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Comparative Study of Mineralogical Characteristics of Natural and Synthetic Amethyst and Smoky Quartz

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Abstract: With the development of synthetic gem technology, a large number of synthetic rock crystals, such as natural and synthetic amethyst and natural and synthetic smoky quartz, have emerged in the market. Research on how to identify natural and synthetic amethyst, and natural and synthetic smoky quartz is of great significance. This paper systematically studied the mineralogical characteristics of natural and synthetic amethyst and natural and synthetic smoky quartz through X-ray powder diffraction, energy spectrum analysis, infrared spectroscopy, Raman spectroscopy, and ultraviolet visible light absorption spectroscopy. The results showed that the basic gemstone properties of natural and synthetic amethyst, natural and synthetic smoky quartz were very similar. The synthetic amethyst and smoky quartz could be seen bending cracks, with a small amount of bread crumb-like black inclusions under the polarizing microscope. Natural amethyst and smoky quartz had Raman characteristic peaks of about 697 cm^{-1} and 1160 cm^{-1}, while synthetic amethyst and smoky quartz had no vibration peaks in these bands. Compared with the synthetic amethyst, the natural amethyst lacked the characteristic infrared absorption peak of 3500 cm^{-1}; compared with natural smoky quartz, synthetic smoky quartz lacked the 3484 cm^{-1} infrared absorption peak.

Keywords: rock crystal; synthetic amethyst; synthetic smoky quartz; mineralogical characteristics

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1. Introduction

The chemical composition of a "rock crystal" is SiO_2, which belongs to the quartz family in mineralogy. As one of the most common rock-forming minerals in the Earth's crust, quartz often can contain Fe, Al, Ti and other elements as inclusions due to geological processes and changes in growth conditions. These elements will form different types of color center defects after irradiation, resulting in common types of monocrystalline quartz, such as colorless rock crystal, amethyst, citrine, smoky quartz, etc. Rock crystal is favored by people for its crystal-clear appearance and shape, and is widely used in national defense, aviation, jewelry and other industries. Among them, amethyst and smoky quartz are widely used in jewelry and industry.

Research on natural amethyst and smoky quartz has focused on mineralogy, spectroscopy and color genesis [1–5]. The purple color of natural amethyst has been confirmed to be attributed to the formation of $[FeO_4]^{4-}$ hole color center by Fe^{3+} replacing Si^{4+} [6–8] at the deformed tetrahedron, and the introduction of alkali metal ions (Li^+, Na^+ or H^+) to maintain the charge balance [9]. Natural smoky quartz is thought to be Al^{3+} instead of Si^{4+} [10], to form $[A1O_4]^{4-}$ hole color centers [11], and alkali metal ions are also introduced [12]. With the maturity of gem synthesis technology, synthetic amethyst and synthetic smoky quartz continue to be entered into the market. The main synthesis methods are hydrothermal method and by adding mineralizer solution, including NH_4F solution and K_2CO_3 solution [13,14]. Inclusions and twins in crystals grown in NH_4F solution can be easily identified by conventional gemology, so the common synthetic amethyst and smoky quartz on the market are grown in K_2CO_3 solution [15]. Synthetic amethyst and smoky quartz have the same chemical composition and crystal structure as natural amethyst and smoky quartz, so it is difficult to identify them by only using to physical indexes.

Previous methods used for the identification of natural and synthetic amethyst, natural and synthetic smoky quartz mainly focused on a comparison of their infrared spectrum [15,16], especially concerning the difference of infrared spectra between synthetic amethyst and natural amethyst [17,18]. A range between 3300–3800 cm^{-1} in the mid-infrared spectral region is considered to be important for distinguishing natural and synthetic amethyst, natural and synthetic smoky quartz [19]. Stefano et al. [16] found that natural amethyst had an absorption peak of 3595 cm^{-1} with the full width at half maxima, (FWHM) about 3.3 cm^{-1}, using a FTIR spectrometer with high resolution (0.5 cm^{-1}). However, 3595 cm^{-1} does not usually appear in synthetic amethyst; 3684 cm^{-1}, 3664 cm^{-1}, 3630 cm^{-1} and 3543 cm^{-1} often occur in synthetic amethyst and have been certified to occur in amethyst grown in neutral NH_4F solutions [17]. It is difficult, in synthetic amethyst grown in K_2CO_3 solution, to detect a band of around 3543 cm^{-1} using a low-resolution (4 cm^{-1}) FTIR spectrometer. The 3595 cm^{-1} absorption peaks in natural amethyst can sometimes be detected using high-resolution (0.5 cm^{-1}) FTIR spectral instrumentation, but the difference from natural amethyst is that the FWHM is about 7 cm^{-1} ($\pm$1 cm^{-1}) [19]. Natural smoky quartz often has 3595 cm^{-1} and 3484 cm^{-1} absorption peaks, while synthetic smoky quartz lacks these two absorption peaks, and there are obvious 3380 cm^{-1}, 3365 cm^{-1} and 3305 cm^{-1} in the 3300–3800 cm^{-1} band [11]. In summary, there is a lack of systematic comparative study on the spectral and chemical compositions of natural and synthetic amethyst, and natural and synthetic smoky quartz.

This paper focuses on the spectral and mineralogical characteristics of natural and synthetic amethyst, and natural and synthetic smoky quartz. On the basis of summarizing previous research results, this work provides new data on the mineralogy and spectroscopy characteristics of natural and synthetic amethysts, and natural and synthetic smoky quartz by using X-ray powder diffraction, an X-ray fluorescence spectrometer, an infrared spectrometer, a micro-Raman spectrometer, and an ultraviolet visible light absorption spectrometer. The purpose of this paper is to better distinguish the difference between natural and synthetic amethyst, and natural and synthetic smoky quartz, providing a new technical method and basis for the identification of synthetic amethyst and smoky quartz, and provide a new approach for the identification of other synthetic gems.

2. Materials and Methods

2.1. Materials

Natural amethyst (Cry-1), synthetic amethyst (Syn Cry-1), natural smoky quartz (Cry-2) and synthetic smoky quartz (Syn Cry-2) were collected. They ranged between 1 to 2 cm in size (Figure 1). The origin of the natural amethyst and smoky quartz was Rio Grande Do Su, Brazil, and the samples were purchased from Brazilian jewelry suppliers. Synthetic amethyst and smoky quartz were obtained from synthetic rock crystal, produced by Chinese synthetic rock crystal factories, Hangzhou Dingli Crystal Factory, China. The synthesis method was the hydrothermal method, and the mineralizer solution was K_2CO_3 or KOH solution.

2.2. Methods

Standard gemological properties of the four samples were detected, including refractive index and hydrostatic SG-specific gravity/density.

The instrument used for the powder X-ray diffraction test was a Bruker D8 Advance from Germany, using Cu Kα radiation with a scan speed of 4°/min and a scanning range of 2 θ from 10 to 70°.

XRF data were collected with an EDX-7000 XRF Spectrometer produced by Shimadzu, Japan. Test conditions: vacuum, qualitative scanning, 1 mm.

Infrared spectra were obtained using an FT-IR Spectrometer Tensor 27, produced by Bruker, Germany. The scanning range was 400–4000 cm^{-1} (reflection).

Raman spectra were collected using an HR Evolution micro-Raman spectroscope produced by HORIBA, Japan. The excitation laser was 532 nm and the scanning range was 100–3000 cm^{-1}.

UV-Visible absorption spectra were collected with a UV-3600 UV-VIS-NIR Spectrophotometer produced by Shimadzu, Japan. The scanning range was 200–800 nm. Sampling interval: 1.0 s.

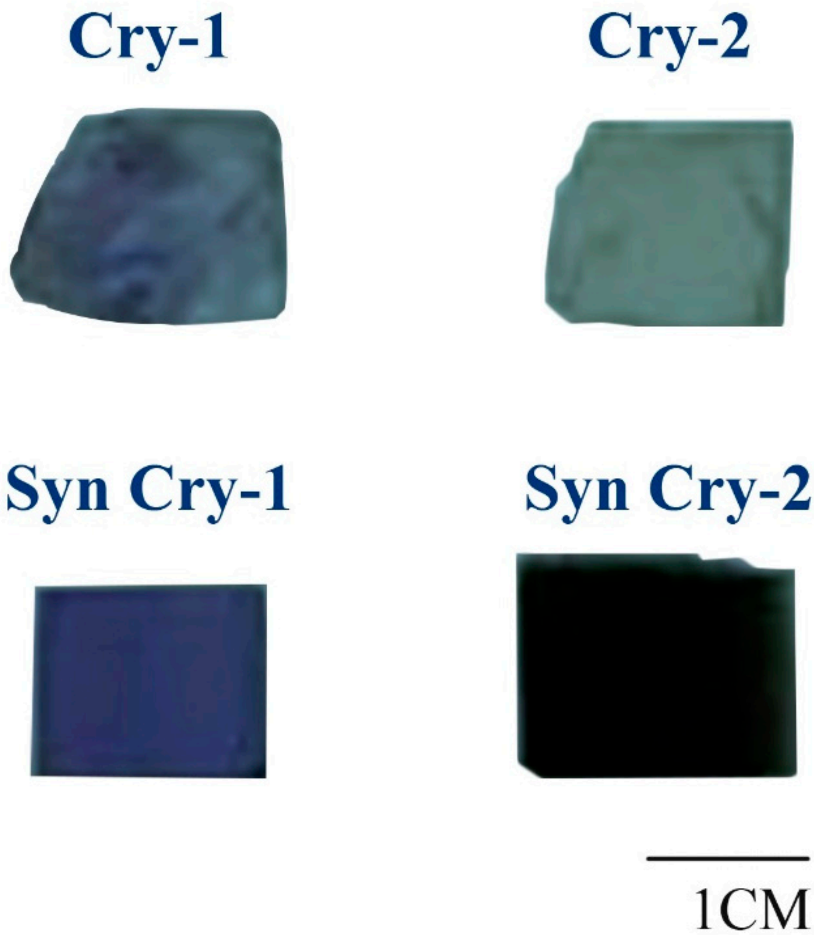

Figure 1. Photos of Cry-1, Syn Cry-1, Cry-2 and Syn Cry-2 samples.

3. Results and Discussion

3.1. Gemological Properties

The natural amethyst and smoky quartz are light in color and unevenly distributed, while the synthetic amethyst and smoky quartz are dark and evenly distributed due to the influence of the concentration of colorants. Both natural and synthetic amethyst, and smoky quartz samples have glass luster, and the upper and lower sides are relatively flat and transparent. The refractive index and specific gravity of the four samples are Cry-1 (RI: 1.545~1.553, SG: 2.64), Syn Cry-1 (RI: 1.546~1.554, SG: 2.64), Cry-2 (RI: 1.543~1.553, SG: 2.63) and Syn Cry-2 (RI: 1.543~1.552, SG: 2.65). The hardness of all samples is similar to that of the knife (Mohs 7). In summary, the gem mineralogy parameters of natural and synthetic amethyst, and natural and synthetic smoky quartz are basically the same. Therefore, it is hard to distinguish the natural from the synthetic by basic gemological characterization.

3.2. X-ray Powder Diffraction Analysis

The XRD patterns of Cry-1, Syn Cry-1, Cry-2 and Syn Cry-2 are shown in Figure 2, and the standard data for SiO_2 (PDF card No. 85-0795) are shown as a reference. It is clear that all the diffraction peaks for the samples are consistent with the SiO_2 diffraction peak positions corresponding to the crystal (ICSD No. 85-0795). Jade 5 software was used to calculate the cell parameters of the sample; results are shown in Table 1. As shown in Table 1, the cell parameters of natural and synthetic amethyst, and smoky quartz are close to those of standard crystals, but there is some deviation, which may be caused by the isomorphic substitution of other ions.

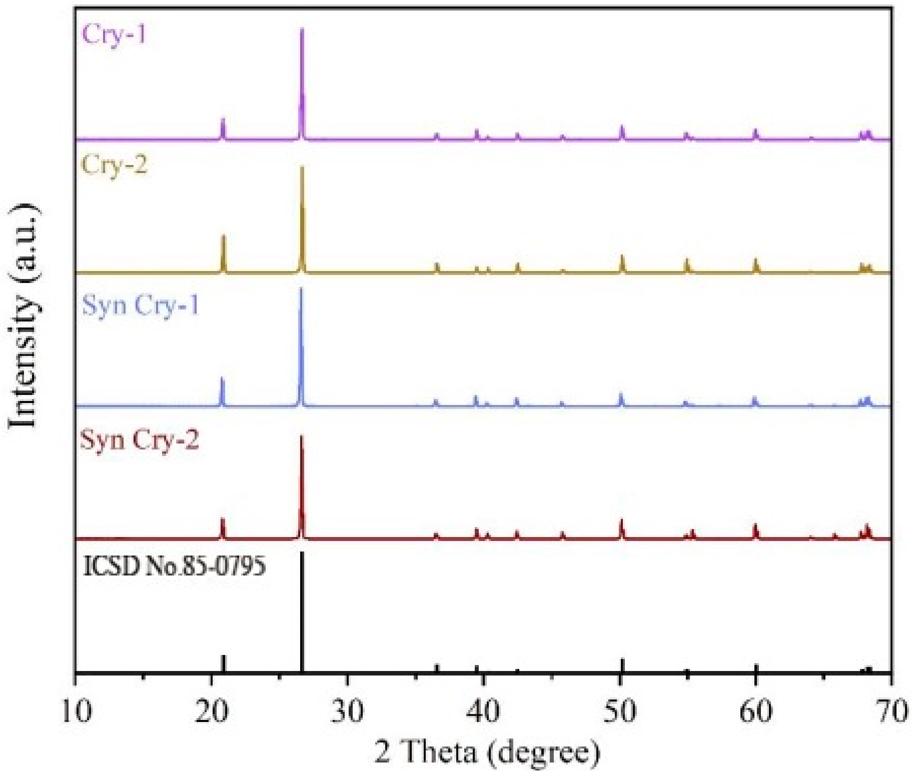

Figure 2. The XRD patterns of Cry-1, Cry-2, Syn Cry-1 and Syn Cry-2 samples.

Table 1. The cell parameters of Cry-1, Cry-2, Syn Cry-1 and Syn Cry-2 samples.

Samples	a, b (Å)	c (Å)	V (Å^3)
Cry-1	4.91451	5.40554	113.07
Cry-2	4.91342	5.40288	112.96
Syn Cry-1	4.91441	5.40553	113.06
Syn Cry-2	4.91438	5.40569	113.06
PDF No. 85-0795	4.9108	5.4028	112.8

3.3. XRF Investigation

The XRF results for Cry-1, Syn Cry-1, Cry-2 and Syn Cry-2 samples are shown in the supporting document. The main elements in natural and synthetic amethysts are Si and O, with total amounts as high as 99.69% and 99.714%, respectively. The crystal often contains Al impurity, which will produce a $[AlO_4]^{4-}$ hole color center. Adding KOH or K_2CO_3 mineralizer can effectively avoid the influence of Al impurity elements in the crystal. Therefore, the content of the K element in Syn Cry-1 sample is higher than that of the natural sample, by up to 0.088%. The content of the K element in synthetic amethyst is higher than that in natural amethyst, which can be used as a basis to distinguish natural and synthetic amethyst.

The top eight chemical components of Cry-2 are: Si, Ca, Os, K, Pr, Cu and Ag; the main elements are Si and O, with a content amount of more than 99.816%. The top eight chemical components of Syn Cry-2 in the sample are: Si, Ca, S, Cu, K, Bi and Mn; the main elements are Si and O, with a content amount of more than 99.693%. However, it is worth noting that the content of K element in natural smoky quartz is as high as 0.036%, slightly higher than that in synthetic smoky quartz. The reason for this phenomenon may be that the natural smoky quartz is formed in a potassium-rich environment. In the process of crystal mineralization, the halide of the Na element replaces the potassium feldspar, which causes the potassium feldspar to undergo greisenization, leading to the enrichment of the K element in the crystal. It can be seen from the XRF results that there is no obvious difference between the element types and contents of natural and synthetic smoky quartz, so it is impossible to distinguish them by this method.

3.4. FT-NIR Analysis

Figure 3a shows the infrared reflection spectra of Cry-1 and Syn Cry-1 samples. The infrared spectra of the two samples are similar because they contain higher Fe and OH^-. Before 1500 cm^{-1}, the intensity and location of various vibration peaks of the two are similar, and the synthetic amethyst has a characteristic absorption peak at 3500 cm^{-1}, which belongs to the stretching vibration band of H_2O [20,21]. The natural amethyst is missing here, which can be used as an important basis for the identification of the two.

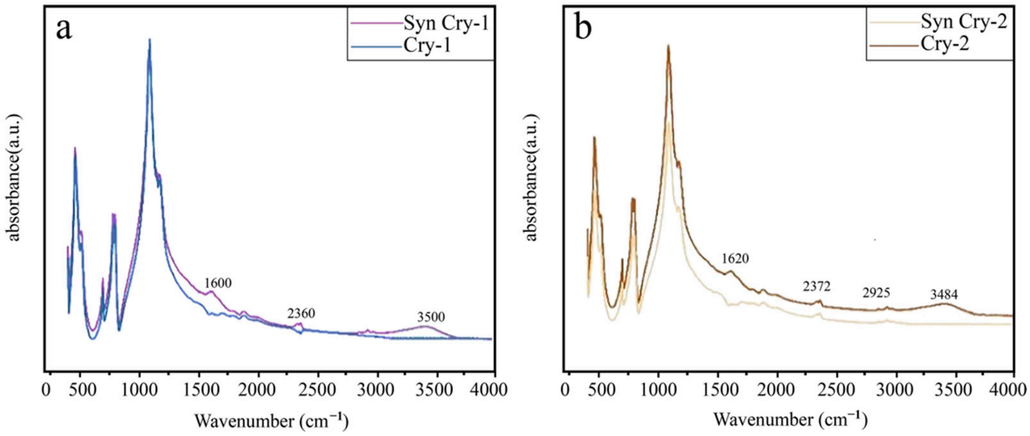

Figure 3. The infrared reflection spectra of Cry-1 and Syn Cry-1 samples (**a**), and the infrared reflection spectra of Cry-2 and Syn Cry-2 samples (**b**).

The infrared reflection spectra of the Cry-2 and Syn Cry-2 samples are shown in Figure 3b. Before 2000 cm^{-1}, the intensity and location of various vibration peaks of the two are similar, and the peak of water can also be seen at 1600 cm^{-1}. Natural and synthetic smoky quartz have absorption peaks near 2372 cm^{-1} and 2925 cm^{-1}. Natural smoky quartz has a characteristic 3484 cm^{-1} absorption peak, while synthetic smoky quartz lacks this peak, which can be used as an important basis to identify them.

3.5. Raman Analysis

Figure 4 shows the Raman spectra of the Cry-1 (4a), Syn Cry-1 (4b), Cry-2 (4c) and Syn Cry-2 (4d) samples. By comparing the Raman spectra of rock crystals, it is found that the characteristic peaks of both natural and synthetic amethyst, and natural and synthetic smoky quartz are basically around 260 cm^{-1}, 350 cm^{-1}, 390 cm^{-1}, 465 cm^{-1} and 807 cm^{-1}, of which around 465 cm^{-1} is the position of the strongest Raman spectrum vibration peak; the most obvious feature of crystals. The Raman peak near 260 cm^{-1} is related to the vibration of the silicon-oxygen tetrahedron, and 350 cm^{-1}, 390 cm^{-1} and 465 cm^{-1} are related to the bending vibration of Si-O [22].

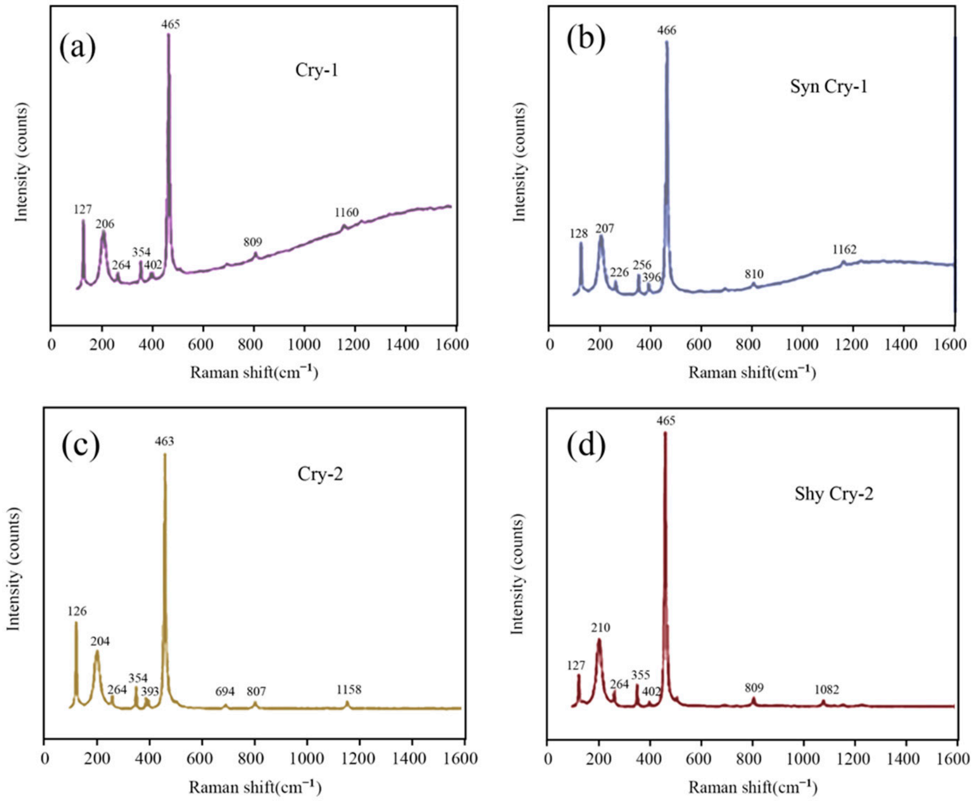

Figure 4. The Raman spectra of Cry-1 (**a**), Syn Cry-1 (**b**), Cry-2 (**c**) and Syn Cry-2 (**d**) samples.

3.6. UV-VIS Analysis

Figure 5 shows the UV-VIS spectra of the Cry-1 (5a), Syn Cry-1 (5b), Cry-2 (5c) and Syn Cry-2 (5d) samples. It can be seen from Figure 5 that the ultraviolet visible absorption spectra of amethyst and synthetic amethyst have similar trends, with an absorption peak at 350 nm and a wide absorption band at 540 nm, which can absorb a large amount of yellow-green light, making the crystal appear purple. The absorption peak at about 350 nm corresponds to the O-Fe^{4+} charge transfer, and the wide absorption band at 540 nm corresponds to Fe^{3+} holes and Fe-trapped electrons. The broad absorption peak of synthetic amethyst at about 550 nm is caused by the hole-color center generated by the internal Fe^{3+} after radiation. This is consistent with the conclusion that there is Fe in the synthetic amethyst, as determined from the XRF test section. The UV-VIS absorption spectra of natural and synthetic smoky quartz are different. The strong absorption peak of natural smoky quartz at 460 nm may be due to Al^{3+} isomorphism replacing Si^{4+}, and then being radiated to form a hole color center $[AlO_4]^{4-}$, which results in a smoke color. The synthetic smoky quartz has a strong absorption peak at 480 nm, especially for the blue violet light region, and then the absorption intensity gradually decreases, and the overall absorption range is long; the absorption broadband almost covers the entire visible light wavelength. In addition, the UV spectral absorption intensity of synthetic smoky quartz is much higher than that of natural smoky quartz, because the synthetic smoky quartz is darker than that of natural smoky quartz, and the concentration of chromophores also accordingly increases.

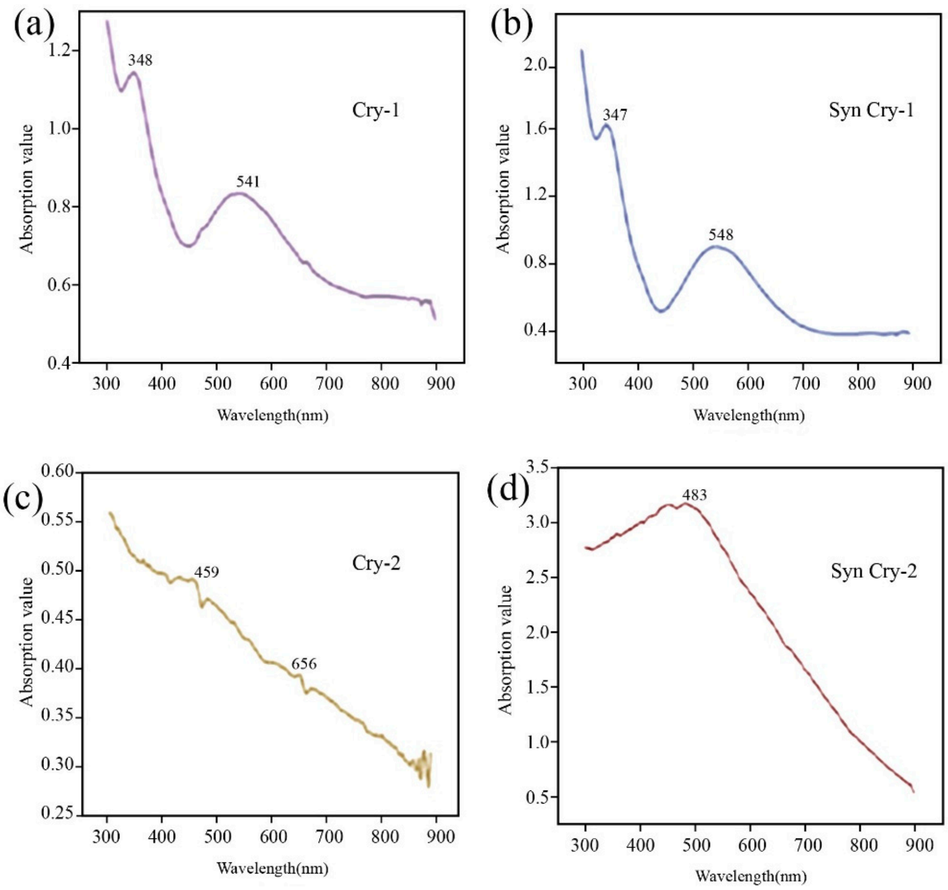

Figure 5. The UV-VIS spectra of Cry-1 (**a**), Syn Cry-1 (**b**), Cry-2 (**c**) and Syn Cry-2 (**d**) samples.

4. Conclusions

In this paper, the gemological and mineralogical characteristics of natural and synthetic amethyst, and natural and synthetic smoky quartz were studied, including basic gemological properties, chemical composition, crystal structure and spectral characteristics. The results indicated that the basic gemstone properties of natural and synthetic amethyst, and natural and synthetic smoky quartz are very similar. The synthetic amethyst and smoky quartz samples displayed bending cracks and a small amount of bread crumb-like black inclusions under the polarizing microscope. Natural amethyst and smoky quartz had Raman characteristic peaks of about 697 cm^{-1} and 1160 cm^{-1}, while synthetic amethyst and smoky quartz had no vibration peaks in these bands. Compared with the synthetic amethyst, the natural amethyst lacked the characteristic infrared absorption peak of 3500 cm^{-1}, and, compared with natural smoky quartz, synthetic smoky quartz lacked the 3484 cm^{-1} infrared absorption peak. This study provided data support for the effective identification of natural and synthetic amethyst, and natural and synthetic smoky quartz.

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