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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 sensored 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, a pigment 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.

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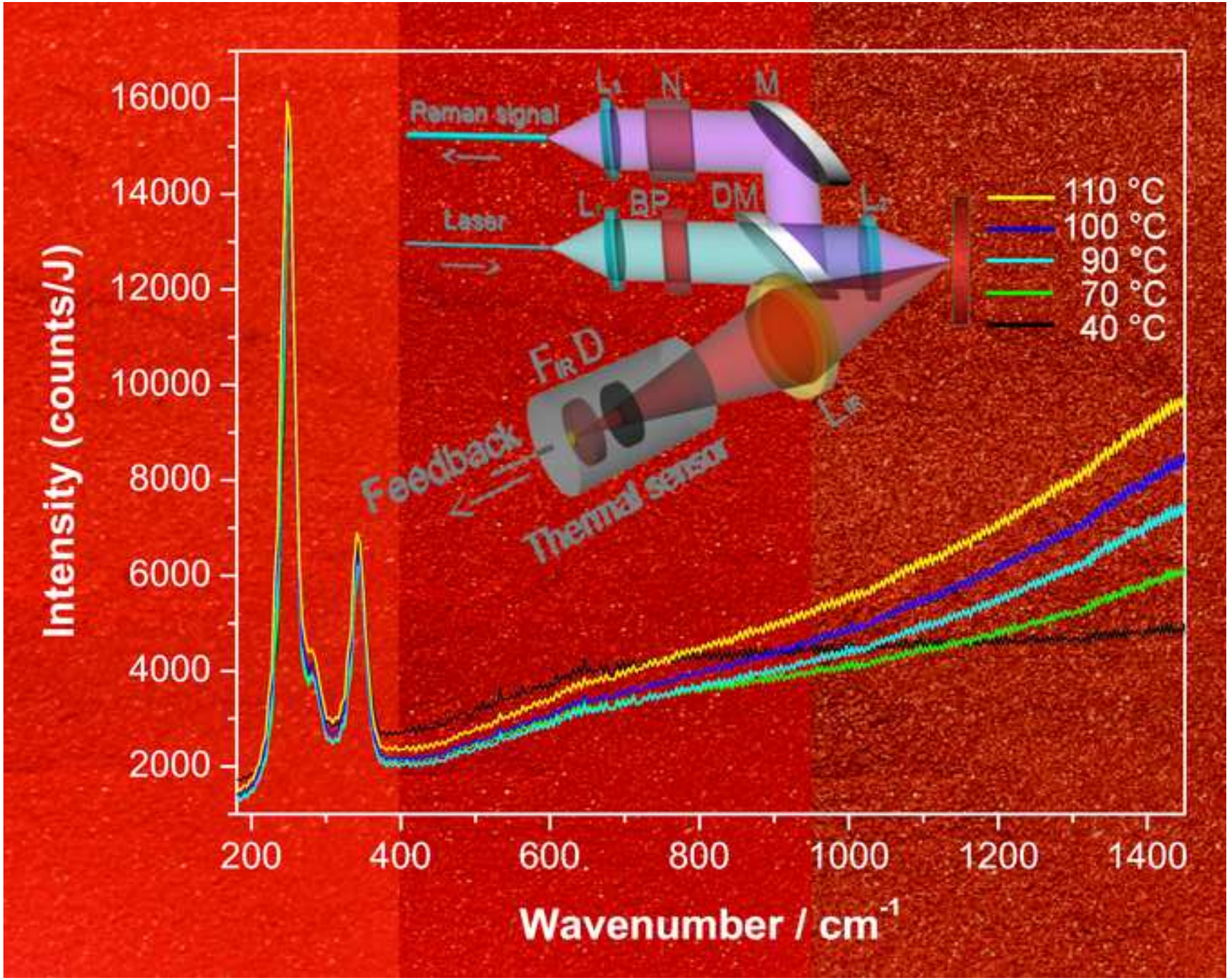
In this work we propose an innovative portable NIR Raman device (excitation wavelength at 1064 nm) in order to avoid thermal stress of the materials analyzed. In particular a specific probe was developed and tested in order to perform temperature controlled Raman measurements using a pyroelectric sensor which provided the feedback for suitably modulating the output power of the laser source and then limiting undesired heating effects within the irradiated volume. The experimentation carried out on materials presenting a pronounced thermal and photosensitivity such as cinnabar allowed showing the effectiveness and reliability of the present approach in preventing thermal alterations effects during Raman measurements, speeding up the identification of materials as well as monitoring variations in the crystals anharmonicity over temperature ranges. This is the first case of performing temperature controlled Raman measurements preventing overheating as well as monitoring the chemical transformations of artistic materials in situ by using a sensored portable instrumentation. For this reason we strongly think that this topic could be of interest for the scientific community taking "sensors and actuators B" journal as reference for publications.

Graphical Abstract (for review)



Highlights:

1) A novel Raman probe including thermal control has been developed
2) Online thermal monitoring prevents material alterations in Raman spectroscopy
3) Automatic control of temperature and laser exposure temporal profile is provided
4) T-controlled Raman probe discloses new authomated mapping possibilities of painted surfaces

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 sensored 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, a pigment 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. INTRODUTION

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, phase changes, and combustion with unacceptable visible effects on the painted surface understudy [11-15] and spectral effects. 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, a notoriously photothermally sensitive pigment.

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 heating effects within the irradiated volume. The experimentation carried out on samples of the mentioned pigment allowed showing the effectiveness and reliability of the present approach for preventing thermal alterations during Raman spectroscopy and speeding up the identification of materials.

2. INSTRUMENTATION AND METHOD DEVELOPMENT

A compact Raman device was assembled using a OEM spectrometer 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} (BaySpec Inc., CA, USA). The exciting source was ultra-narrow linewidth diode pumped CW Nd:YAG(1064 nm) laser with a maximum output power of 500mW and a beam diameter of 300 μm (Innovative Photonic Solutions, NJ, USA). This laser source 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 pigments purchased from Zecchi, Florence, Italy, which exhibits high photothermal instability. The samples were prepared by flattening the powder in small cells.

Trigonal red structure of cinnabar (α-HgS) is stable at lower temperatures but it can transform into its cubic polymorph metacinnabar (β-HgS) when temperature of 673 °K is reached [16].

A schematic view of the Raman probe setup is shown in figure 1. The fiber-coupled Nd:YAG laser beam, collimated by the lens L_1, 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 L_2. The Raman-scattered light, collected and collimated by the lens L_2, 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 L_3 into a 200 μm core diameter optical fiber leading to the spectrometer. The ZnSe lens, L_{IR}, provides an image of the "hot-spot" of the target onto the thermopile sensor, which is also provided of a field diaphragm, D, in order to match the laser spot dimension, and a IR filter, F_{IR}, in order to cut-off the ambient light.

A thermopile sensor with active area of about 750×750 μm^2, angle of view of about 10°, response time of 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:

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

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 cinnabar samples was 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. We found $\varepsilon = 0.61$.

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:

$$P(t) = K\left[T_{exp} - T(t)\right]^{\frac{1}{4}} \tanh\left(\frac{t}{\tau}\right) \qquad (2)$$

where K and τ are constants, T_{exp} is the expected temperature set. The exponent ¼ was selected in order to smooth the power modulation while was phenomenogically adapted in order to achieve the rapid convergence of the control process (see the applicative cases below) while the tanh factor was introduced in order to make gradual the laser power rise during the onset phase by exploiting the saturating zone of its behavior ($t/\tau \sim 2$). T_{exp} was set sufficiently below the critical temperature of the phase change and spectral alteration of the Raman spectrum under laser irradiation, as determined through preliminary irradiation tests.

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 K and τ and to plot $T(t)$ and $P(t)$.

2.1 Application results

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 a control accessory was implemented 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 optimization step concerned the selection of the parameter K in Eq. 2. Let us consider the case of cinnabar and assume a given temperature T_{exp}=60 °C and a fixed τ= 1s. As shown in figure 2a, K values between 0.1-0.12 W/°K$^{1/4}$ allowed to smoothly approach T_{exp} after 10 s (for K=0.12) and later on (for K=0.1), with a corresponding smooth power control, after the initial rapid rise (see black and red curves). On the contrary, the feedback of the thermal sensor for higher values of K (0.13-0.15 W/°K$^{1/4}$) produced increasing oscillations of the excitation power and consequent growing temperature modulations. Very interestingly, even in such a not optimized situation, temperature overshoots were limited to a few Celsius degrees with transient overheating of about 5 °C. However, a careful selection of K is needed in cases where the Raman spectra are collected in proximity of a given critical temperature.

The further 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 K= 0.12 W/°K$^{1/4}$, τ values between 1-4000 ms generate the profiles P(t) and T(t) displayed in figure 3. 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 τ>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 polimateric 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.

Temperature and laser power behaviors for various T_{exp} of figure 4 were achieved for cinnabar by selecting the K between 0.08 (at 40°C) and 0.2 (at 110 °C), τ = 1s, and a total excitation exposure of 1300 J/cm^2. These conditions were used for collecting the Raman spectra reported in the following. As observable, the temperature approached quite quickly the values of T_{exp} set and was then maintained almost constant during the whole energy release to the target, whose duration depends on the selection of T_{exp}.

Cinnabar exhibited a visible gradual darkening while the temperature increased then the sample returned back to the original colour after cooling. Such a discoloration was observed well-below the critical threshold for the transition to metacinnabar, which occurs around 400 °C [16]. Thus, no phase changes were identified in Raman spectra, whereas the phenomenon was clearly detected by means of online reflectance (R) measurements at 1064 nm. As shown in figure 5, temperature between about 20-215 °C produced a reflectance decrease of about 13%, which corresponds to a consequent increase of the photothermal coupling to the target. The initial reflectance at ambient temperature was about 72%, slightly higher but not far from the reported one for cinnabar-based paint layers [18].

The above described behavior suggests the possibility to use R as a possible further independent parameter, which can be exploited in order to stop the irradiation whenever ΔR overcomes a given value, thus strengthening the present technique of damage prevention, which could be guaranteed even in case of accidental underestimation of T. Such a double safety control line will be implemented in our Raman device in the next future after investigating its possible usefulness for other photosensitive pigments.

2.1.2 Raman spectra of cinnabar in optimized laser excitation conditions

Figure 6 shows the Raman spectra of cinnabar sample acquired using the control setting just described (figure 4). An increase of the background with the temperature is clearly observable, which is attributable 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. Cinnabar has band gap energy of 2.1 eV [20] against photon energy of 1.16 eV. 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 S/N ratio. Various algorithms [19, 21] and laser modulation techniques [22] were proposed for reducing the thermal background in Raman spectra. As shown in figure 6, 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.

Figure 7a shows the major Raman bands of cinnabar at 252, 283 and 345 cm^{-1} commonly assigned to Hg-S stretching modes [23]. An evident broadening of the can be noticed observed in the spectra at increasing temperatures, which is reasonably attributable to the to the anharmonic component associated with the thermal expansion [16]. Figure 7b 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 90 to 110°C (Fig. 4), which provide a further evidence of anharmonicity.

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 phototermally 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 reducing the temperature set thus avoiding consequent band shapes distortion and errors in band positions. In particular, under the temperature setting of 40°C, Raman spectra of cinnabar pigment with a moderate and substantially flat thermal background have been acquired.

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.

Finally, the possibility to associate the reflectance at 1064 nm with the thermal monitoring in order to detect damage precursors of cinnabar, such as in particular reversible discoloration, was also preliminarily explored. The results achieved confirmed that the variation of the reflectance of the sample surface provides a safety redundancy against photothermal alterations during Raman spectroscopy.

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

4. ACKNOWLEDGEMENTS

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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 K on the thermal control (fixed τ = 1s): temperature (a) and laser power (b) as a function of time for different values of K, from 0.1 to 0.15.

Fig. 3 Influence of the parameter τ on the thermal control (fixed K = 0.12 W/°K1/4): temperature (a) and laser power (b)as a function of time for different values of τ, from 1 to 4000 ms

Fig. 4 Behaviors of the thermal control with optimized K and τ= 1s for different Texp sets: temperature (a) and laser power (b) trends over time

Fig. 5 Reflectance @ 1064 nm of cinnabar as a function of temperature.

Fig. 6 Raman spectra of cinnabar pigment acquired at T_{exp} between 40 and 110 °C: an increase with the temperature of the blackbody emission thermal background is clearly observable in the spectra.

Fig. 7 Raman spectra of cinnabar at increasing values of T_{exp} evidencing band broadening and shift (a) effects and corresponding broadening trend (b).

Fig.1

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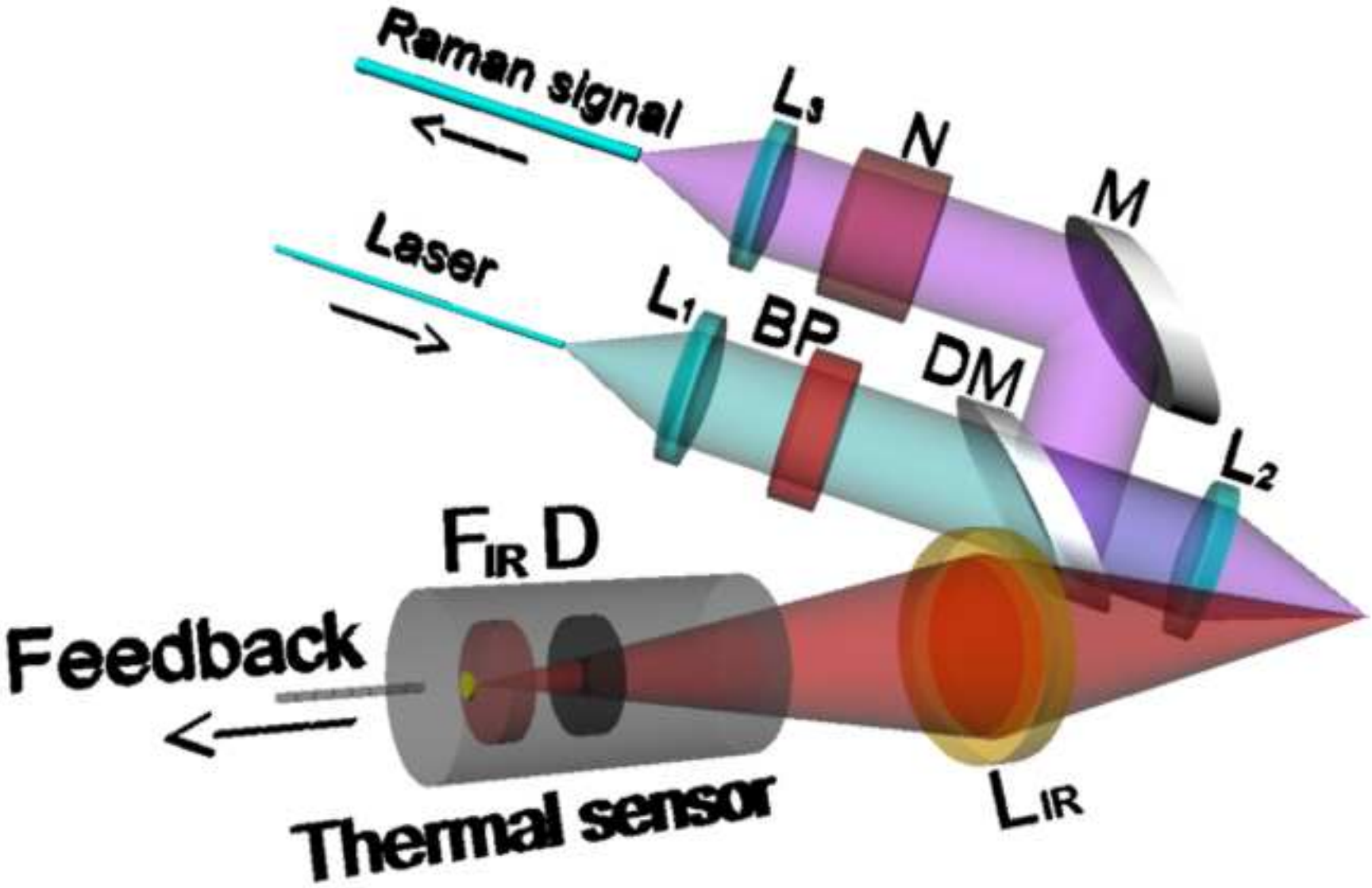


Fig.2a

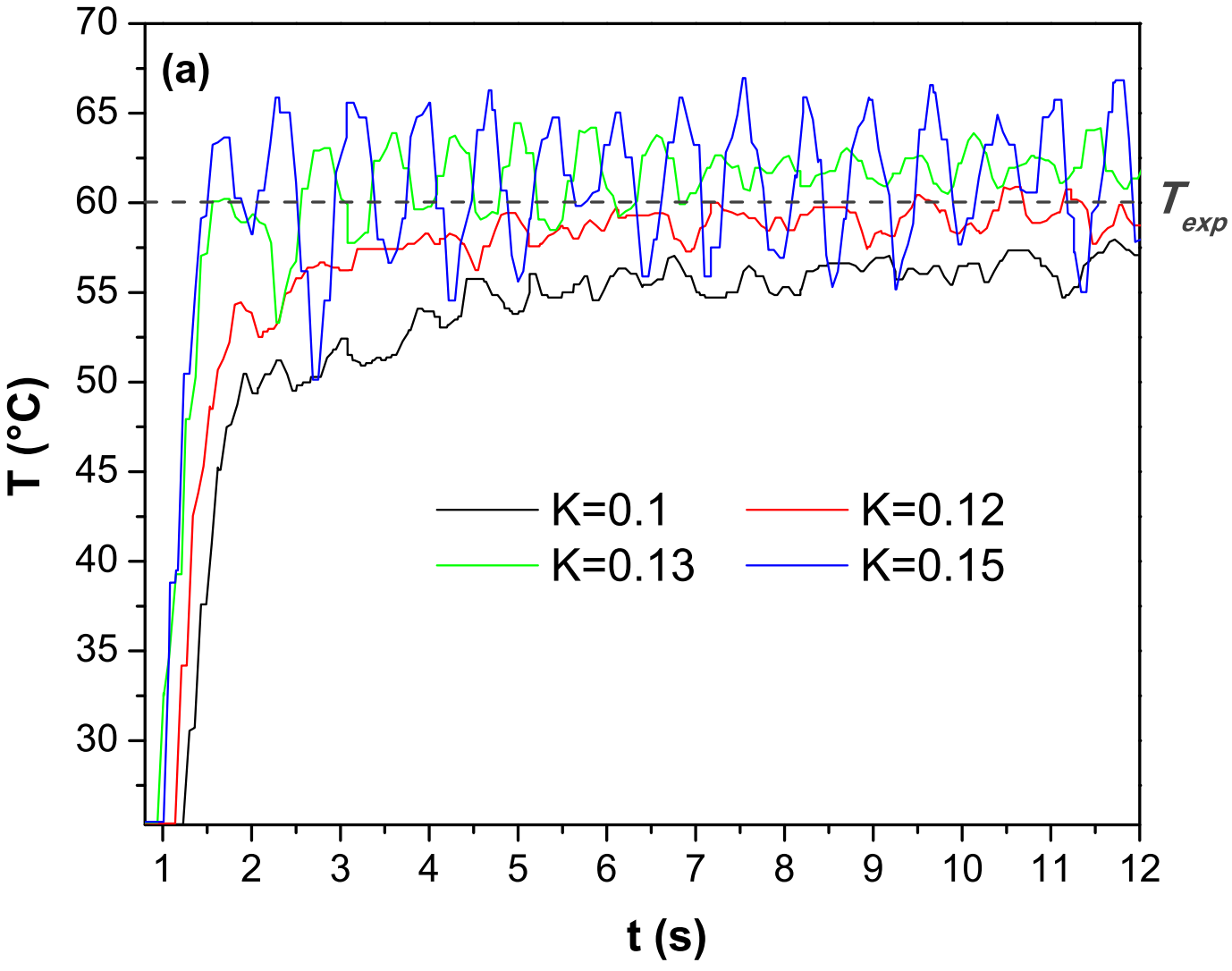
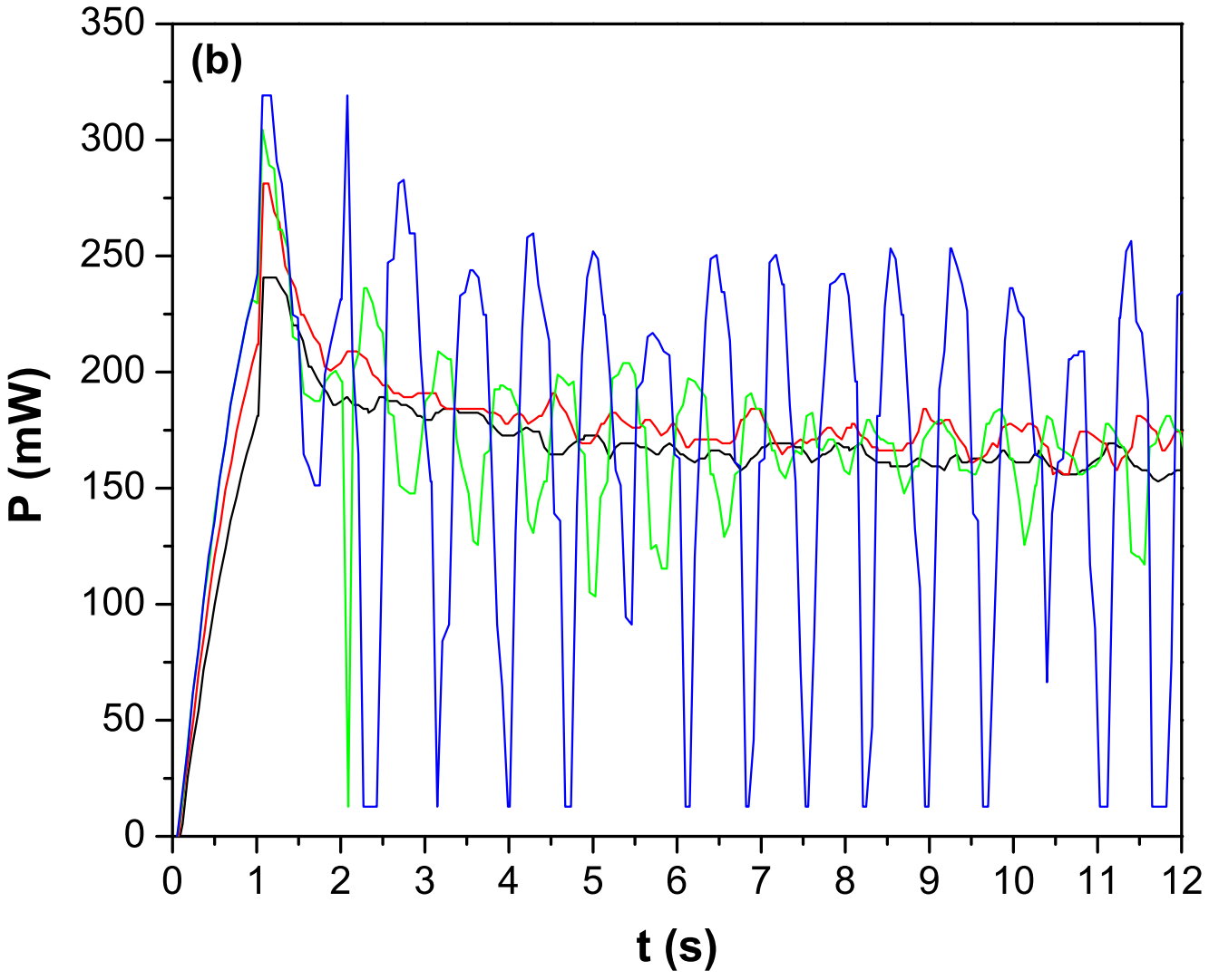

(a)
T (°C)
t (s)
70
65
60
55
50
45
40
35
30
1
2
3
4
5
6
7
8
9
10
11
12
T_{exp}
K=0.1
K=0.12
K=0.13
K=0.15

Fig.2b



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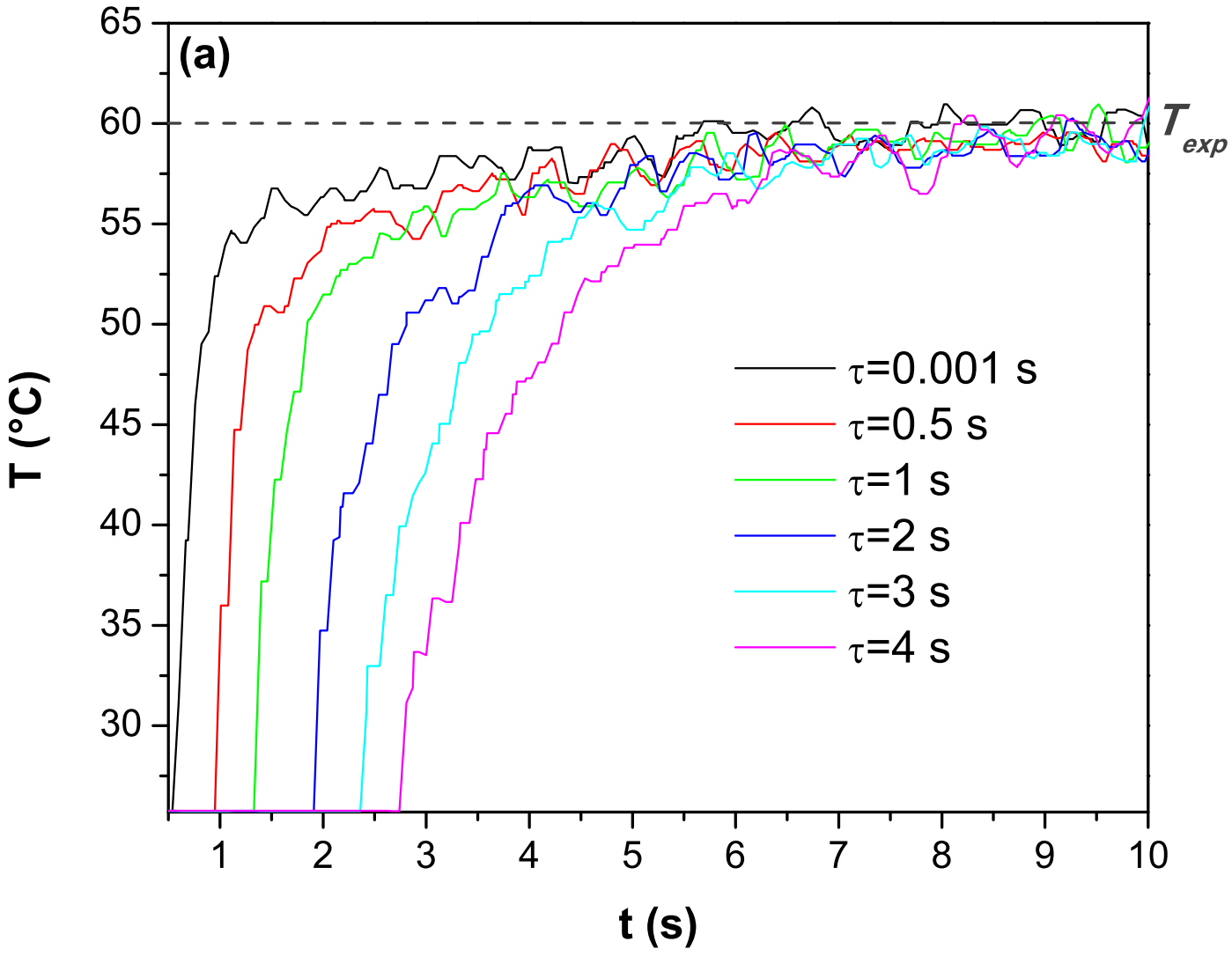
(a)
T (°C)
t (s)
T_{exp}
τ=0.001 s
τ=0.5 s
τ=1 s
τ=2 s
τ=3 s
τ=4 s
65
60
55
50
45
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1
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Fig.3b

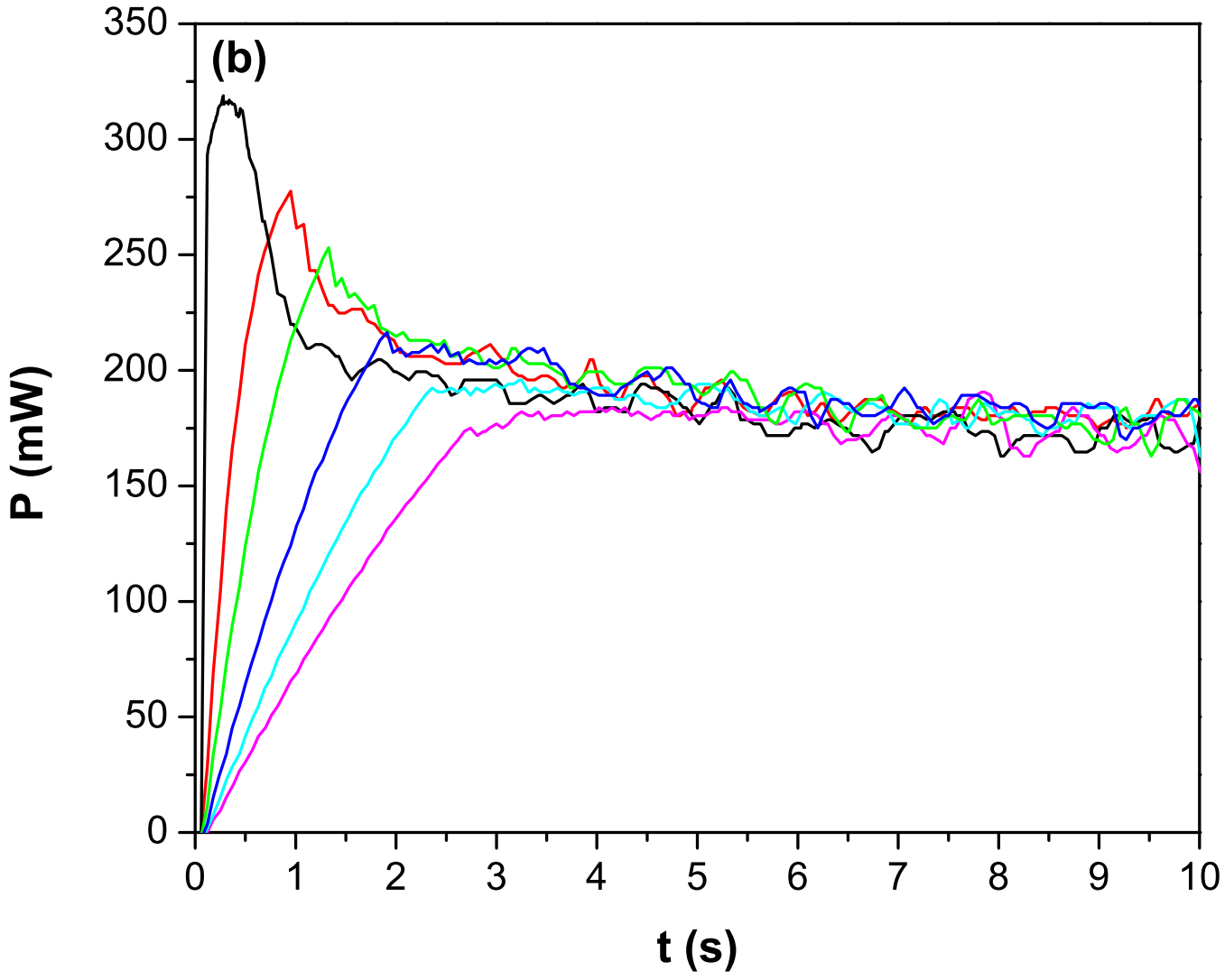
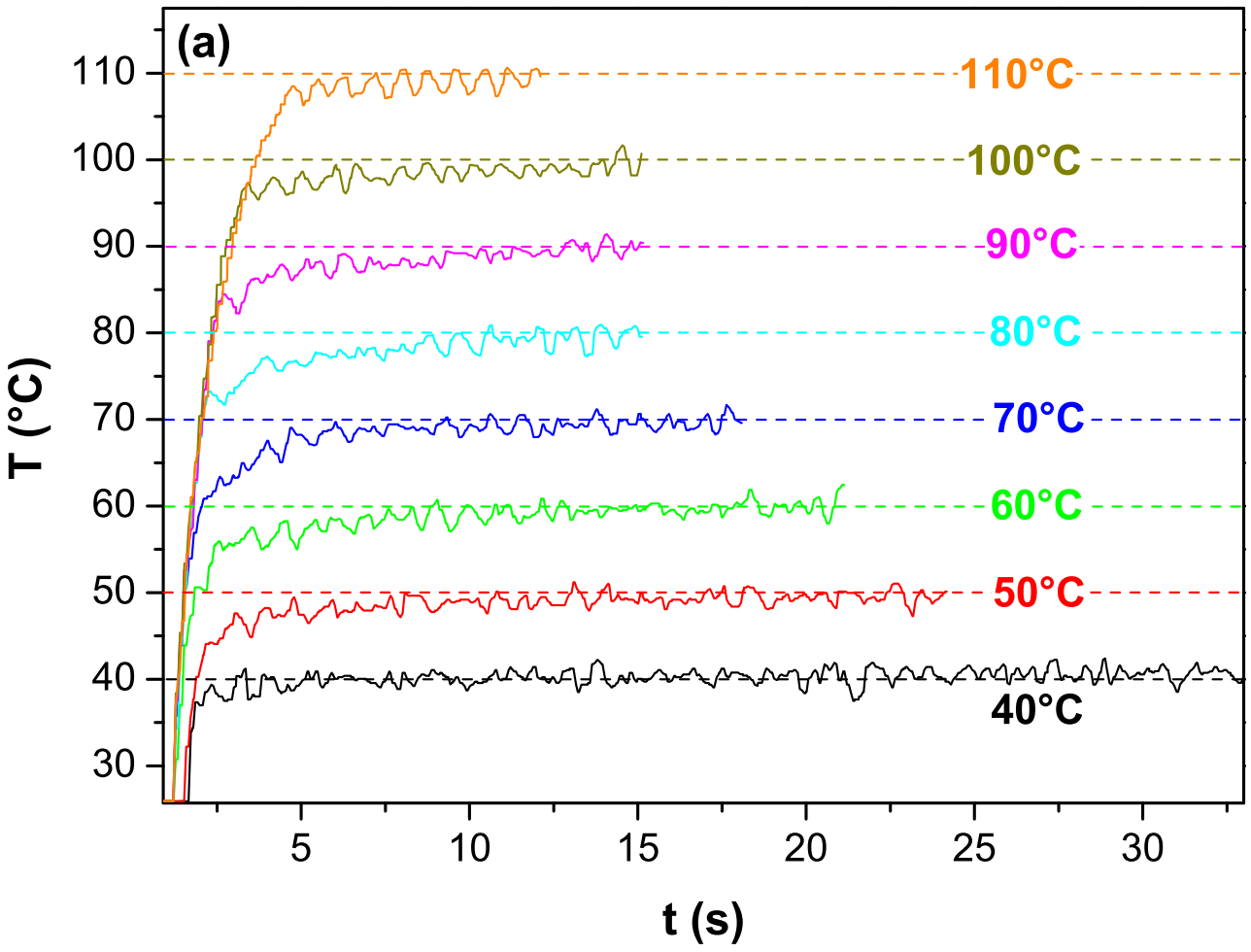


Fig.4a


(a)
110°C
100°C
90°C
80°C
70°C
60°C
50°C
40°C
T (°C)
t (s)
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100
90
80
70
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40
30
5
10
15
20
25
30

Fig.4b

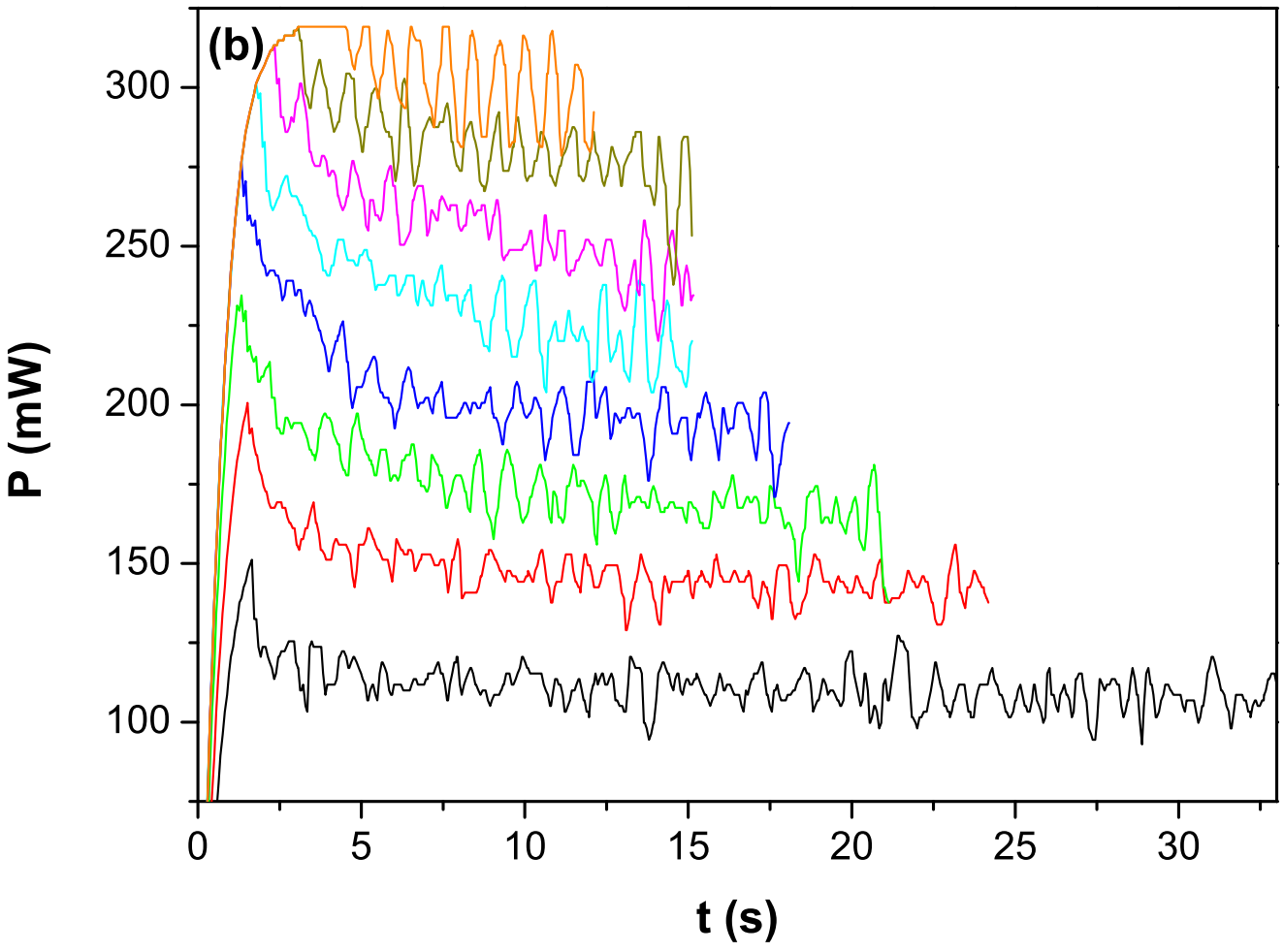

Fig.5

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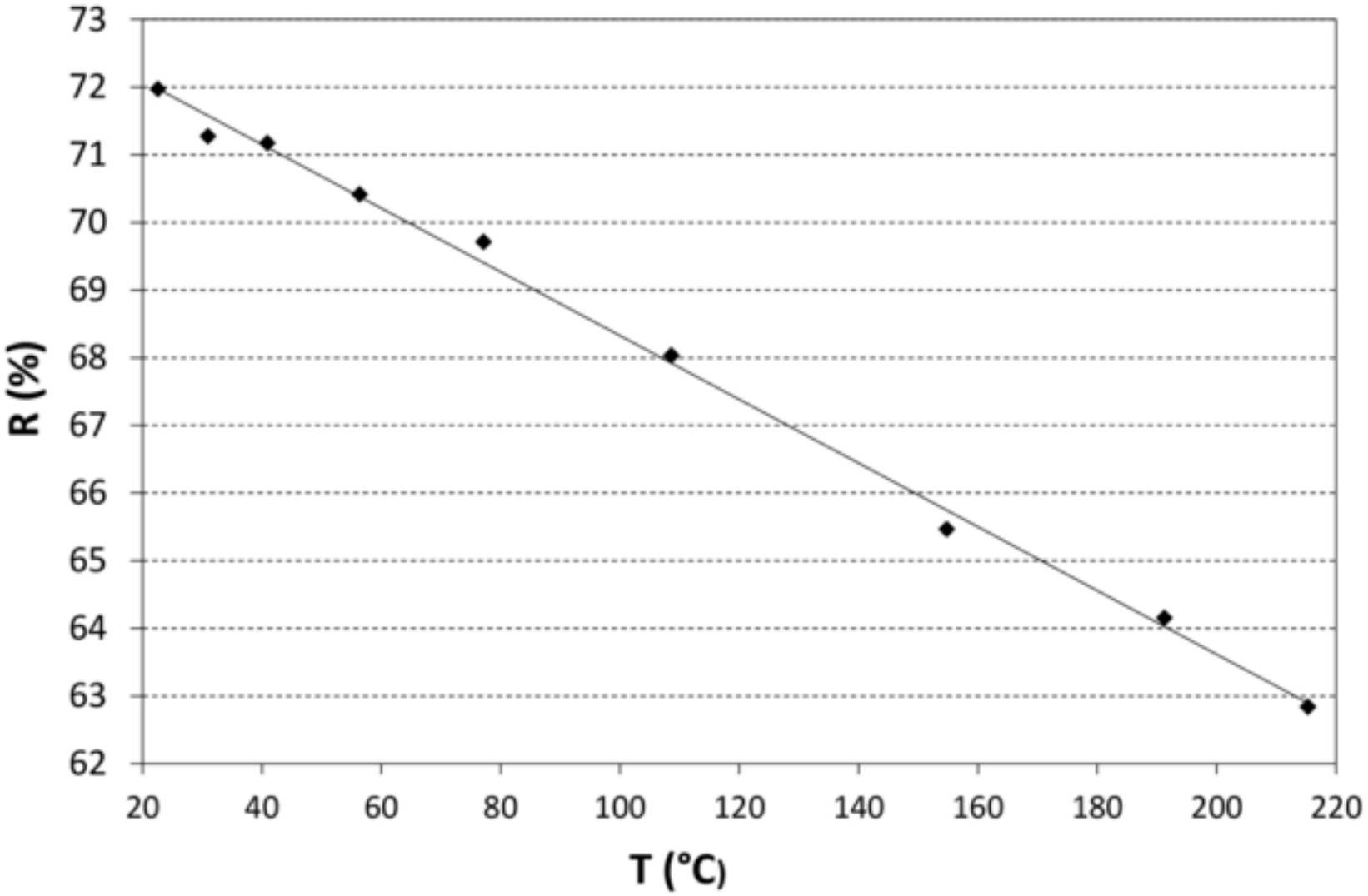
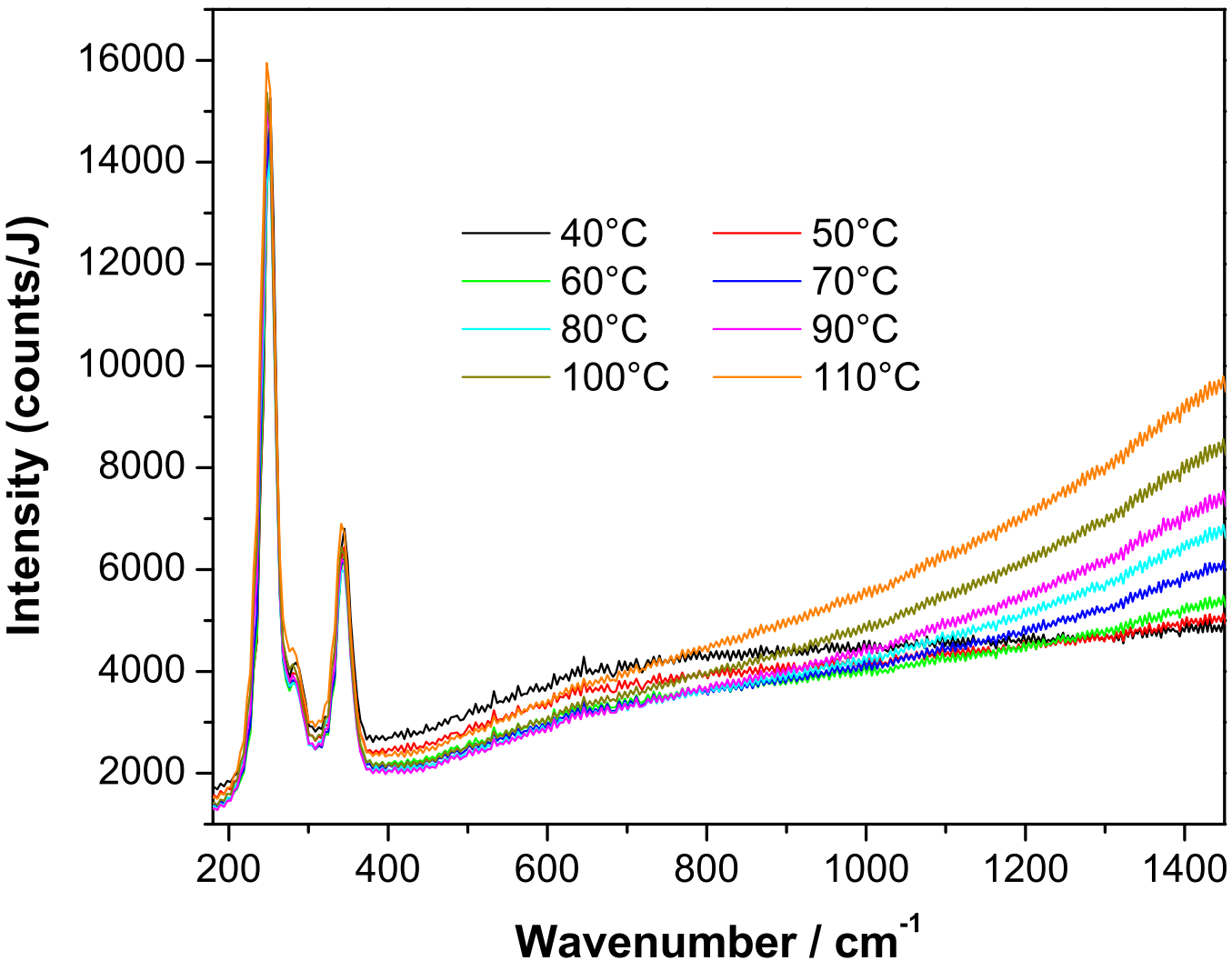


Fig.6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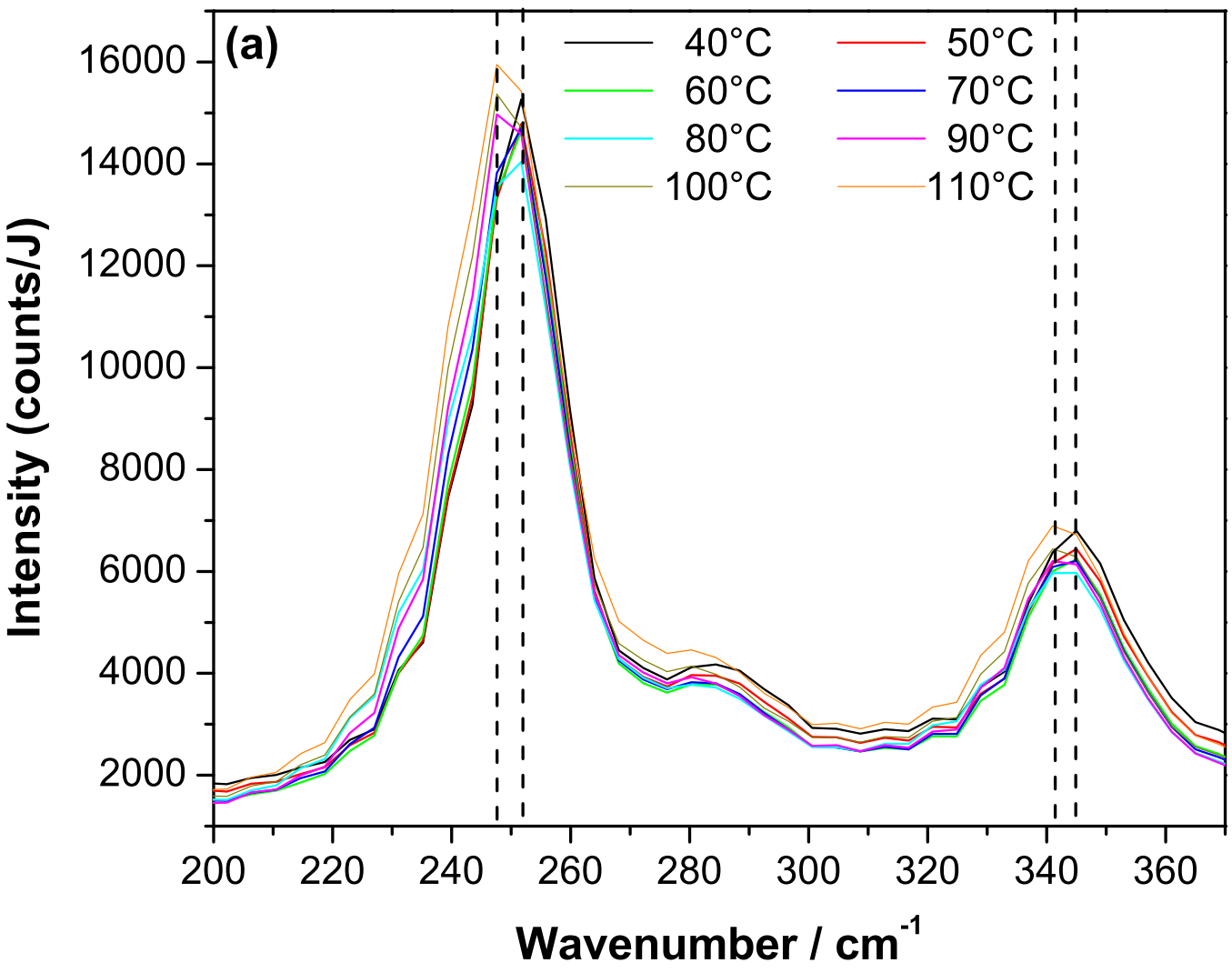
14000
12000
10000
8000
6000
4000
2000
200
400
600
800
1000
1200
1400
Wavenumber / cm-1
40°C
50°C
60°C
70°C
80°C
90°C
100°C
110°C

Fig.7a


(a)
40°C
50°C
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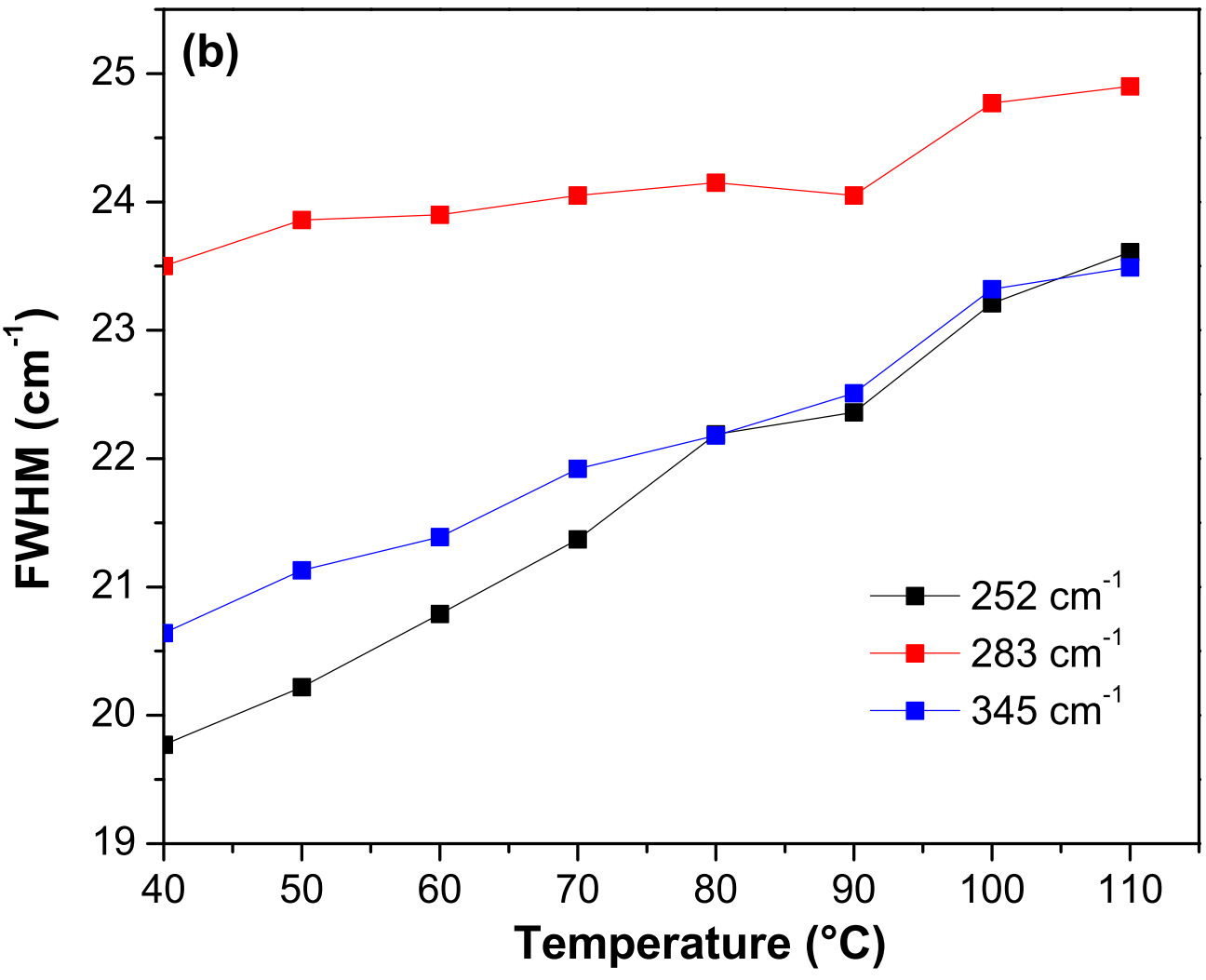
70°C
80°C
90°C
100°C
110°C
16000
14000
12000
10000
8000
6000
4000
2000
Intensity (counts/J)
200
220
240
260
280
300
320
340
360
Wavenumber / cm-1

Fig.7b


(b)
FWHM (cm-1)
Temperature (°C)
252 cm-1
283 cm-1
345 cm-1
19
20
21
22
23
24
25
40
50
60
70
80
90
100
110

Author Biographies

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 Physiscs-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.

Andrea Azelio Mencaglia, born 1958, graduated in physics from the University of Florence, and researcher at the Institute of Applied Physics-CNR. His activity focuses on the hardware and software design and development of optoelectronic devices, biosensor, and environmental sensors for microclimate control. He has been involved in several RTD projects by developing novel devices, investigating and optimising light-material interaction processes for elemental and molecular chemometry. Author of about one-hundred ISI-WoS publications and many other in proceedings, books, and journals.

Salvatore Siano, senior researcher at the Institute of Applied Physics-CNR since 2007. His research activity is focused on laser, optoelectronic, and neutron techniques for material characterisation and processing in cultural heritage and biomedical fields. He has been strongly involved in several tens of RTD, networking, and dissemination projects by developing novel laser systems, investigating and optimising laser-material interaction processes for archaeometry and conservation, as well as surgical applications. Member of the editorial boards of four ISI-WoS journals, contract professor, and scientific expert in a number of analytical and conservation campaign carried out on unique ancient and Renaissance masterpieces.