

FTIR spectroscopy of glass-filled rubies

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Introduction

Glass filling is one type of the ruby treatment that represent the low or high temperature heat treatment process with a number of additives or fluxes. After solidification, these additives or fluxes form glassy substance in fissures and cavities and also on the surface of the treated stone.

It is important to recognize the presence of the treatment in the stone and also to determine the extent of the glass filling. The gemological identification of glass-filled rubies is mostly based on microscope observation and the internal features of glass-filled rubies are already described in details (Pardieu, 2006). The determination of the extent of glass-filling is shown in the LMHC Information Sheet #3.

In our study we focus on the FTIR spectroscopy of the glass-filled rubies and the additional information that such spectra can provide. The FTIR spectroscopy is known as the non-local method that can give the information about the whole sample. The FTIR spectra of lead-glass filled rubies with 2600 and 3500 cm^{-1} absorption bands were observed by Panjikar and GIT (2007). Then Pardieu et al. (2010) also reported the same bands. But the origin of those bands was not specially studied.

Samples and Methods

In our research, we studied 11 polished gem-quality lead-glass filled rubies, 10 flux treated rubies and also 18 glass samples with different compositions.

FTIR spectra were recorded using FSM-1201 FTIR spectrometer in spectral range 400-4000 cm^{-1} , spectral resolution 4 cm^{-1} , averaging 100 scans.

Also the stones were studied by microscope and microprobe/EDXRF to confirm the presence of the lead glass in fissures. Some lead glass-filled rubies were annealed at 1700 $^{\circ}\text{C}$ to check the stability at high temperatures of the lines observed in FTIR spectra.

Results

FTIR spectra for all lead glass-filled rubies show three broad absorption bands at 2250, 2600 and 3500 cm^{-1} . The spectra of different glasses (see Figure 1) consist of the broad bands at 3500-3600 cm^{-1} and additional peaks at 2900-3000 cm^{-1} for lead glass and soda-lime glass. Also peaks 2250 and 2650 cm^{-1} observes in fused quartz.

According to the Scholze (1991) broad band at 3500 cm^{-1} can be attributed to the absorption of the H_2O molecules. Peaks at 2250 and 2600 cm^{-1} are related to Si-OH vibrations as noticed by Efimov et. al (2003) for glasses.

The bands in FTIR spectrum of lead-glass filled ruby is mainly related to water and Si-OH vibrations. No lead-related vibrations were noticed. So the similar lines could be observed in lead glass- and lead-free glass-filled rubies. However, the glasses in rubies annealed to high temperature do not show OH-related absorption.

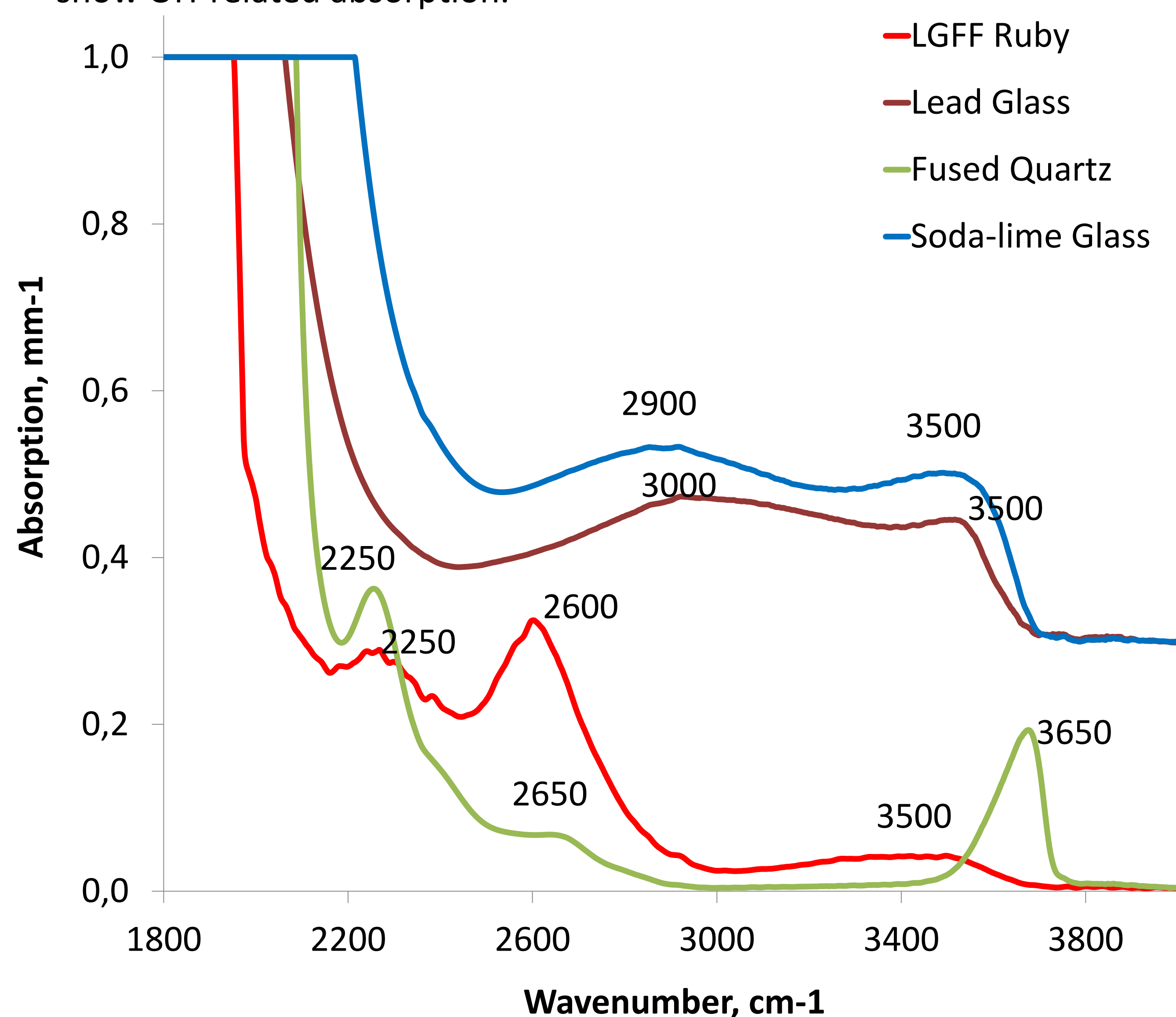


Figure 1. The FTIR spectra of lead glass-filled ruby (marked red) and different types of pure glasses (fused quartz glass, lead glass, soda-lime glass).

Figure 2 shows the FTIR spectra of lead glass-filled rubies with different filling extent. The absorptions at 2250, 2600 and 3500 cm^{-1} are related to glass and we see that the absorption varies from one sample to another because of the different glass contents in ruby. So absorptions on 2250, 2600 and 3500 cm^{-1} can be used as a criterion to determine the filling extent on the base of infrared spectroscopy.

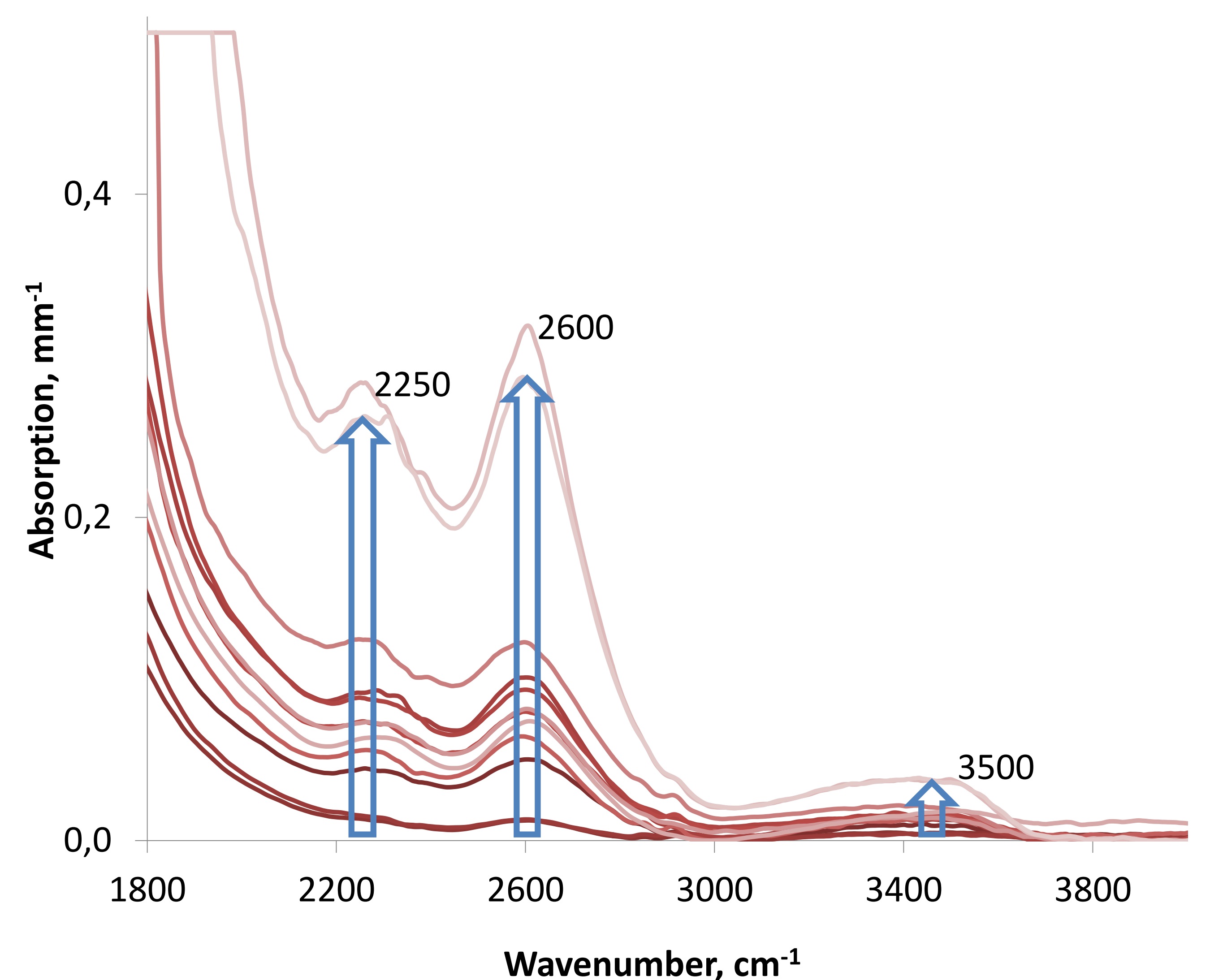


Figure 2. The FTIR spectra of Lead-glass filled rubies with different filling degree.

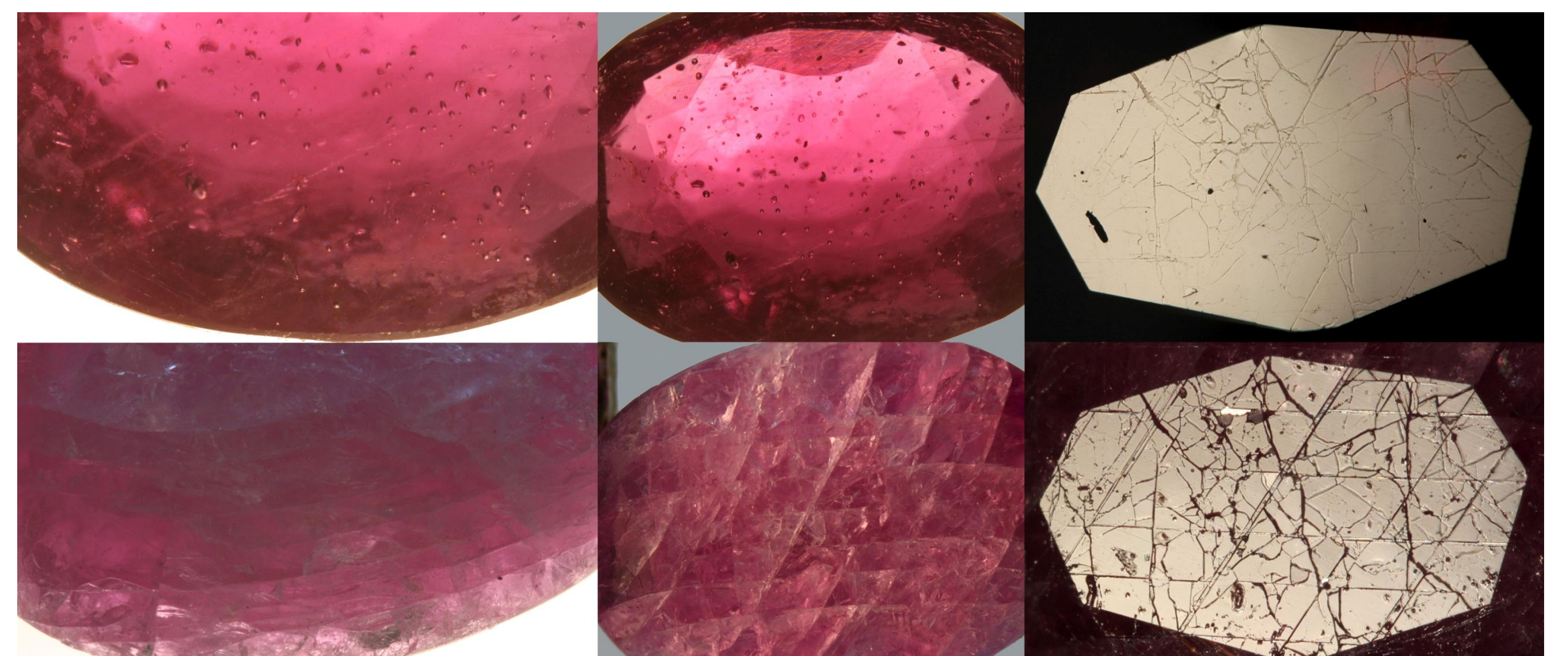


Figure 3. Lead-glass filled ruby (top) after the high temperature heat treatment (bottom).

Discussion

FTIR spectroscopy for rubies can be used to determine several features. The specific absorptions of H_2O and Si-OH vibrations in FTIR spectrum of the ruby are related to the presence of glass (lead or lead-free) and low temperature annealing (below 750 $^{\circ}\text{C}$). These absorption bands vanish in the process of high-temperature annealing (>1100 $^{\circ}\text{C}$) and does not occur in the spectra of annealed rubies (for example rubies annealed with borax and other fluxes) (see Figure 3).

So the bands in FTIR spectra could become a good indication of glass filling and low temperature annealing.

Absorption bands at 2250, 2600 and 3500 cm^{-1} have the direct correlation with the quantity of the glass filler in ruby. Thus it can be used as a criterion of the filling extent. We can present the scale that allows to determine the filling degree by FTIR spectrum.

The determination of the filling degree using FTIR spectroscopy turns out to be much more precise and rapid than the present methods based on the observation of the filled fissures in microscope in reflected and transmitted light or methods based on the radiographs suggested by Hainschwang (2009).

References

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