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Development of Mid-Infrared Absorption Spectroscopy for Gemstone Analysis

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Abstract: Absorption spectroscopy has been widely used in gemstone societies as it enables the identification of the origin and post-treatment of gemstones in a non-destructive way. The infrared (IR) range is critical for studies of gemstones such as corundum, emerald, and diamond. Regarding the corundum sample, absorption peaks related to the -OH bond could be used as an index for heat-treatment detection, and different types of inclusions could be identified by analyzing the IR absorption spectrum. The most widely used method for measuring IR absorptions is Fourier-transform infrared spectroscopy (FTIR), which was designed based on the working of the Michelson interferometer. However, FTIR has a few limitations, such as a long measurement time and difficulty in sample placement, which limits its full automation capability. In this study, a mid-infrared (MIR) spectrometer relying on the upconversion phenomenon of non-linear crystals was used to measure the absorption spectra. Corundum with heat treatment features and/or with different common types of inclusions were measured by both transmission and reflection modes. After comparison with the FTIR spectra captured on the same sample set, the same target peaks could be captured with a shorter measurement time and easier operation. The developed MIR spectrometer could directly measure the absorption spectrum in the 2–4.5 µm (2200–5000 cm^{-1}) range within a few seconds. Meanwhile, as both transmission and reflection modes were available, both loose and mounted gemstones could be measured, supporting the widespread use of this device in large-scale production and its ability to achieve full automation.

Keywords: colored stone; diamond; absorption spectroscopy; mid-infrared spectroscopy

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1. Introduction

Research relying on mid-infrared (MIR) range absorption spectroscopy has been widely conducted in gemstone societies for analyzing corundum, emerald, and diamond samples. For corundum samples, heat treatment has been broadly used as a post-processing technology to improve their appearance. When the effect of heat treatment was first discovered, traditional methods such as using blowpipes were applied. After years of development, modern treatments have relied more on combustion and/or electrical resistance furnaces that have a controllable interior treatment environment. Heat treatments are normally carried out under different treatment environments depending on the conditions and type of the gemstone sample. In particular, the heating temperature, time duration (may vary from hours to days), steps in changing the temperature, and heating atmosphere (reduction or oxidization) can be critical in determining the ultimate heat treatment condition [1–4]. The color change produced in the sample tends to last after heat treatment due to a change in its internal chemical composition. As the color change under heat treatment is more stable than that induced by UV irradiation, which is usually related to a reversible photochromic mechanism, the heat treatment method is more widely used in the corundum market. However, after heat treatment, the material of the gemstone is modified; thus, its value tends to be lower than that of natural stones. Technologies to identify such post-processing induced modifications need to be developed in the gemstone industry.

During the formation process of corundum, most naturally-colored stones contain a certain amount of water, which can be represented in the form of OH [5]. Moreover, the FTIR spectra of untreated corundum samples have shown a series of OH absorption peaks in the MIR range of ~3000–3600 cm^{-1} [6–8]. The water content in these samples, which reduces after heat treatment, can be used as an index to detect whether the gemstone has been thermally treated.

Regarding emeralds, most of them, regardless of their origin, contain fissures that may affect their appearance in cut stones. To overcome this issue, an artificial clarity enhancement process is carried out. This process dates back over 3000 years ago. Over the past few years, clarity enhancement in emeralds has made significant progress. Common clarity-enhancing substances include oils, essential oils, resins, polymers, and pre-polymers. Among these, the resin Opticon is typically used to improve the emeralds' appearance [9] because of its longer-lasting effect compared with that of natural oil, as well as its ability to seal breaks from the surface [10]. The above-mentioned filling materials can be detected by FTIR spectroscopy through the screening of the organic peaks at approximately 3000 cm^{-1} [11]. Regarding diamonds, the boron center can be used as an indicator for type IIb diamond screening. The presence of boron in diamonds can be determined by absorption bands in the MIR range of 1290, 2460, 2802, and 2936 cm^{-1} [12]. Based on the above reasons, and because the most fundamental rotational and vibrational states of molecules are within the MIR range, spectroscopic behavior in this region is critical for gemstone identification in relation to treatment screening and mineral identification [13].

The most common technique used to measure absorption in the MIR region is Fourier-transform infrared spectroscopy (FTIR) [14–16]. A Michelson interferometer is used to split and recombine the beam from a light source, while wide bandwidths can be covered normally from 2.5 to 25 μm. The absorption peaks in the FTIR spectrum can be used to represent the types of chemical bonds within the material and/or the vibration mode of the bonding [17]. In the gemstone industry, FTIR spectra are already widely used for research on colored stones to identify possible treatments and inclusions. However, a few limitations in FTIR spectroscopy are present. Sample alignment is a major challenge, especially for gemstone measurement, as the faceted gemstones deviate the beam path due to multiple refractions, which results in a complicated and unreliable absorbance calibration process. Data acquisition becomes time-consuming because scanning across the MIR region typically takes several minutes. The corresponding complicated sample alignment and time requirements severely restrict its use in daily production. FTIR is normally used for loose stone measurement based on the transmission mode, certain portions of gemstones that need to be analyzed for identification purposes are already mounted; these portions can only be measured by the reflection mode. Therefore, developing an easy-to-use MIR spectrometer with both transmission and reflection modes is critical for sample analysis and screening.

Recently, a new type of MIR spectrometer was developed based on upconversion technology; this spectrometer transfers the incoming spectra in the MIR wavelengths to the near-visible wavelength range [18,19]. The mechanism of the upconversion technique is based on the sum-frequency generation (SFG) by the second-order nonlinearity of selected crystalline materials. After an MIR light enters a non-linear crystal, the electric field interacts with the field inside the crystal. The newly generated wave will have a frequency equal to the sum of the frequencies of the incoming MIR spectra and the crystal field. Based on energy conservation, the spectrum profile of the incoming MIR spectra will be maintained and converted to a correlated peak in the near-visible range that can be detected by a regular CCD/CMOS detector with high signal-to-noise (SNR) ratio and fast response speed. Using this technology, room-temperature-based fast absorption measurements in the MIR wavelength range are possible.

In this study, we developed a rapid absorption spectroscopy-based screening device that operated in the MIR range (2–4.5 μm) in both the transmission and reflection modes. The primary purpose of this device is to screen and identify gemstones in room-temperature environments rapidly. A novel type of MIR spectrometer based on upconversion technology was used in preparing this design. A rapid screening prototype unit was developed by integrating the MIR spectrometer with a globar light source covering the target MIR wavelength range. The setup enabled the passage of light through the sample to enhance the flexibility of the sample alignment, allowing the faceted gemstones to be easily measured. Comparing the FTIR measurement results captured on the same sample set revealed that the prototype MIR absorption spectrometer reduced the data acquisition time for the measurements from a few minutes to seconds while maintaining its ability to identify critical features.

2. Experimental Setup

The systematic layout of the MIR absorption spectrometer based on the transmission mode is shown in Figure 1a. A stabilized Globar MIR light source with a blackbody radiation spectrum from 500 nm to 9000 nm (SLS203L, Thorlabs, Newton, NJ, USA) was used to illuminate the sample. MIR light was delivered to the sample, which was placed on a pre-aligned stage. After passing through the sample, the transmitted light was collected using a MgF_2 plano-convex lens (LA6002, Thorlabs, Newton, NJ, USA) with a focal length of 50 mm. The collected signal was focused on a signal collection optical fiber and then delivered to an MIR spectrometer (S2050, NLIR, Farum, Denmark). Based on our test results, adding a focusing lens would improve the efficiency of excitation and light collection, which would further lower the required power of the light source and shorten the spectroscopy integration time. The fiber chosen for both light source delivery and transmitted signal collection was a ZrF_4 fiber with a core diameter of 450 μm (MZ41L1, Thorlabs, Newton, NJ, USA), which covered the operation wavelength range from 285 nm to 4.5 μm.

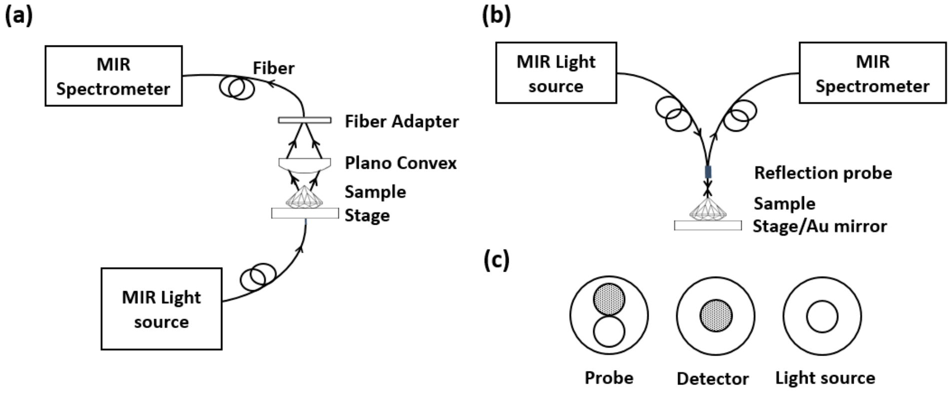

Figure 1. Systematic layout of MIR absorption spectrometer based on (**a**) transmission and (**b**) reflection mode, and (**c**) bifurcated fiber bundle as used in reflection mode measurement.

The systematic layout of the MIR absorption spectrometer based on the reflection mode is shown in Figure 1b. The same Globar light source was used to illuminate the sample by coupling it into a bifurcated fiber bundle (BFYZ4S05, Thorlabs, Newton, NJ, USA) composed of a light source fiber and signal detector fiber, both with 450 μm ZrF_4 core materials. The light source fiber delivered illuminated light to the sample, and the detector fiber collected the reflected signal and delivered it to the MIR spectrometer. A fiber collimator (F028SMA-3450, Thorlabs, Newton, NJ, USA) was connected to the end of the bifurcated fiber bundle with a focal length of 5.94 mm, and the beam diameter was aligned in the range of 1–2 mm by adjusting the distance between the sample and collimator. An Au mirror (PF10-03-M01, Thorlabs, Newton, NJ, USA) was mounted under the sample to reflect incoming light, enabling double absorption through the gemstone sample and improving the signal-to-noise ratio of the absorption measurement as shown in Figure 2. An aperture was placed on top of this mirror to maintain the optimal central position of the stone. For both the reflection and transmission modes, the fibers were connected through the SMA connector for the light sources and the MIR spectrometer. Finally, the recorded spectra were analyzed using a customized algorithm, and a screening/identification result was generated.

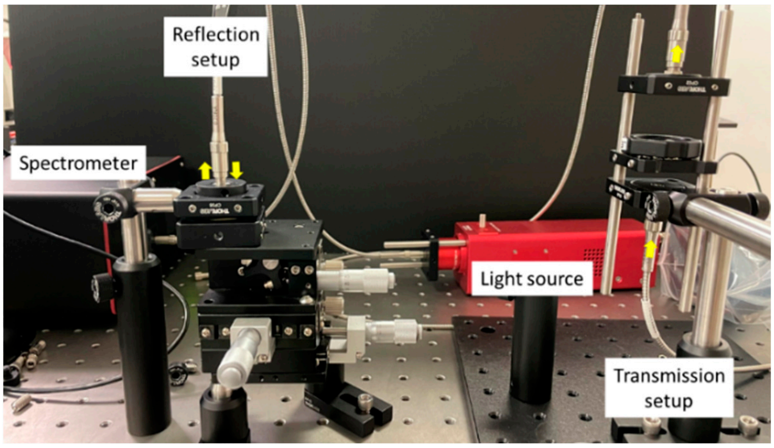

Figure 2. Prototype of MIR absorption spectrometer based on transmission and reflection model.

To generate consistent and stable results, the output power of the MIR light source and the integration time of the spectrometer were defined. The output power of the MIR light source was set to 6 mW, and the spectrometer collected the transmitted spectra using a setting of 250 ms integration with 20 times averaging, and 25 ms integration with 20 times averaging for reflection mode measurement. The corresponding background spectra were then subtracted from each measurement. To validate the performance of this prototype spectrometer in the gemstone screening process, the following mineral species were selected since they contain absorption features in the targeting wavelength range (2–4.5 µm): sapphires with heat-treatment features (Table 1), emerald samples with and without clarity enhancement (Table 2), and type Ia/IIb diamonds (Table 3). The test results acquired from those samples were used to represent the performance of the designed MIR absorption spectrometer; in the meantime, the application of the spectrometer can also be applied to other mineral species as well.

Table 1. Corundum Samples for Absorption Spectroscopy Analysis in the Mid-Infrared Range.

Sample	Variety	-OH Peak	Inclusion	Country of Origin	Weight (ct)	Color
A	Sapphire	N/A	Kaolinite	Sri Lanka	1.580	Yellow
B	Sapphire	N/A	Gibbsite	Burma (Myanmar)	1.593	Blue
C	Sapphire	3109 cm^{-1} series	N/A	Madagascar	0.811	Yellow
D	Sapphire	3109 cm^{-1} series	N/A	Sri Lanka	1.242	Yellow
E	Sapphire	3109 cm^{-1} series	N/A	Sri Lanka	0.936	Yellow
F	Sapphire	3309 cm^{-1} series	N/A	Australia	3.271	Blue

Table 2. Emerald Samples for Absorption Spectroscopy Analysis in the Mid-Infrared Range.

Sample	Variety	Clarity Enhancement	Weight (ct)
A	Emerald	N/A	0.85
B	Emerald	Opticon-hardened	0.79

Table 3. Diamond Samples for Absorption Spectroscopy Analysis in the Mid-Infrared Range.

Sample	Variety	Type	Weight (ct)
A	Diamond	Ia	0.13
B	Diamond	IIb (boron center)	0.38

The tested samples were from research sets collected from the Gemological Institute of America (GIA). These sets were all previously conclusively identified using various gemological and advanced techniques, including visual observation, ultraviolet–visible (UV–Vis) spectroscopy (Lambda 950, Perkin Elmer, Waltham, MA, USA), FTIR (Nicolet iS50, Thermo Fisher Scientific, Fair Lawn, NJ, USA), and Raman spectroscopy (inVia, Renishaw, West Babylon, NY, USA). In this study, FTIR data were collected with the resolution was set at 4 cm^{-1} with 1.928 cm^{-1} data spacing and each sample was scanned 64 times. The performance of the newly designed MIR absorption spectrometer was verified by comparing its results with the FTIR measurement results.

3. Results

3.1. Corundum Sample Screening

Measurements were first carried out on six corundum samples, including samples from Sri Lanka, Madagascar, Australia, and Myanmar (Table 1). Those samples were tested for inclusion identification and post-heat treatment screening. Corundum samples with two types of inclusions were tested first: (1) kaolinite inclusions ($Al_2Si_2O_5(OH)_4$), for which a yellow sapphire mined from Sri Lanka with the kaolinite inclusion (sample A, Table 1) was used here as an example, and (2) gibbsite inclusions ($Al(OH)_3$), for which a blue sapphire mined from Myanmar (sample B) was chosen to represent this type. As shown in Figure 3, a series of sharp peaks at approximately 3697, 3669, 3652, and 3620 cm^{-1} are visible in sample A. These are the signature peaks for kaolinite [20,21]. For sample B, two dominant peaks at 3622 and 3528 cm^{-1}, with three subordinate peaks at 3566, 3399, and 3379 cm^{-1}, were used as indices for gibbsite inclusion [22,23].

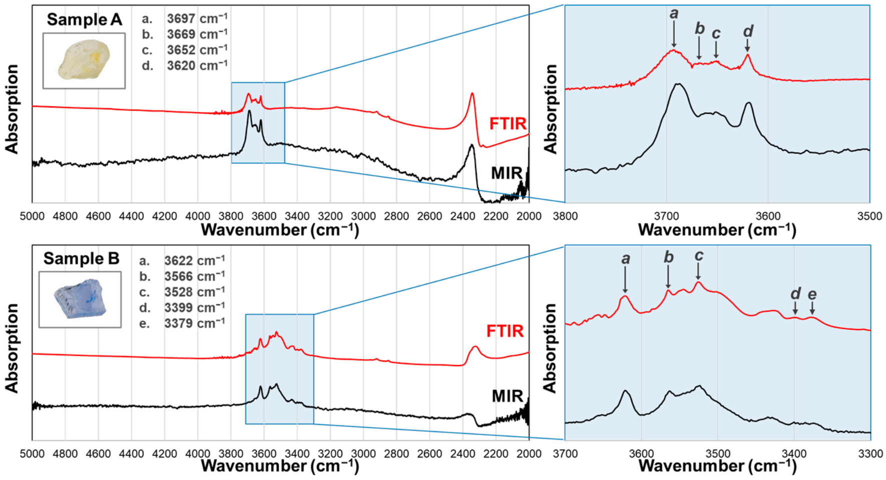

Figure 3. MIR absorption spectra for corundum sample A (**top**) containing the kaolinite inclusion, and sample B (**bottom**) containing the gibbsite inclusion.

To prove the effectiveness of this setup for corundum heat-treatment screening, four yellow sapphire samples mined from Madagascar (C), Sri Lanka (D, E), and Australia (F) were also tested. Samples C–E show a dominant peak at approximately 3161 cm^{-1} and two subordinate peaks at approximately 3242 and 3356 cm^{-1}, whereas sample F shows a dominant peak at 3309 cm^{-1} with two subordinate peaks at 3232 and 3184 cm^{-1}. These features were revealed by FTIR analysis and were found to be related to the structural OH groups in the corundum sample. More specifically, the 3161 cm^{-1} peak series involved charge compensation with Si^{4+} and/or bound with Mg^{2+} [8,13], and the 3309 cm^{-1} series was related to structural Ti-OH stretching [24–26]. As this OH bond was unstable at elevated temperatures, the presence and/or the trend of changing intensity of the dominant 3161 and 3309 cm^{-1} peaks in the mid-IR region of the sapphire could be used as indicators for any possible heat treatment.

The spectra collected using the MIR absorption spectrometer for samples C, D, and E with the 3161 cm^{-1} peak series (dominant peak at 3161 cm^{-1} and two weak subordinate peaks at 3242 and 3356 cm^{-1}) featured under both the transmission and reflection modes are shown in Figure 4. The horizontal and vertical axes indicate the wavenumber and absorption calculated based on the transmission spectra, respectively. The FTIR spectra (red) were used as a reference to verify the MIR measurement results. The noise around 3700 cm^{-1}, as shown in the FTIR analysis, was the environmental noise caused by the moisture and carbon dioxide content in the air. The 3161 cm^{-1} peak could be correctly identified for all three samples using the transmission results of the MIR absorption spectrometer. A comparison test between the transmission and reflection modes was carried out on Samples D and E. As shown in Figure 4b, the reflection mode tends to amplify the signal, possibly because of the double absorption inside the sample during the measurement. Sample F, with the 3309 cm^{-1} peak series (3309 cm^{-1} as the dominant peak and three subordinate peaks at 3186, 3232, and 3368 cm^{-1}), was characterized under the reflection mode (Figure 5). After comparing the FTIR spectra captured for the same sample, the dominant and side peaks could be captured with a shortened measurement time of <1 s per sample.

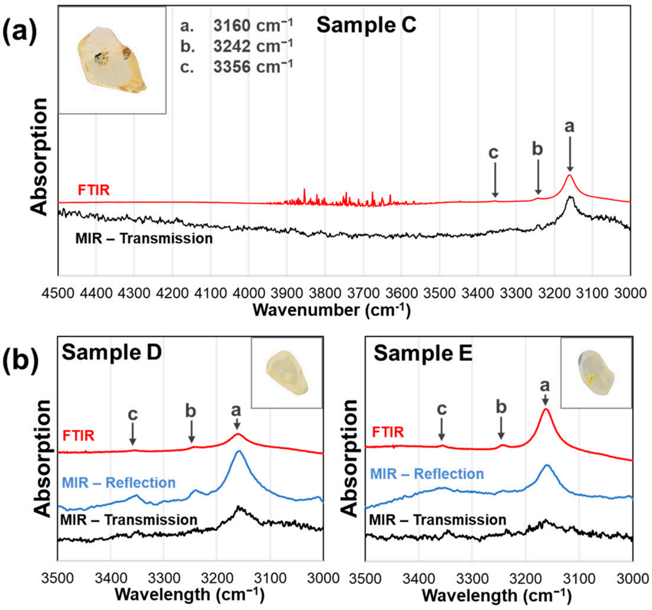

Figure 4. (**a**) Transmission-mode-based MIR absorption spectra for corundum Sample C and (**b**) transmission- and reflection-mode-based MIR absorption spectra for corundum Samples D (**left**) and E (**right**) containing the 3309 cm^{-1} series absorption peaks as indicators for heat treatment.

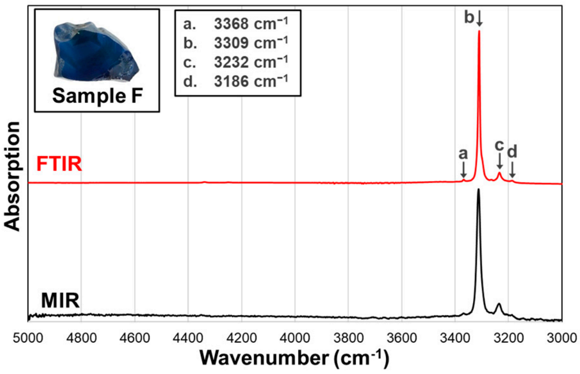

Figure 5. Reflection-mode-based MIR absorption spectra for corundum Sample F containing the 3309 cm^{-1} series absorption peaks as indicators for heat-treatment.

3.2. Emerald Clarity Enhancement Screening

Two emerald samples were measured in the reflection mode. As discussed in the previous section, the clarity of the emerald stones could be enhanced by adding oil or other types of organic resin fillers. Among all types of filler materials, Opticon has been used widely because it can be applied with or without a surface hardener for crack repairing, and it does not evaporate as readily as cedarwood oil does. FTIR has been used to detect the presence of a filler material substance in emerald, and absorption peaks in the region between 3100 and 2850 cm^{-1} can be used as characteristic features of polymers. Since the wavelength range was within the coverage of our MIR absorption spectrometer, two emerald stones with and without Opticon-hardened treatment for clarity enhancement were measured, and the obtained spectra were compared (Figure 6). The reflection-mode-based experimental prototype presented in Figure 2 was used. The stone was illuminated from the top while being placed down on the table, and the spectra were simultaneously collected from the top lens. The untreated emerald sample exhibited a relatively flat region between 2850 and 3100 cm^{-1}, while the Opticon-hardened sample showed a series of absorption peaks at 2962, 2927, and 2873 cm^{-1}. These peaks were indicative of polymer-filling materials [27]. It was concluded that the organic filler could be screened out based on the reflection mode with a measurement time of less than 1 s per sample.

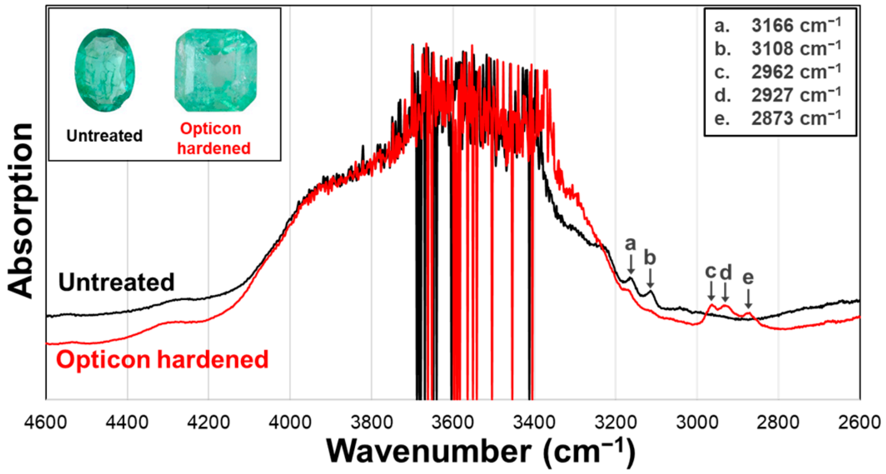

Figure 6. MIR absorption spectra for untreated (black) and Opticon-hardened (red) emerald samples based on reflection mode.

3.3. Diamond Type Identification

A similar experiment was carried out on faceted diamond samples, while stones were placed in a table side down position during the reflection measurement. Two diamond samples (type IIb and type Ia) were tested in the reflection measurement mode. Boron centers were used as the representative peak for the type IIb sample screening, with a dominant peak at 2802 cm^{-1} and side peaks at 2931 and 4091 cm^{-1}. As shown in Figure 7, all three boron peaks are present in the measured type IIb diamonds. For the type Ia diamond sample, a peak at 3107 cm^{-1} attributed to the N_3VH^0 defect [28] was also detected.

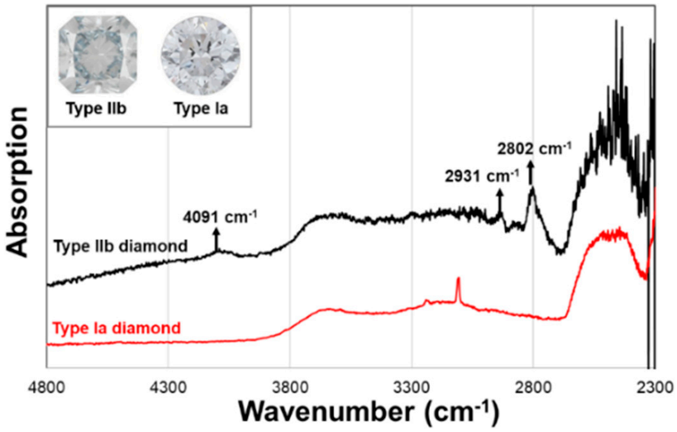

Figure 7. MIR absorption spectra for type Ia (red) and type IIb (black) diamond samples based on reflection mode.

4. Conclusions

In this study, we developed a novel absorption spectrometer in the MIR range based on a newly developed upconversion technology that enabled fast operation in a room-temperature environment with both transmission and reflection modes based on the upconversion technology. The MIR absorption spectrometer covered the range of 2–4.5 µm (2200–5000 cm^{-1}), and the measurement time was limited to seconds. Both transmission- and reflection mode-based measurements were carried out on the corundum sample set first; samples with an absorption peak series with dominant peaks at 3161 and 3309 cm^{-1}, typically used as indicators for possible heat treatment, as well as for two common inclusions (gibbsite and kaolinite), were observed. The spectra collected in the reflection mode tended to have a better SNR and shorter measurement time than those in the transmission mode. The separation of the emerald samples with and without clarity enhancement and the identification of the type IIb diamonds were successfully conducted.

Compared with the measurement results under the FTIR approach, which corresponded to the traditional scanning type spectrometer, the data acquisition speed was substantially improved, and all the peaks in the series were correctly identified in the results under the proposed prototype. By enabling both transmission and reflection modes, the proposed setup showed potential for a fast-screening process for both loose and mounted gemstones, supporting the development of large-scale automated gemstone screening processes. Future research will focus on evaluating the feasibility of the proposed prototype device for screening mounted gemstones. In the meantime, a test on other mineral species with MIR absorption features, such as colored stone samples and CVD diamond, is ongoing. A trial to further extend the wavelength range of the proposed spectrometer to the FIR range is currently underway.

Author Contributions: Conceptualization, H.T. and Z.W.; methodology, software validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, Z.W.; supervision, project administration, funding acquisition, H.T. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

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