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DATE 11 July 2016

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SUBJ FTIR Analysis to Distinguish 4H and 6H Polytypes of SiC Crystals

Summary

We were provided with an unknown SiC Princess-cut crystal and provided with a known 6H and a known 4H Princess-cut gemstone. I had suggested that an alternative to classifying the unknown gemstone to XRD might be FTIR infra-red spectroscopy. The principal results of our attempt to use FTIR to classify the unknown polytype structure of the provided gemstone are:

- The FTIR absorption spectra of the SiC crystals are weak and any surface contamination due to organic materials tends to overwhelm the true SiC spectra. The crystals must be carefully cleaned before successful results are obtainable.
- The FTIR spectra were too weak to obtain useful results using the ATR apparatus on which we press the gemstone face against a diamond window.
- We were able to acquire FTIR spectra reproducibly in the transmission mode.
- The known 4H and 6H polytypes are distinguishable, but not in the manner suggested by a published paper in an astrophysics journal discussing the measured spectra of SiC particles in space.
- The unknown crystal is of the 4H polytype.
- The A, B, C, B repeat sequence of the bi-layers that characterizes the 4H polytype appears not to be repeated with 100% success in all crystals. There are minor differences in the spectra of the known 4H and the unknown crystal that suggest

that there is a slight difference between the two crystals in the success rate of repetition of the A, B, C, B sequence. It is not known which crystal has the higher successful repeat rate.

Samples and Background

We received 3 Princess-cut Moisannite crystals from Mike Christensen on 12 May 2016. One had a diameter of 8 mm and was known to be a 4H polytype SiC crystal. One had a diameter of 7 mm and was known to be a 6H polytype SiC crystal. The third was of an unknown polytype with a diameter of 7.4 mm. We were asked if we could distinguish SiC crystals having 4H and 6H crystal structures. I suggested that we could try to find a way to make the distinction using FTIR spectroscopy.

The SiC crystal is made of bi-layers of atoms stacked in one of several sequences. There are three types of bi-layer pair arrangements, A, B, and C. The C arrangement causes a 60° rotation or twist of the lattice. There is a structure that can be arranged to repeat or be periodic with only two pair of bilayers, which is called the 2H polytype. The 2H polytype has only alternating A and B bilayer structures. There is also a 4H polytype which incorporates a C orientated bilayer structure within a periodic repeating structure of 4 bilayers. This has a repeating arrangement A, B, C, B. There is also a 6H polytype with the repeating arrangement A, B, C, A, C, B.

I had discovered a published paper called Infrared properties of SiC particles, by H. Mutschke, A. C. Andersen, D. Clement, Th. Henning, and G. Peiter published in Astronomy and Astrophysics, 2 March 1999, whose purpose was to calculate the resonant absorption frequencies of SiC particles found in distant space. The paper had a table of the experimentally measured frequencies expressed in wavenumbers (cm^{-1}) based on multiple experimental measurements for 2H, 4H, 6H, 3C, and 15R polytypes of SiC crystal particles. All of the measured frequencies given for the 6H and 4H polytypes were very nearly the same, except for one frequency due to a resonance parallel to the principal axes. The 6H polytype had a resonant frequency of 788.1 cm^{-1} in this case and the 4H polytype had a frequency of 783.6 cm^{-1}, which I thought we could use to distinguish these polytypes.

FTIR Spectroscopy Analysis

All FTIR data were collected using a JASCO 6100 infra-red spectrometer equipped with a Golden Gate GS-10515 Attenuated Total Reflectance (ATR) Cell with KRS-5 lenses. The FTIR spectrometer has a ceramic mid-infrared source and a temperature controlled DLATGS detector. The Michelson interferometer has KRS-5 lenses and the detector has DTGS windows. Spectra were analyzed using BioRad's KnowItAll Informatics System, Jasco IR Edition. Spectra were matched using the libraries contained in Fiveash Data Management's ATR Polymers and Adhesives Database. Usually samples are scanned 128 times to obtain a high-signal-to-noise ratio at a resolution of 4 cm^{-1}. In this study, we used a higher resolution 2 cm^{-1} and a larger number of scans.

FTIR infra-red spectroscopy analysis of the crystals was tried with the front face of the Princess-cut crystals pressed against the diamond window of the ATR apparatus. This did not work well at all. There was too little signal from the crystal surface and the results were entirely erratic. Any organic contamination on the surface overwhelmed any signal from the crystal itself.

We then tried to analyze the crystals in transmission mode with the infra-red beam incident normal to the large face and exiting the crystal at the pointed end. Once again even the slightest organic contamination of the crystal caused this transmission analysis to produce spurious results. We had to develop a very careful cleaning procedure for the SiC crystals. When this was done, the spectra became relatively consistent and reproducible.

The resulting transmission spectra of the weak absorptions of the SiC crystals are shown in Figs. 1, 2, and 3 for the 6H, 4H, and the unknown crystal, respectively. The absorption spectrum of the 4H crystal is very distinct from that of the 6H crystal in the 400 to 1300 cm^{-1} range. The most striking difference is that the 4H polytype crystal has a strong local minimum in the absorption at about 1148 cm^{-1}. There is also a pair of local maxima in absorption at 1035 and 1017 cm^{-1}, a broad minimum at about 978 cm^{-1}, and a strong minimum at about 506 cm^{-1}.

The spectra from the unknown crystal shown in Fig. 3 are much more like the spectra of the 4H crystal than the spectra of the 6H crystal. One of the spectra, the green one is very similar, while somewhat more significant differences show up in the blue and black spectra which are very nearly identical to one another. Instead of having the broad absorption minimum at 1148 cm^{-1}, the blue and the black spectra have two local minima at 1154 and 1112 cm^{-1}. There is a shoulder in the 4H crystal spectra and in the green spectrum from the unknown crystal that suggests an absorption at 1112 cm^{-1}, which is weaker than that found in the blue and black spectra of the unknown crystal. Where the 4H crystal has two similarly strong maxima at 1035 and 1017 cm^{-1}, there is a broad single top to the local absorption maximum in the green spectrum of the

unknown crystal and an asymmetric peak for the blue and black spectra indicating the 1035 cm^{-1} maximum is suppressed relative to the 1017 maximum. The unknown crystal has somewhat more absorption at about 850 cm^{-1} compared to the 4H crystal. All of the spectra show the strong and broad minimum in absorption at about 506 cm^{-1} seen in the 4H crystal.

The unknown crystal is concluded to be 4H crystal, though it is also clear that there are some minor stacking variations in the unknown crystal relative to the known 4H crystal. The ideal 4H crystal has the repeating A, B, C, B, structure. However, it may be that this structure really only repeats in this way almost all the time, but it occasionally does not. Perhaps the successful repeat of that A, B, C, B sequence is 98% in one crystal and 95% in another. Something like this may then cause minor differences in the spectra of two 4H crystals such as we saw in the unknown and the known 4H crystals in this case. It is not known to us which of these two crystals may have the higher successful repeat sequence either.

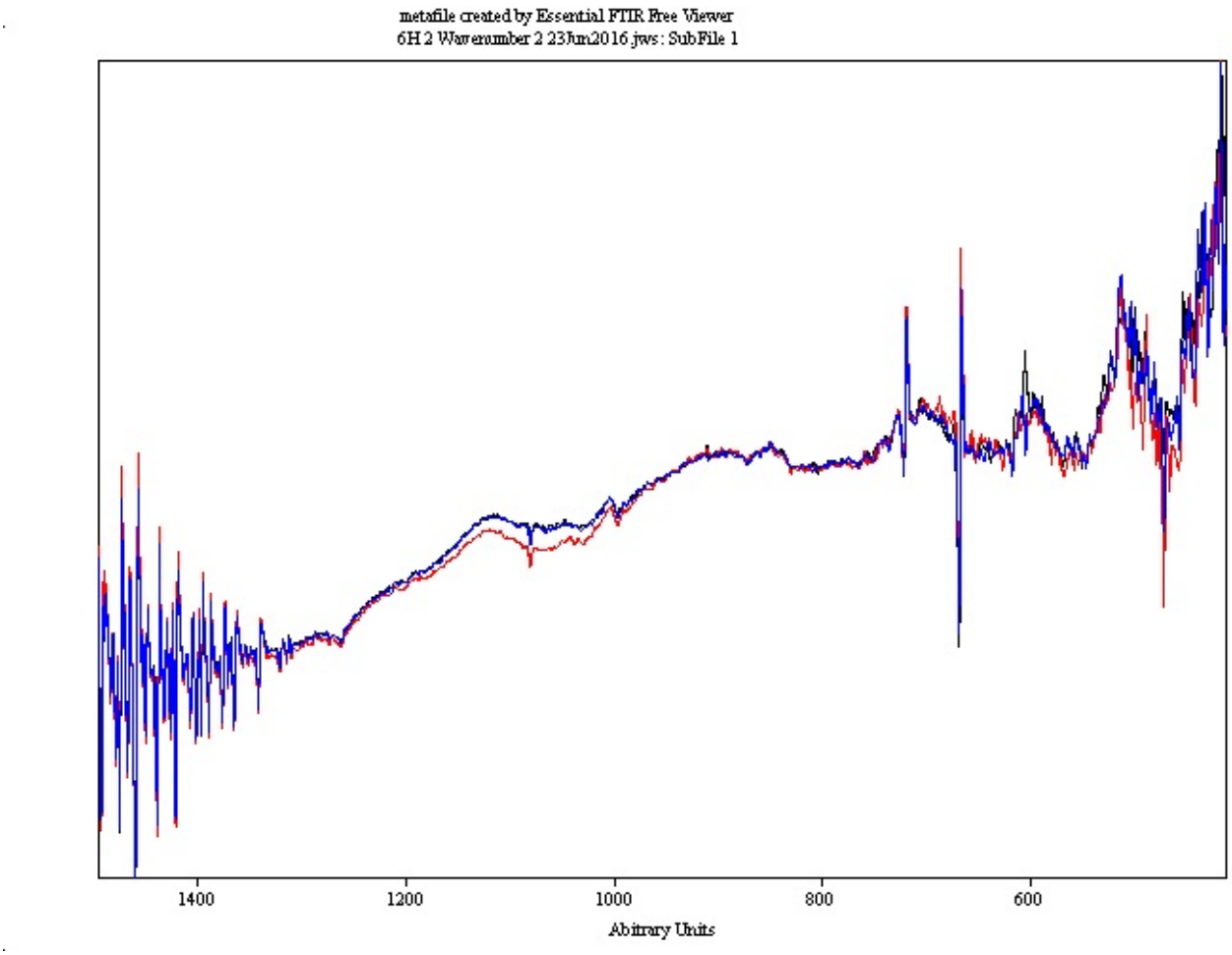

Fig. 1. Three spectra of the known 6H polytype Princess-cut SiC crystal are shown here. The spectra are shown in red, blue, and black, with the blue and the black hard to distinguish because they are so similar. The x-axis units are cm^{-1}, not arbitrary as falsely stated by the software used to overlay the spectra. There are broad local maxima in the absorption at about 1115, 707, 600, and 513 cm^{-1}, a sharp local maximum at 1006 cm^{-1}, and sharp local minima at 1080 and 998 cm^{-1}.

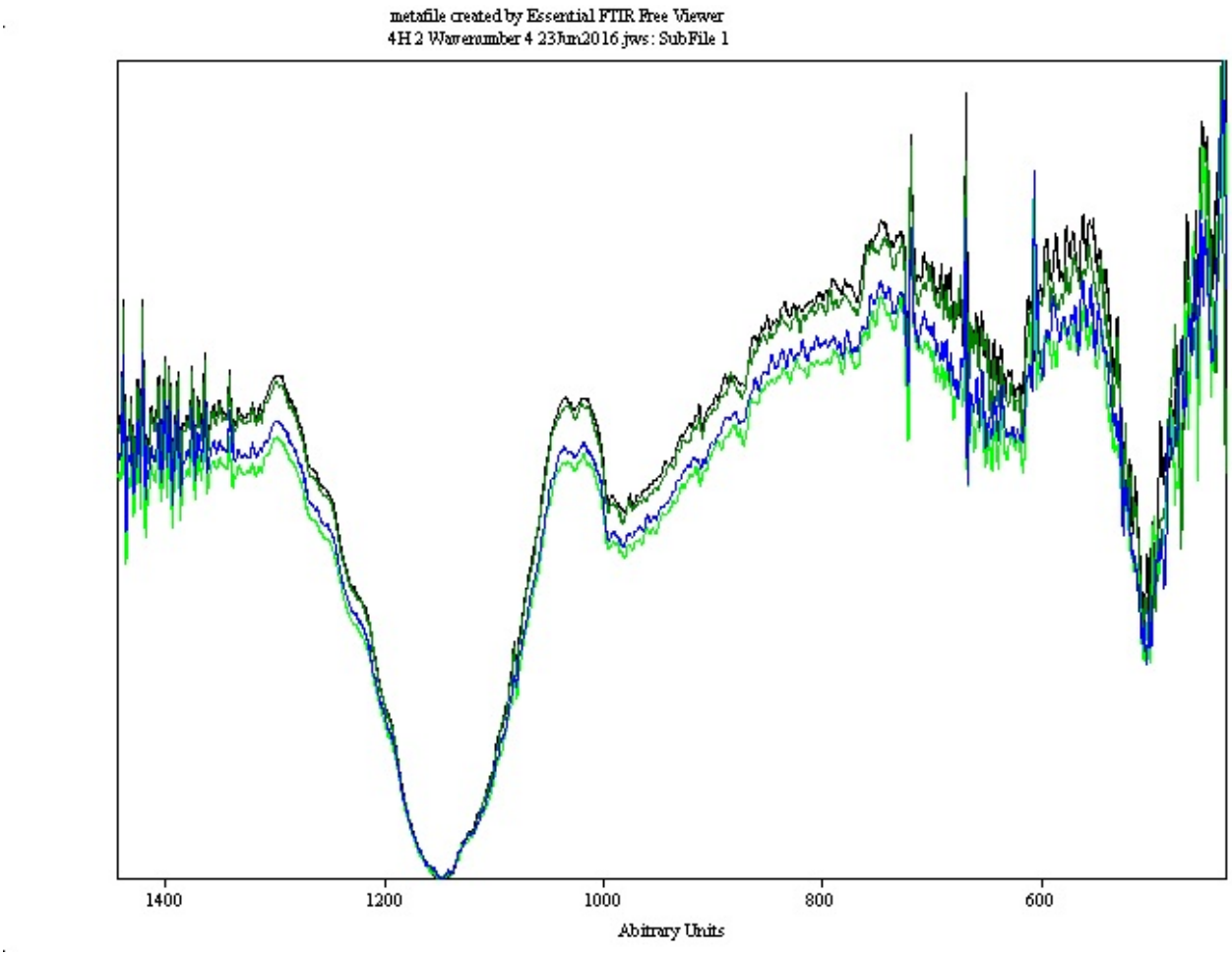

Fig. 2. The known 4H polytype SiC Princess cut SiC crystal results of four spectra are shown here in black, dark green, blue, and lighter green. The most notable difference with the 6H spectrum is the strong, but broad, minimum in the absorption at 1148 cm^{-1}. This is followed by two local maxima at 1035 and 1017 cm^{-1}, a broad local minimum at 978 cm^{-1}, a sharp local minimum at 873 cm^{-1}, a broad local maximum at 974 cm^{-1}, a broad local minimum at about 623 cm^{-1}, a broad local maximum at 554 cm^{-1}, and a broad local minimum at 506 cm^{-1}.

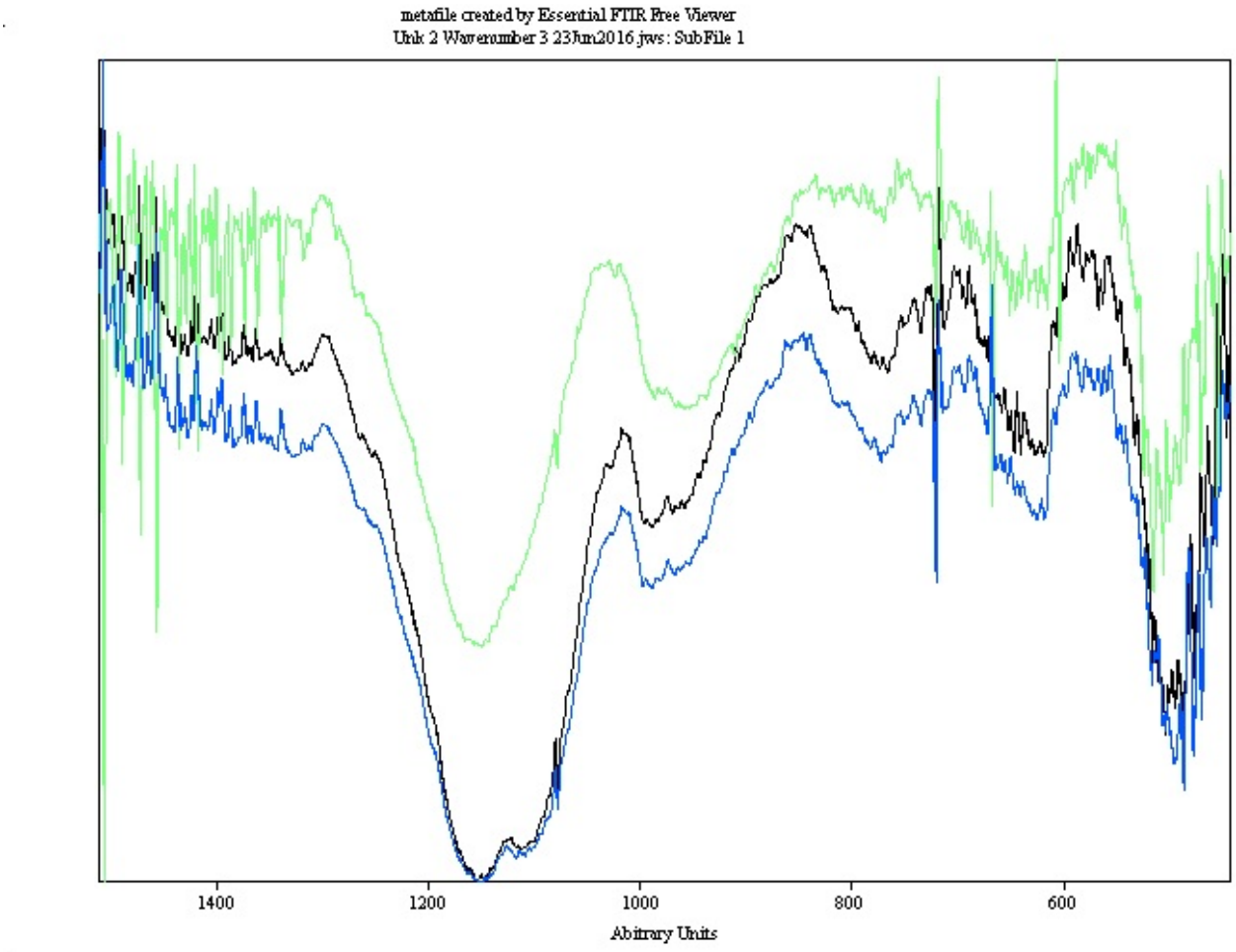

Fig. 3. Three FTIR transmission spectra of the Princess-cut SiC crystal are shown. The spectra are very similar to those of the known 4H polytype SiC crystal. There are minor differences, such as the doublet nature of the major absorption minimum near 1148 cm^{-1}, with the slightly deeper minimum of absorption at 1154 cm^{-1} and another local minimum of 1112 cm^{-1}, in two of the three spectra . The third spectrum in green has a minimum at 1154 cm^{-1}, very close to the minimum of 1148 cm^{-1} observed in the 4H polytype. The absorption minimum at 978 cm^{-1} found in the 4H polytype is also found here to be similar, but slightly altered with a small, sharp absorption peak at 974 cm^{-1} in the midst of the broader minimum. The green spectrum looks very much like the 4H polytype spectra, while there are still other differences in the blue and black spectra, such as the suppression of the local absoption maximum at 1035 cm^{-1} relative to the one at 1017 cm^{-1}. There is relatively more absorption at about 850 cm^{-1} in the unknown crystal than in the 4H crystal. All of the spectra of the unknown crystal have absorption maxima at about 570 cm^{-1} similar to the 4H crystal and a minimum of absorption of about 506 cm^{-1}.