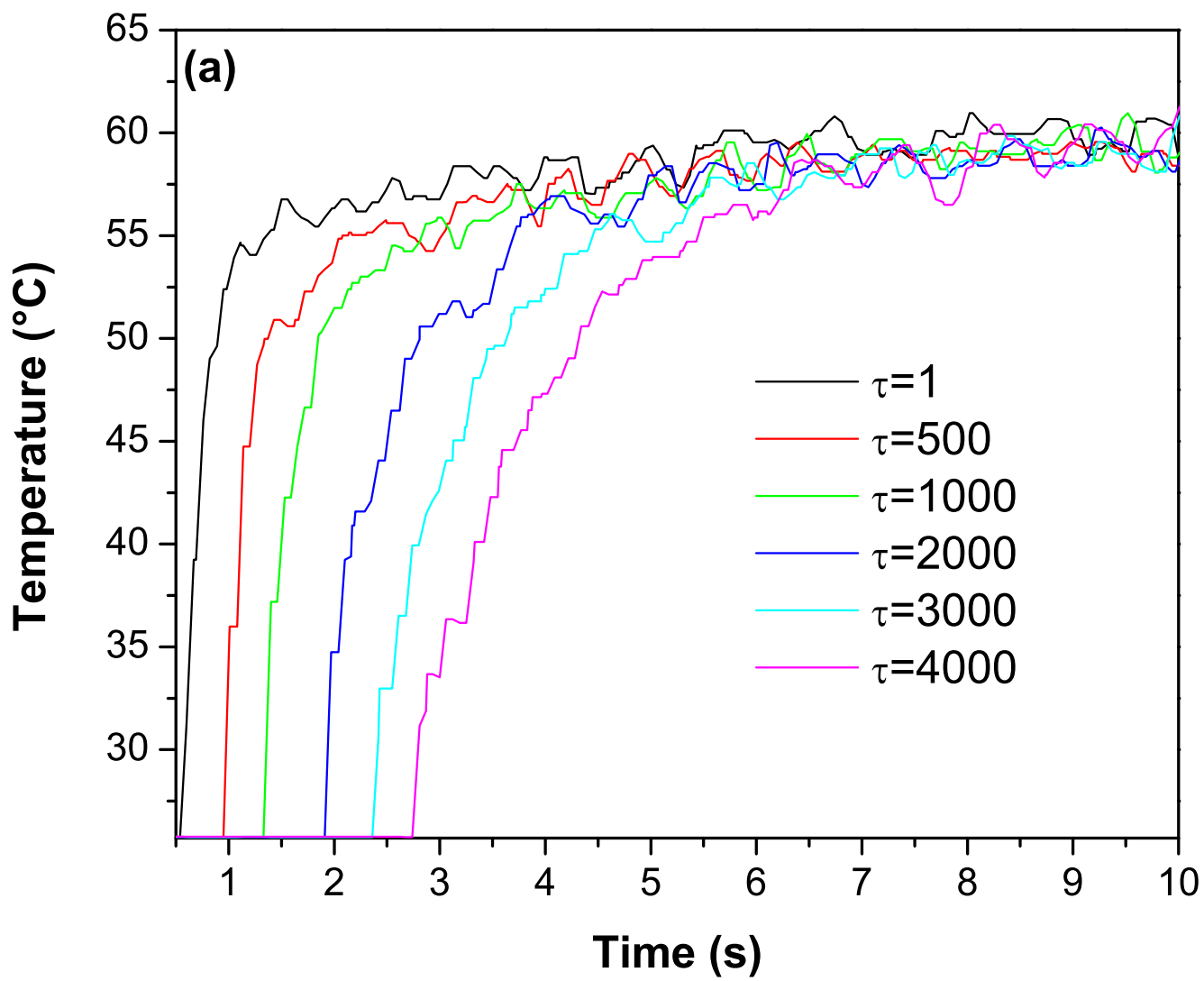
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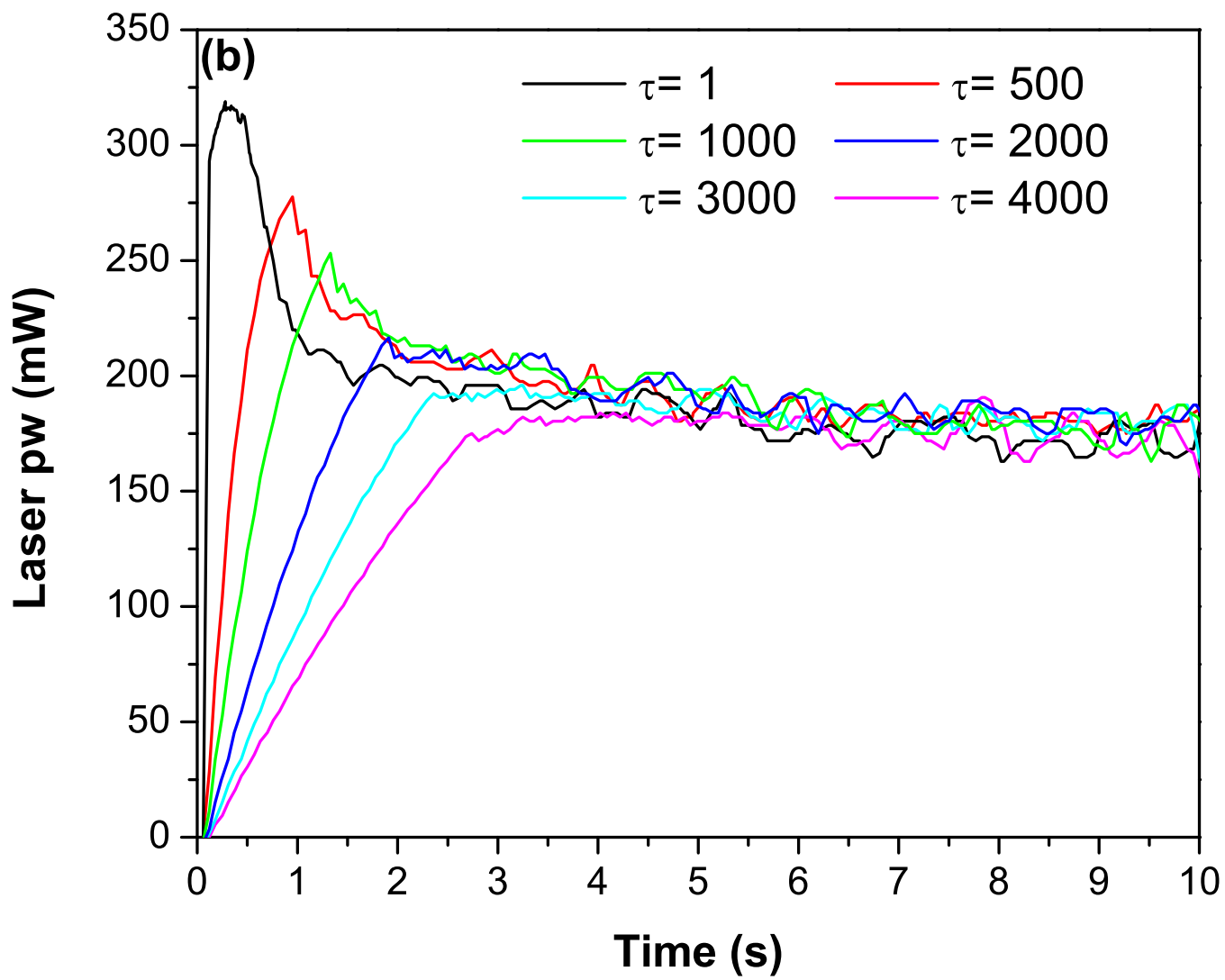
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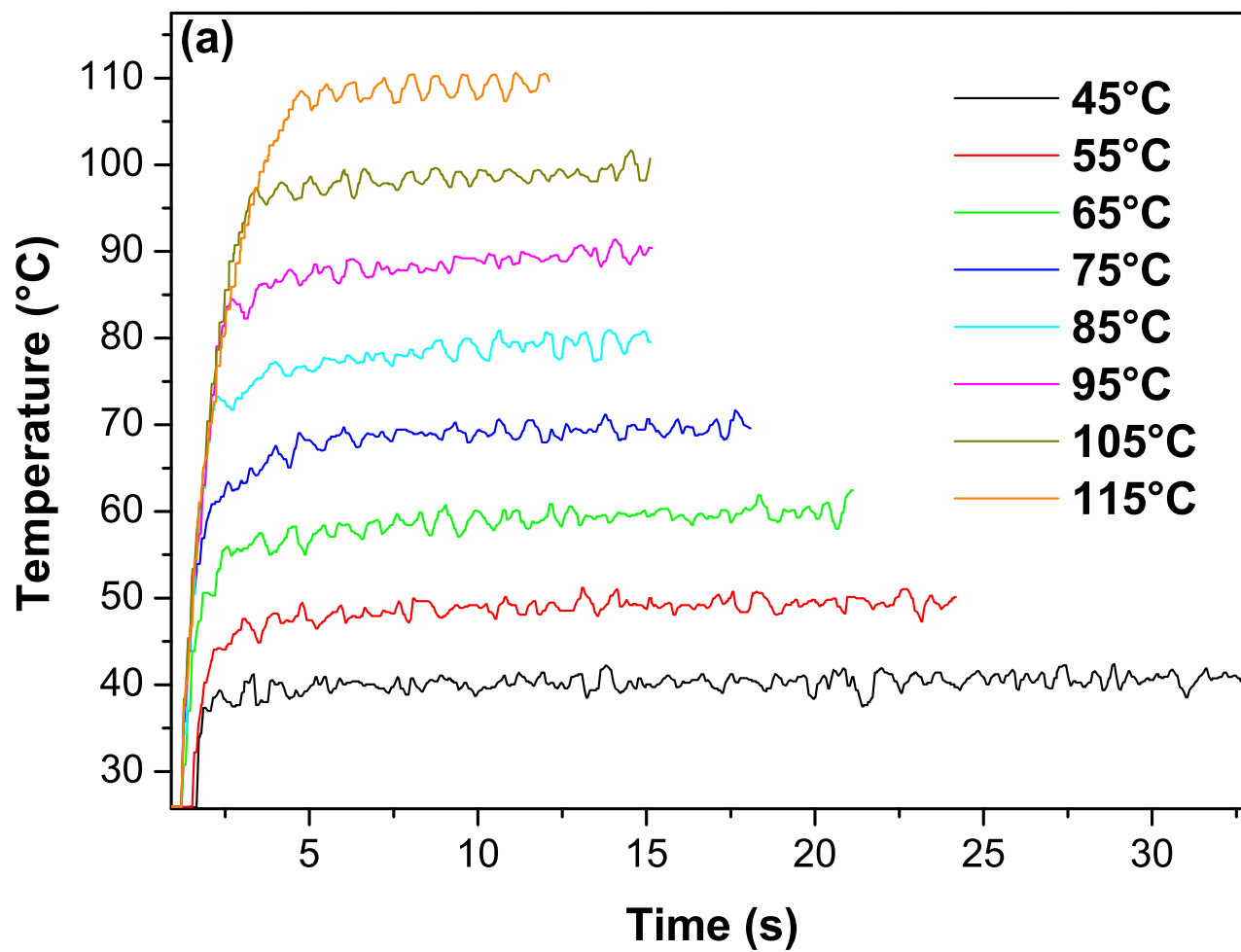




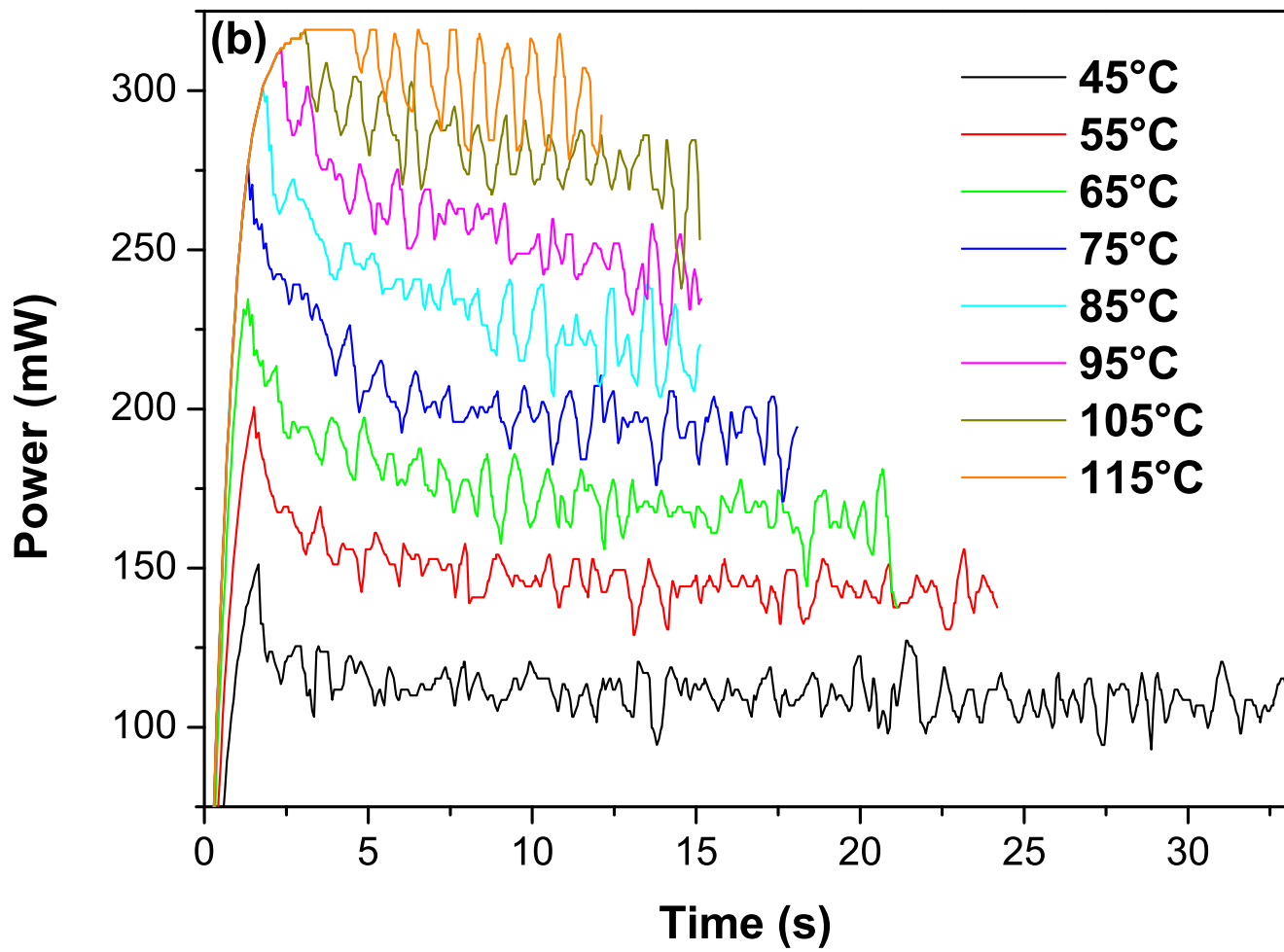
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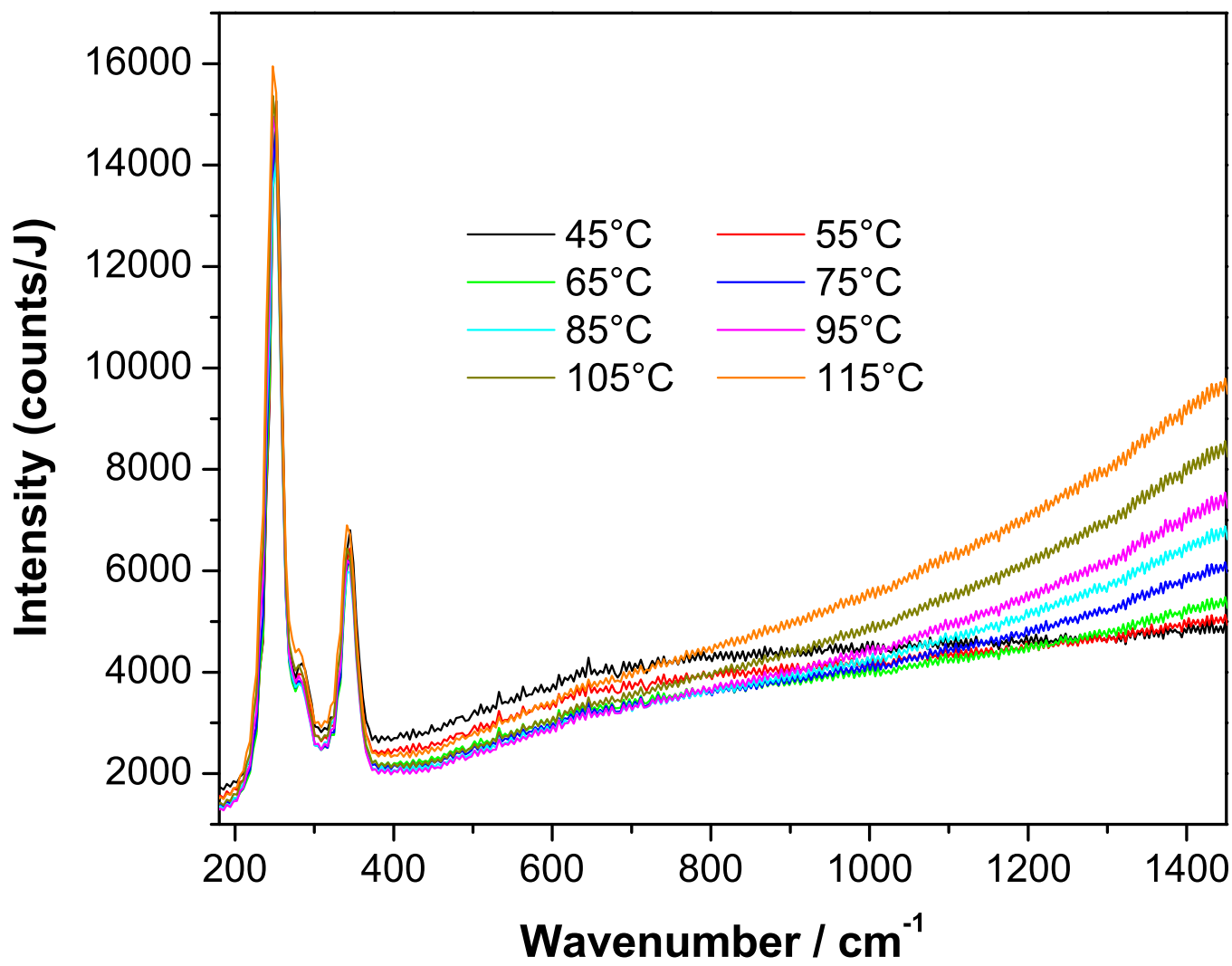
Figure(s)



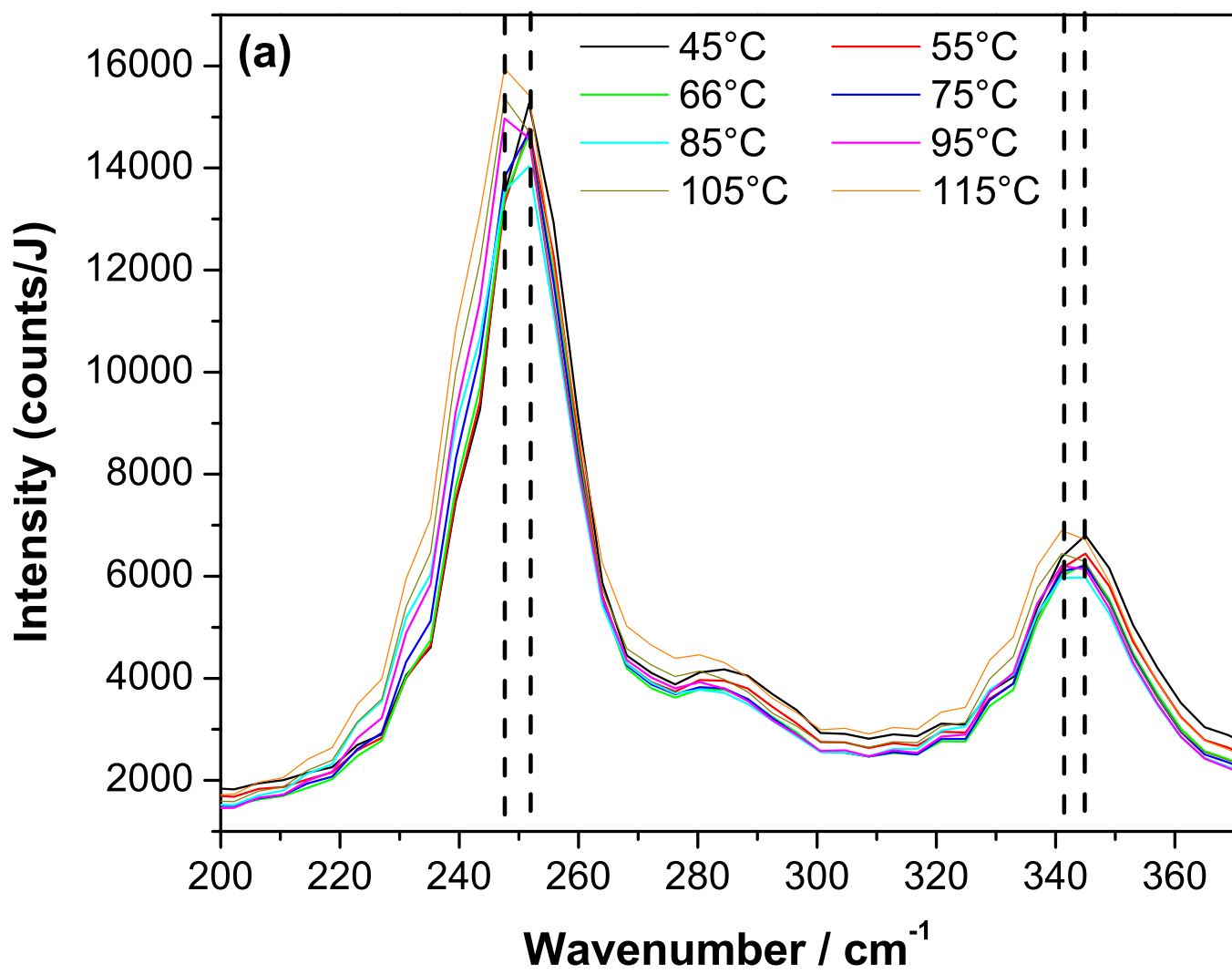
Figure(s)

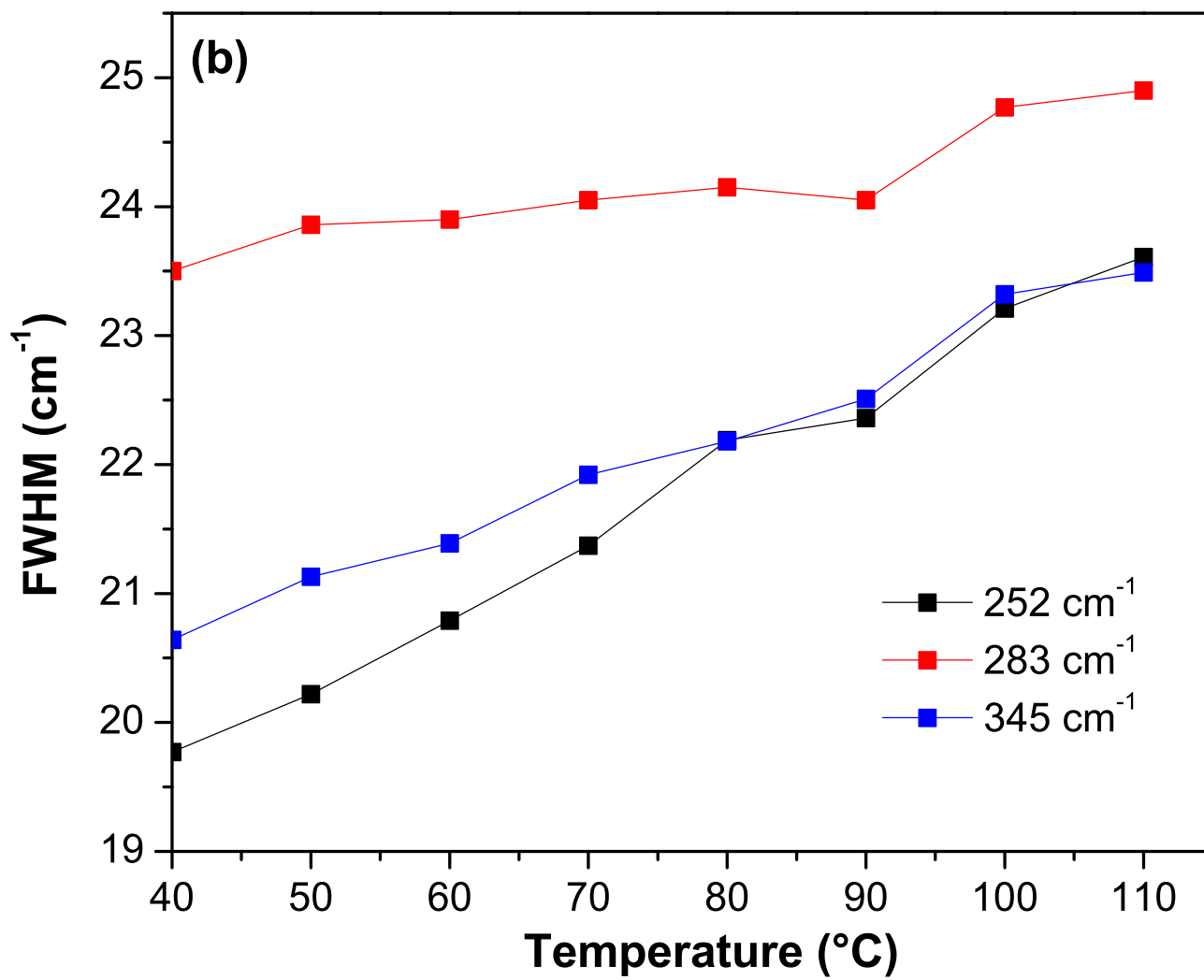


Figure(s)

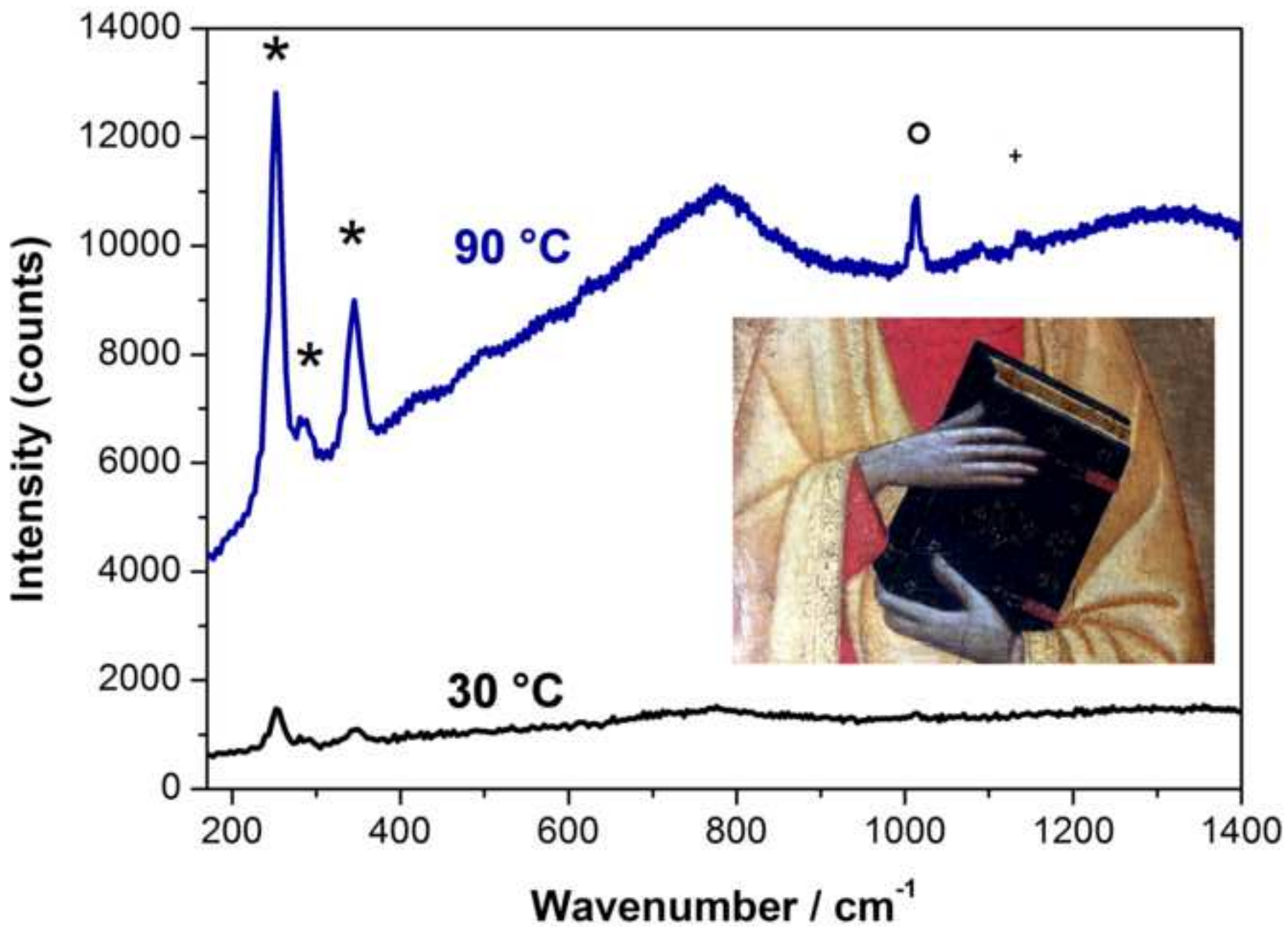


Figure(s)





Figure(s)
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Iacopo Osticioli, born in 1979, graduated in chemistry from the University of Florence, PhD in conservation science from the university of Florence, and researcher at the Institute of Applied Physics-CNR. His research activity is focused to the innovation and the application of modern spectroscopic and imaging techniques for the study and characterization of artistic materials and in particular Raman, LIPS and fluorescence spectroscopy. He has been involved in several RTD projects by developing novel devices, analytical protocols as well as chemometric methods in archaeometry. Author of about forty ISI-WoS publications and many other in proceedings, books, and journals.

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