Conference paper

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High-temperature Raman spectroscopy

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Abstract: Raman spectroscopy has a long-standing reputation as a powerful tool for structural investigation of the various materials. However, application of this technique to study the melt structure directly under high-temperature requires its certain modification. The methods of the registration of high-temperature Raman spectra were considered. Particular attention was paid to considering the systems on time-resolved filtering of the thermal radiation.

Keywords: Raman spectroscopy; spatial filtering; SSC-2018; time-resolved filtering.

Introduction

Presently, high-temperature synthesis is one of the widespread methods of production of a wide variety of materials. It is obvious that properties of these materials depend directly on the structure, physical and chemical parameters of melt, as well as the processes and reactions which occur in the melt during variation of its composition, temperature or pressure. Thus, study of the melt structure at high temperatures and mechanisms of its reorganization depending on temperature is of great interest both fundamental and applied viewpoint. Since the discovery of the Raman scattering phenomena in 1928 [1, 2], Raman spectroscopy became a powerful tool for structural characterization of materials and actively used in various fields of science. Because Raman scattering is an extremely weak effect (approx. 1 in 10^7 photons of the incident radiation), the key challenge of high-temperature Raman measurements is registration of weak Raman signal against a strong thermal emission of the melt and heater assembly. Figure 1 shows thermal radiation effects on modeled Raman spectrum (initial Raman spectrum was modeled as a superposition of several Gaussian lines). Figure 1a, in particular, demonstrates effect of constant component of thermal radiation in the frequency range under consideration whereas Fig. 1b shows normalized presentation of the same curves after subtracting thermal radiation background. Thus, the first figure (Fig. 1a) imitates the raw (measured) spectra before their treatment and the second one (Fig. 1b) shows an influence of fluctuation of thermal radiation on quality of the spectra. All the presented curves were obtained assuming that thermal radiation intensity (1) and its fluctuation (2) are described by following equations [3]:

$$I_{\text{therm}} = A \cdot \left[\exp\left(\frac{h\nu}{kT} - 1 \right) \right], \tag{1}$$

$$\delta_{\text{therm}} = \sqrt{I_{\text{therm}}}. \tag{2}$$

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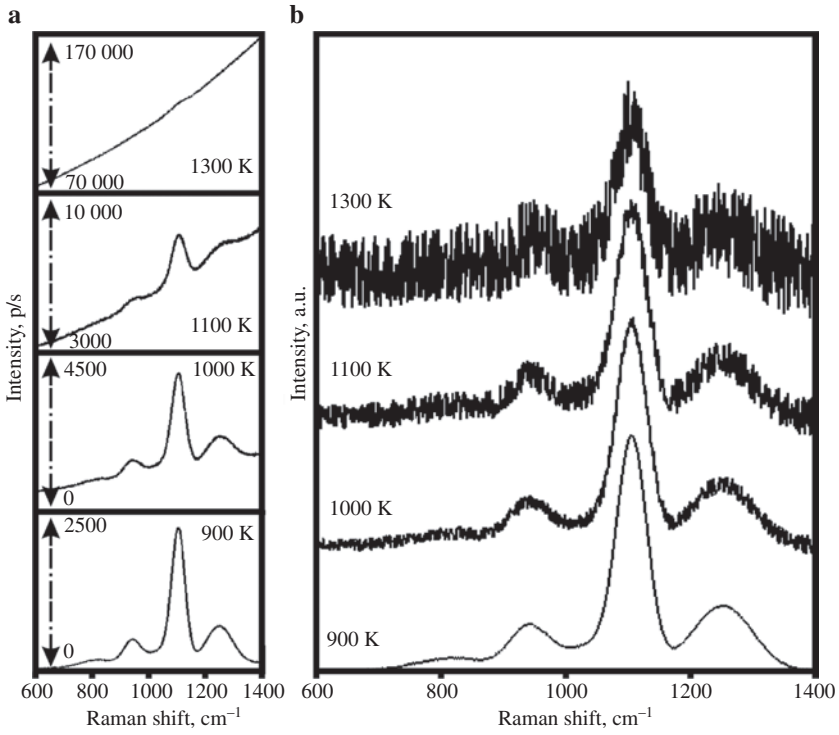

Fig. 1: Thermal radiation effect on the Raman spectra (simulation results). (a) Demonstrates effect of constant component of thermal radiation in the frequency range under consideration; (b) normalized presentation of the same curves after subtracting thermal radiation background.

Here, A is the constant coefficient, which depends on the used Raman system and it can be determined by measuring thermal radiation intensity at various wavenumbers within the given frequency range, h is Planck's constant, k is Boltzmann's constant, v is frequency and T is absolute temperature. Equation (2) is valid when a photomultiplier tube (PMT) operating in a photon-counting mode is used as a detector of scattered light (in this case the distribution of the pulse count measured during the given time interval obeys the Poisson law and a mean square fluctuation of thermal radiation is a square root of its intensity).

As seen in Fig. 1a, increasing the constant component of thermal radiation with increase in temperature results in gradual veiling Raman features until their disappearing at very high intensity of thermal background. If the intensity of the total luminous flux does not cause detector saturation, an intensity of thermal radiation should be measured and subtracted from high-temperature Raman spectrum. This simple procedure allows easy exclusion of the influence of constant component of thermal radiation. As seen in Fig. 1b, however, the constant component of thermal radiation is not the only problem. Fluctuations of thermal radiation also negatively affect the quality of the spectrum due to their random nature (especially at high temperatures when they become comparable with the intensity of the Raman bands). The weak Raman bands can completely be masked by fluctuations of the parasitic light. In accordance with eq. (2), suppression of thermal radiation intensity is a direct way to reduce the fluctuation. At present, there are two methods of suppression of thermal radiation which make it possible to obtain high-quality high-temperature Raman spectra.

Spatial filtering systems

Spatial filtering of thermal radiation is a most popular technique to suppress parasitic light during *in situ* Raman studies of melt structure. In this case, the high-temperature Raman spectra are measured using micro-Raman systems with confocal optics (Fig. 2). In these systems, the focusing of the laser beam on the

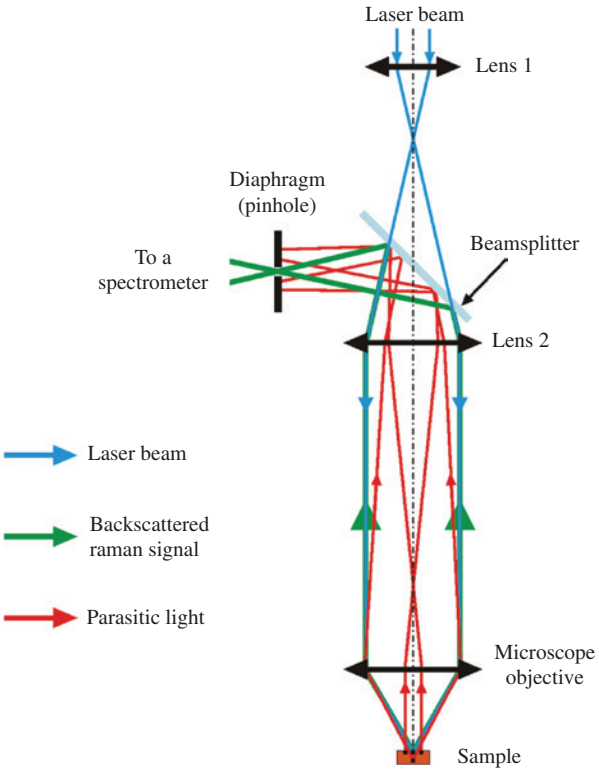

Fig. 2: Schematic diagram of a confocal Raman system.

sample and the collection of the scattered light are achieved with the objective of an optical microscope. A short-focus microscope objective has a high numerical aperture and enabling to focus the laser beam into a very small sample volume as well as to collect the light scattered by this volume under a wide angle. As a result, the Raman spectra with high signal/noise ratio can be obtained. In the confocal systems, thermal emission of the sample and heater assembly is suppressed by spatial filtering using the additional pinhole diaphragm. This diaphragm passes the light emitted directly by the small excited volume and cuts off those beams emitted outside the excited volume. If the diaphragm does not used, thermal emission of the sample becomes very intense at temperatures <1000 K. Thermal radiation of the sample within the small excited volume, however, will affect strongly enough the Raman spectrum when temperature exceeds ~1400–1500 K, even if the pinhole diaphragm is used. Therefore, it is useful to register the Raman spectrum and the thermal radiation alone, without the laser radiation used for excitation of the spectrum. It is obvious that thermal radiation should be measured under the same experimental conditions as the Raman spectrum (microscope objective, recording time, etc.).

As for the heater, the use of the short-focus objective of an optical microscope to focus laser radiation on a sample and collect scattered light requires specific design of a heating furnace, which should protect the objective against harmful effects of high temperatures and melt evaporation products. Therefore, high-temperature micro-Raman systems, as a rule are equipped with commercially available compact electric furnaces (e.g. temperature controlled stages production of Linkam Scientific company) or original home-made micro heaters [4–6].

Time-resolved filtering

Another less abundant but as effective as the first method of suppression of thermal radiation is based on application of the pulsed laser for excitation of the Raman spectra and gated registration system synchro-

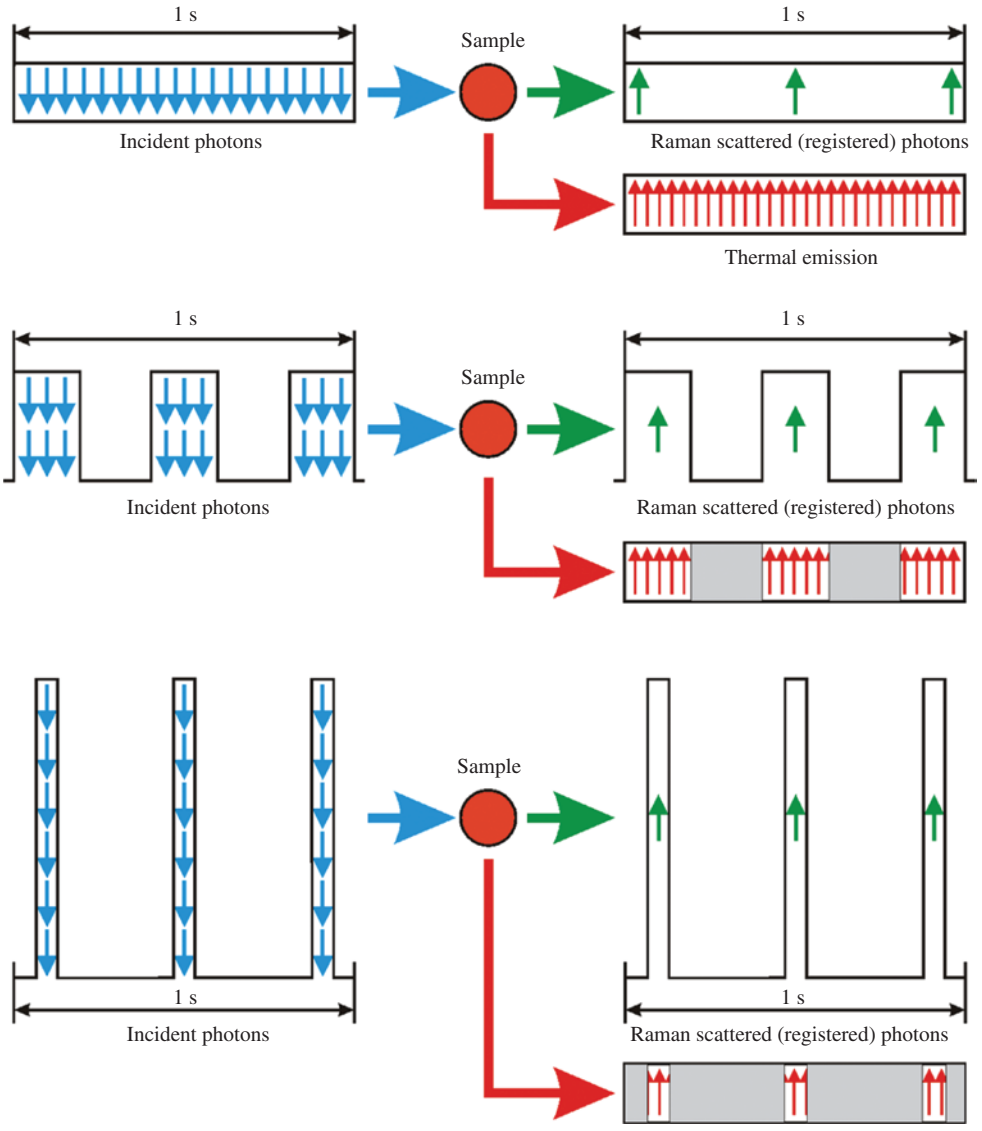

Fig. 3: Schematic presentation of the time-resolved filtering of thermal radiation.

nized with the laser pulses. The main idea of the registration of high-temperature Raman spectra by means of time-resolved filtering of thermal radiation is illustrated in Fig. 3. As seen in this figure, the measured intensity is a sum of Raman signal and thermal radiation, when both laser and registration system operate in a continuous mode (upper diagram). Hereinafter the laser radiation intensity is understood the mean amount the laser photons incident on a sample per unit time (1 s) and Raman intensity is the mean amount the scattered photons detected by registration system per unit time (1 s). Under conducting high-temperature measurements, intensity of thermal radiation will significantly exceed intensity of the scattered light and as a result will negatively affect the quality of the measured spectrum. If the laser operating mode changes from continuous to pulsed one in the way that the number of the laser photons incident on the sample per unit of time remains the same, the scattered light intensity remains the same too. The distribution of the scattered photons in time, however, will change. The registration system will detect scattered light only during the short periods, when the sample is under the laser radiation. Thus, there is a possibility to block the registration system in the absence of laser pulses without losing intensity of the Raman signal. At the same time, thermal radiation intensity will decrease as the pulse duration reduces (see Fig. 3). Thus, the contribution of thermal radiation to the total measured intensity can significantly be reduced by using pulsed laser for

excitation of the Raman spectra and gated registration system synchronized with the laser pulses. It means an opportunity to measure high-quality Raman spectra directly at high temperatures.

Based on the aforesaid, a high-temperature Raman setup equipped with a gated registration system synchronized with the laser pulses was elaborated at the Institute of Mineralogy UB RAS in 1996 [7]. Simplified block-diagram of this high-temperature Raman system is shown in Fig. 4. The second-harmonic of a LTI-701 Nd:YAG laser ($\lambda = 532$ nm) operated at a modulation frequency was used as an excitation source. The pulse duration, pulse energy and pulse repetition rate were 2–4 μs, ~100 μJ and 8.7 kHz, respectively. An uncooled FEU-79 photomultiplier tube (PMT) operating in a photon-counting mode was used as a detector. A photodiode, an amplifier, a rectangular-pulse shaper with a delay line and one-cycle multivibrator are intended for the formation of two strobe pulses with similar duration, which control the operation of two "AND" logical elements. The delay line was included to the scheme to compensate the phase shift between the first strobe pulse and the pulses related to the scattered photons. (The phase shift is due to the finite speed of response of the electronic devices using in the registration system). Two "AND" logical elements divide the pulse stream generated by a PMT detector into two streams. As seen from the diagram presented in Fig. 5, the position of the first strobe coincides with the laser pulse (the first strobe is generated on the front edge of the laser pulse). Thus, the first counter counts the pulses related to both the Raman scattering and thermal radiation during the first strobe. The second strobe is formed on the falling edge of the first one and, therefore, it is shifted by the phase relative to the laser pulse by duration of the first strobe. The second counter counts the pulses related only to thermal radiation because of lacking laser radiation at these moments. Data from the counters is entered to a computer at regular periods into two separate files. One of the files contains the information on the intensity of the total luminous flux (first counter's data) and another one contains the data only on thermal radiation intensity (second counter's data). Simple mathematical calculations provide a constant component of thermal radiation from the data of second file and, this constant component can be subtracted from the full registered spectrum (first file). This procedure finally yields the Raman spectrum without constant component of thermal radiation for a single measurement. In other words, separate measurement of thermal radiation is no longer required in this case.

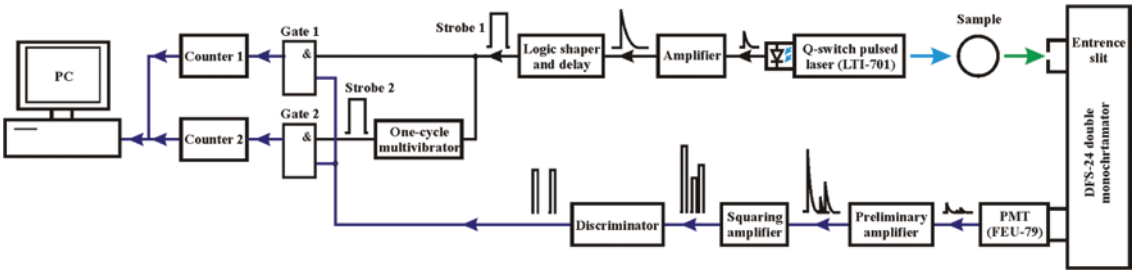

Fig. 4: Simplified diagram of the high-temperature Raman setup equipped with the gated registration system.

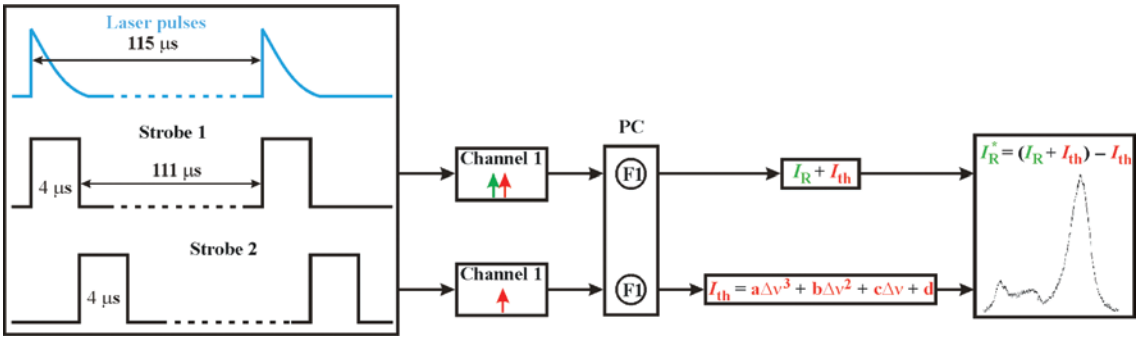

Fig. 5: Timing diagram of the gated registration system.

The scheme of an optic cell of the high-temperature Raman setup is shown in Fig. 6. A plano-convex lens and a small prism placed on it were used to focus the laser beam on a sample. The same lens was used to collect the scattered light. The parallel beam of the scattered light, reflected by a flat mirror, was collected on an entrance slit of a DFS-24 double monochromator by a second biconvex lens. An open-type electrical furnace was used to heat a sample. The temperature inside the furnace was controlled by a platinum thermocouple placed in immediate proximity to the crucible bottom. A small Pt crucible with the sample was placed in a central part of the furnace, where the temperature gradient is minimum (the height of a heating element is 10 times higher than the crucible vertical size). The internal diameter of the heating element was determined by the solid angle of the scattered light to prevent the screening of the scattered light by the sidewalls of the heating element.

As indicated in Fig. 6, a long-focus lens (210 mm) was used for both the focusing laser radiation on the sample and collecting scattered light. This is because of the need to protect the plano-convex lens against the high temperature and chemically active vapors of melt during high-temperature experiments using an open electrical furnace. In our experimental setup, this protection was provided by a buffer distance. It should be noted, that our high-temperature setup required no replacement of the plano-convex lens for more than 20 years of its operation.

Theoretical background for the high-temperature Raman setup spectroscopy with gated registration system was developed by Kudryavtsev and Sobol. They have shown [3] that $I_{\text{Raman}}(\Delta\nu, T) \geq 10\delta_{\text{therm}}(\Delta\nu, T)$ slack inequality can be used as a criterion of reliable registration of intensity of scattered light in the presence of thermal radiation background. This inequality can be rewritten as follows:

$$F(\Delta\nu, T) \geq 10 \tag{3}$$

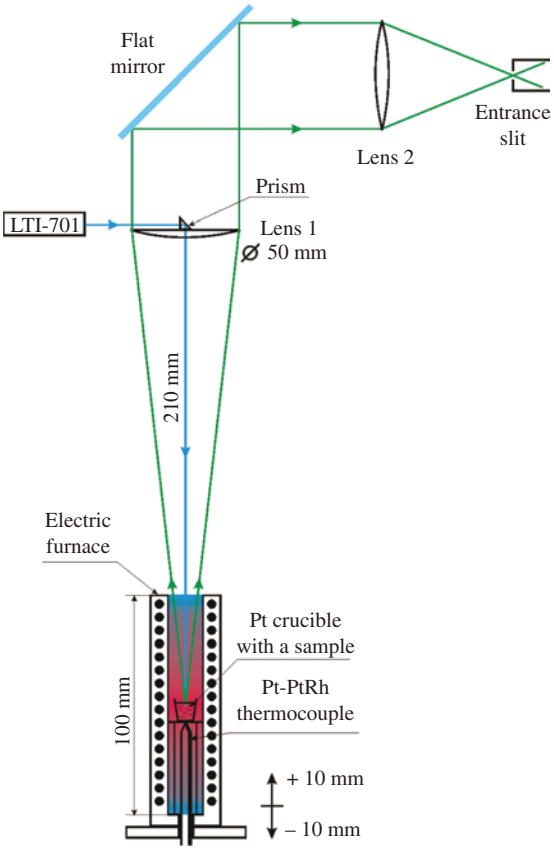

Fig. 6: Schematic illustration of the optic arrangement for high-temperature Raman scattering measurements.

where I_{Raman} is the intensity of the Raman band, $\Delta\nu$ is the Raman shift, T is the temperature, δ_{therm} is the mean square fluctuation of thermal radiation intensity, defined by expression (2), and F is the ratio of the Raman signal to fluctuation of the thermal radiation. Both the intensities, I_{Raman} and I_{therm} are measured at the same wavenumber.

Figure 7a shows $F(T)$ function measured using continuous and gated registration systems. One can see that $F(T)$ function measured with gated registration system lies higher than that measured using continuous registration system and never achieves the limit of 10 in a temperature range under consideration. At the same time, the upper limit for registration in a continuous mode is ~1300 K.

Figure 7b demonstrates two Raman spectra of the sample with composition of $33Na_2O$-$67SiO_2$ measured using continuous and gated registration systems. Both the spectra were registered at 1300 K. The upper spectrum (ii) was obtained using continuous registration system. One can see that quality of this spectrum is too weak to draw any clear conclusions on the melt structure and its modification depending on temperature even though it was measured at the temperature that satisfies the expression (3). At the same time, the

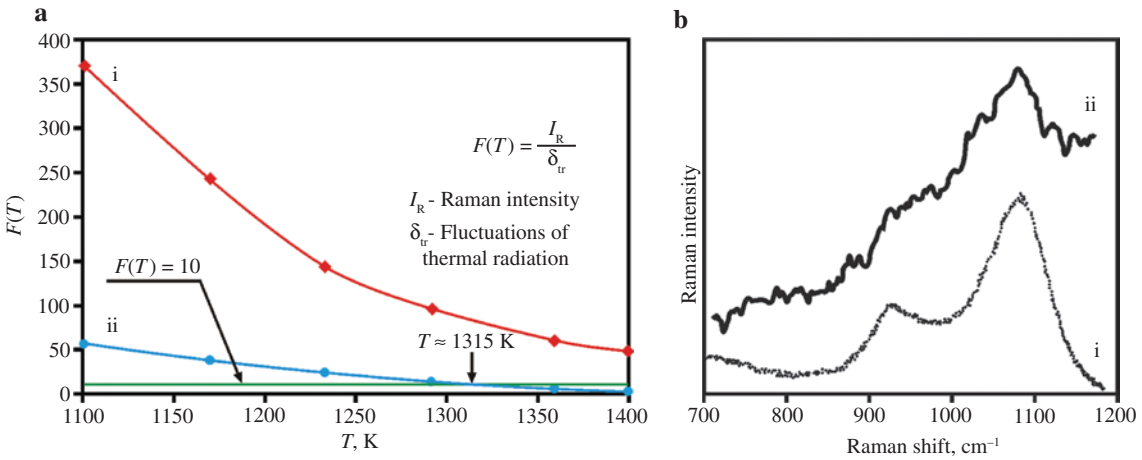

Fig. 7: (a) I_{Raman}/δ_{therm} ratio as a function of temperature, (b) high-temperature Raman spectra of 33 % Na_2O-$67SiO_2$ melts (T=1300 K). (i) Measured using the gated registration system, (ii) measured in continuous registration mode.

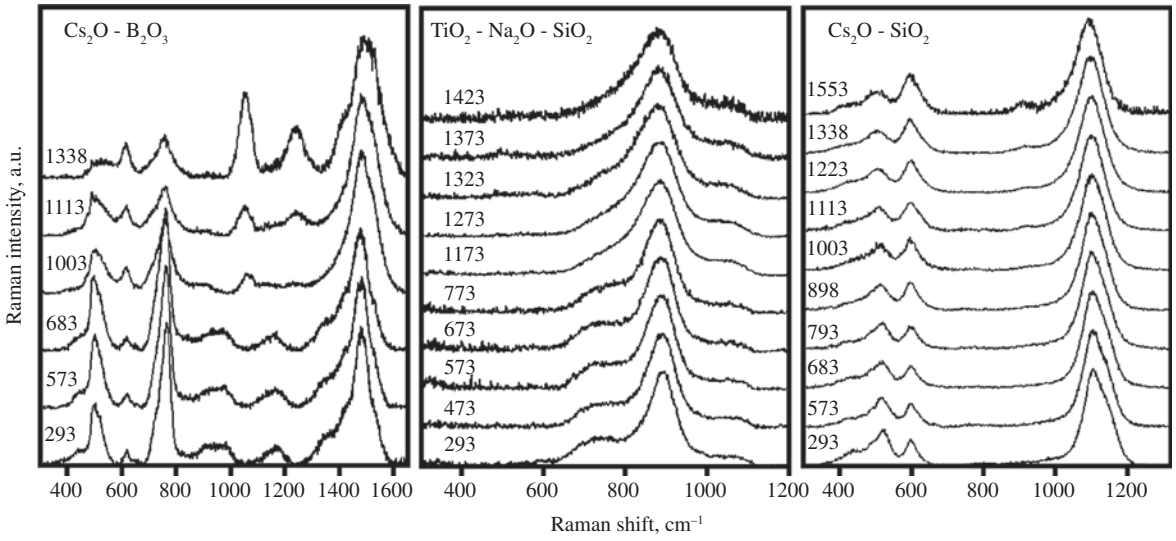

Fig. 8: Raman spectra of various substances measured using the gated registration system at different temperatures.

spectrum (i) registered using the gated registration system demonstrates much better quality and can be used for study of melt structure without a doubt.

Several Raman spectra of samples with various compositions measured at different temperatures are shown in Fig. 8 as an example. As seen from the figure, the use of gated registration system in combination with pulsed laser allowed registration of the spectra with sufficiently good quality in a broad temperature range (up to 1553 K). It is important to note that temperature of 1553 K is not an upper limit for the Raman tools equipped with gated registration system. As shown in [8], application of lasers with higher pulse power and shorter pulse duration and, as a result, the registration systems with a shorter counting time window, make it possible to measure the Raman spectra at much higher temperatures (at least up to 1750 °C). And even so the upper-temperature limit was not related to the design of the Raman setup but was limited by the design of the electric furnace.

Conclusions

Thus, both the spatial and time-resolved filtering are effective methods of suppression of parasitic thermal radiation during high-temperature measurements. The spatial filtering of the parasitic light is solved by improvement of optical systems whereas time-resolved filtering requires certain modification of electric scheme for gated registration system. One can expect that further prospects of development of high-temperature Raman spectroscopy is bringing together both methods in one setup.

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