LABORATORY TECHNIQUE

A Nitrogen Cryostat with Adjustable Temperature and Cold Loading of Samples for the Measurement of Optical Spectra

K. P. Meletov*

*Institute of Solid State Physics, Russian Academy of Sciences,
Chernogolovka, Moscow oblast, 142432 Russia*
e-mail: mele@issp.ac.ru

A cold-loaded cryostat was designed to measure the optical spectra of thermally unstable samples. The temperature stabilization system with a resistive heater provides temperature control in the range of 80−270 K with an accuracy of ±0.3 K. The cryostat was used to measure the Raman spectra of molecular hydrides of silica glass at different temperatures.

Cold loading involves the rapid transfer of samples from the nitrogen reservoir to the working area of the cryostat and is necessary to prevent thermal destruction of thermally unstable samples, for example, metal and molecular hydrides obtained by quenching in liquid nitrogen after they are saturated with hydrogen at high pressure [1, 2]. The presence of molecular hydrogen in hydride samples after synthesis is checked using Raman spectroscopy at the temperature of liquid nitrogen, while the amount of hydrogen absorbed is measured by thermal desorption.

Study of the kinetics of molecular hydrogen desorption at temperatures above the liquid nitrogen temperature is possible using Raman spectroscopy; however, this requires a nitrogen cryostat with cold loading of samples and a controlled temperature. This work presents the simplest cryostat of this type, which was manufactured in laboratory conditions specifically for measuring the Raman spectra of SiO_2-H_2 molecular hydrides of silica glass in the backscatter geometry.

The important parameters of such a cryostat are the operating temperature range, the accuracy of its stabilization, and the flow rate of liquid nitrogen. We offer a simple design of a nitrogen filling cryostat with purging of samples on a cold table with nitrogen vapor. The cryostat is equipped with a temperature stabilization system using a resistive heater controlled by the simplest commercially available TERMODAT-08M3 temperature controller, with a SB10M3 power unit [3]. The cryostat stabilizes the temperature in the range of 80−270 K with an accuracy of ±0.3 K, does not have an optical window, and provides rapid cold loading of samples.

The cryostat device is shown in Fig. 1. It consists of an external cylindrical container 1 for liquid nitrogen made from extruded polystyrene foam. A heat exchanger is located inside the container 2 made from 12X18H10T stainless steel, whose upper part is directly under the work table 3 and resistive heater 4. There is a cylindrical recess on the work table in which the test sample and the temperature sensor are placed. The heat exchanger is covered with an inverted fluoroplastic cap 5 so that the bottom of the hood is located above the upper surface of the heat exchanger. At the bottom of the cap, directly above the sample, is a round hole for the release of nitrogen vapor, and on the side surface, in its lower part, holes are made through which liquid nitrogen 6 fills the space around the heat exchanger. Liquid nitrogen is poured through a funnel between the outer casing of the cryostat and the cap.
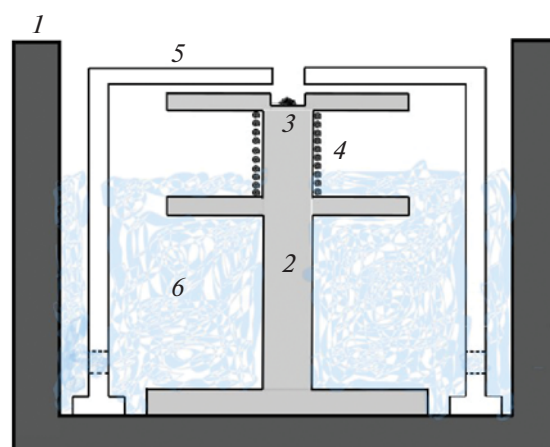
Fig. 1. The cryostat device. *1*, container; *2*, heat exchanger *3*, work table; *4*, resistive heater; *5*, teflon cap; *6*, liquid nitrogen.

After pouring nitrogen and cooling the heat exchanger, cold loading of samples from liquid nitrogen into the recess on the work table of the cryostat is performed. The distance between the sample and the top surface of the cap is approximately 4 mm, which is less than the working distance of the special Olympus lenses with an increase of $50^\times$ (9 mm) and $10^\times$ (18 mm), which are used, in particular, for measuring the Raman spectra in backscattering geometry when working with high pressure chambers with diamond anvils [4]. One important function of the hood is to create a steady stream of cold nitrogen vapors above the surface of the sample site, which prevents the formation of frost and provides good conditions for optical measurements. The sample is cooled both due to heat removal from the working table through the heat exchanger body to liquid nitrogen and due to outgoing cold nitrogen vapors. Stabilization of the surface temperature of the table is provided by a resistive heater, which allows one to change the efficiency of the thermal bridge between liquid nitrogen and the table, as well as to increase the temperature of the passing nitrogen vapor.

The heat exchanger material was selected experimentally. An attempt to use copper was unsuccessful due to its high thermal conductivity of ~400 W/(m K), which led to the need for significant heat generation on the resistive heater to maintain temperatures above 140 K and to a large flow of liquid nitrogen. The use of stainless steel with a lower thermal conductivity of ~20 W/(m K) turned out to be optimal: in this case, the heat exchanger cooled more slowly; however, it became possible to stabilize the temperature up to 270 K at a moderate nitrogen flow rate (~100 ml of nitrogen was added every 30 min).

A resistive heater on a heat exchanger was used to stabilize the temperature, which is controlled by the TERMODAT-08M3 on-off controller with the SB10M3 power unit. The temperature was measured with a Pt100 miniature platinum thermometer with a nominal resistance of 100 Ohms and a temperature range of 77−430 K, which is the standard temperature sensor for the TERMODAT-08M3 controller.

The compact design of the cryostat provides its compatibility with the Olympus BX51 microscope, which is usually used in spectral installations for measuring the Raman spectra in the back reflection geometry.

The Raman spectra of $SiO_2-0.6H_2$ molecular hydride of silica glass were measured in the 80−190 K temperature range using a cryostat; the results are shown in Fig. 2. Spectra measured in the backscattering geometry on an Acton SpectraPro-2500i spectrograph cooled to −70° with a Pixis2K CCD detector and an Olympus BX51 microscope. A cw solid state laser with a power of 100 mW and a wavelength of $\lambda = 532$ nm with diode pumping and an edge filter for this wavelength with a band of 100 cm^{-1} were used for excitation. The laser beam was focused on the sample using an Olympus $10^\times$ lens into a spot with a diameter of ~2.6 μm.

The bottom of Fig. 2b shows the spectrum of the original SiO_2 silica glass measured at the temperature of liquid nitrogen, while the Raman spectrum of the $SiO_2-0.6H_2$ molecular hydride of silica glass at the same temperature is shown above. Under the spectra, thin solid lines show their decomposition into separate bands as performed by the DATALAB program for approximating the contour of the phonon bands of the Voigt curve. The position of the phonon modes is marked by vertical dashed lines and the bands themselves are identified as $^H R_1$ and $^H R_2$, the rotational modes of the hydrogen molecule H_2; $^H G_1$ and $^H G_2$, the phonon modes of $SiO_2-0.6H_2$ glass; and G_2, the phonon mode of the initial SiO_2 silica glass.

The range of SiO_2 silica glass (see Fig. 2b, below) has been well known for many years, while the spectrum of $SiO_2-0.6H_2$ (see Fig. 2b, above) was measured in this work after the first successful synthesis of molecular quartz silica glass [2]. It should be noted that the introduction of molecular hydrogen leads to the occurrence of the H_2 molecule in the spectrum of rotational modes and to some redistribution of the intensity in the phonon spectrum of the glass itself. Moreover, according to the data of [2], no fundamental changes in the structure of quartz glass occur.

The temperature dependence of the frequencies of phonon modes in the 80−190 K range is shown in Fig. 2a. The measurements are limited to a temperature of 190 K, since with more heating the $SiO_2-0.6H_2$ sample decomposed rather quickly due to intense desorption of molecular hydrogen. The temperature dependences of different phonon modes differ: the frequencies of the vibrational phonon modes of a quartz matrix $^H G_1$ and $^H G_2$ of $SiO_2-0.6H_2$ (light dots) decrease with increasing temperature, the frequency of rotational phonon modes ($^H R_2$, $^H R_1$) of H_2 molecules (light squares) increases, and the phonon frequency of the initial quartz glass G_2 (stars) practically does not change. The frequencies of the phonon modes decrease with increasing temperature in the vast majority of solids due to the positive coefficient of thermal expansion; however, in SiO_2 quartz glass it is close to zero in this temperature range [5] and its phonon frequencies practically do not change. The frequency of the rotation modes is inversely proportional to their moment of inertia, which increases in hydrides due to the van der Waals interaction with the SiO_2 matrix [6, 7]; however, with increasing temperature, this interaction weakens, the moment of inertia decreases, and the mode frequency increases.
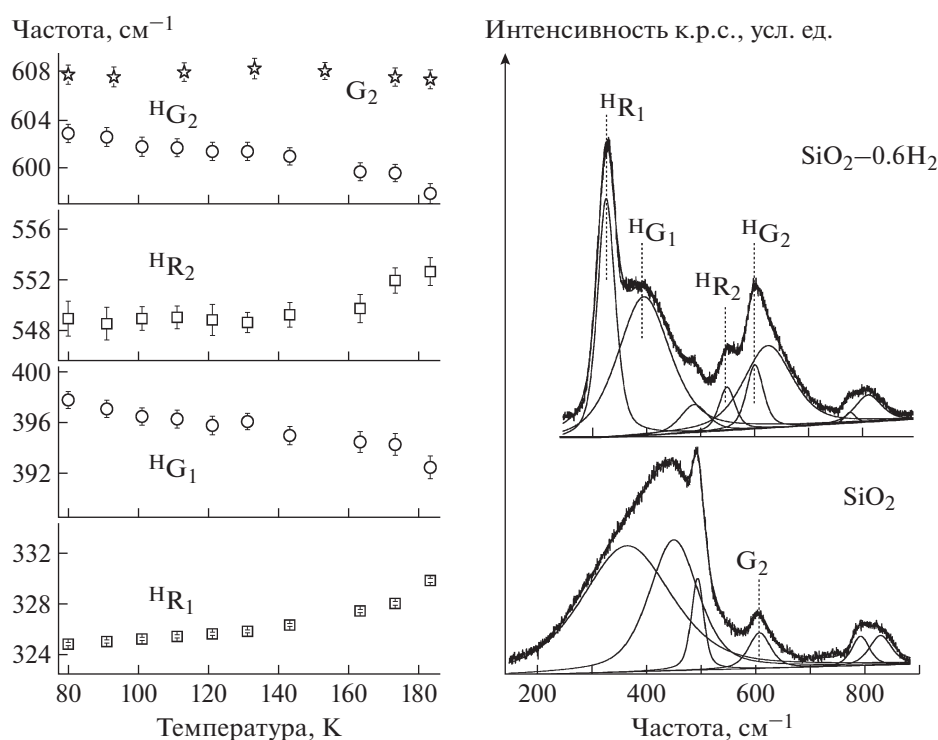
Fig. 2. (a) the temperature dependence of the frequency of phonon modes of SiO hydride$_2$−0.6H$_2$: ^{H}R$_1$ and ^{H}R$_2$, rotational phonon modes of the hydrogen molecule H$_2$; ^{H}G$_1$ and ^{H}G$_2$, vibrational phonon modes of the SiO matrix$_2$; G$_2$, the vibrational phonon mode of pure SiO$_2$; (b) the spectra of SiO2−0.6H2 (above) and pure SiO$_2$ (bottom).

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