

NEAR – FAR IR SPECTRA OF SULFIDE MINERALS RELEVANT TO COMETS D. Moriarty¹, C. A. Hibbitts¹, C. M. Lisse¹, M. D. Dyar², G. Harlow³, D. Ebel³, R. Peale⁴, ¹JHU-APL, Building MP-3 Rm. E161, 11100 Johns Hopkins Rd., Laurel, MD 20723, dpmoriar11@gmail.com, ²Mt. Holyoke College, Kendade Hall Rm. 217, South Hadley, MA 01075, ³American Museum of Natural History, Central Park West at 79th Street, New York, NY 10024-5192, ⁴University of Central Florida, 4000 Central Florida Blvd, Building 12 Rm. 310, Orlando FL 32816

Introduction: The Spitzer Space Telescope observed the mid-IR (~5-40 μm) spectra of ejecta from the hypervelocity impact of the Deep Impact projectile with comet 9P/Tempel-1. Spectral modeling demonstrates that there are abundant minerals present in the ejecta including Ca/Fe/Mg-rich silicates, carbonates, phyllosilicates, water ice, amorphous carbon, and sulfides [1,2]. Precise mineralogical identifications are somewhat hampered by the lack of spectral measurements, particularly of transmission and of the associated derived absorption coefficient, for these materials in the 25 – 40 μm range over which Spitzer is sensitive. Additionally, a broader compositional range of carbonates, sulfides, and clays needs to be measured over this full 5-40 μm spectral range to fully and properly assess the comet's composition.

Here, we present our procedure and preliminary results for transmission spectra from ~ 5 – 200 μm for sulfides relevant to comets, including pyrite, pyrrothite, and pentlandite. This follows on initial progress presented at DPS 2008 and LPSC 2009 [3,4]. We have successfully acquired transmission spectra of these minerals ground to micron and sub-micron sizes. Transmission measurements of the micron-sized sulfides are particularly difficult to obtain because the minerals oxidize rapidly during grinding and subsequent handling unless special care is taken, using purged and water-free preparation environments.

Laboratory Procedures: We have used transmission spectroscopy, measuring the absorption of light by mineral samples suspended in an optically neutral matrix, to derive the imaginary component of the complex index of refraction. Measuring the transmission of materials over Spitzer's full spectral range requires the use of a potassium bromide (KBr) matrix for measurements from 1.5 – 24 μm and a polyethylene (PE) matrix for 20 – 200 μm . Transmission is obtained by dividing the spectrum of a sample-bearing pellet by that of a sample-free blank. Successful measurements have been achieved only after a continual process of refining our sample preparation methodology.

Sample preparation, pellet creation, and transmission measurements are similar for both the KBr and PE pellets. First, it is essential that the sample grain size is smaller than the wavelength of light to reduce scattering. We obtained 8 high-purity, well-characterized powdered sulfides from the American Museum of Nat-

ural History. To achieve the necessary micron to sub-micron particle size, we ground ~ 75 mg of each sample in an isopropanol slurry using a McCrone micronizing mill. Because sulfides of this grain size are especially prone to oxidation due to the large surface area of the grains, we performed all sample preparation in N₂-purged glovebags. The use of isopropanol as opposed to water for the grinding slurry also reduces oxidization of the sulfides. After grinding, the sample slurry is dried in the purged glovebag using a constant purge of N₂. Once dry, the micronized sulfide is transferred to a purged vial containing desiccant, sealed with parafilm, and stored under vacuum until it is to be sealed into pellets.

Because many of the sulfides used are nearly opaque at the wavelengths of interest, only a very small amount of sample is used in each pellet to avoid optical saturation. We have found that for both mid and far IR measurements, it is necessary that the pellet contain < 1% sample by mass. Three mixtures are made from each sulfide at different mass weightings. These contain 0.25, 0.50, and 1.0 mg of sample. KBr pellets begin with 250 mg of KBr. PE pellets begin with 170 mg of PE. We use a Mettler Toledo XS105 balance accurate to ~0.02 mg in this range.

It is essential to obtain a uniform mixture of the desired sample and matrix. Clumping of the sample in the mixture can result in large effective particle sizes causing opaqueness, self-shadowing, or regions free of sample. Each of these effects confuse the spectral interpretation and usually result in a lower measured absorbance. Mixture uniformity is achieved using twenty minutes of hand-mixing with a mortar and pestle, or with the use of a dental amalgamator which vigorously shakes the mixture in a small, sealed stainless steel vial along with small steel ball bearings.

A pellet is created using a hydraulic press and 13mm die. Mixtures are loaded into the die inside the glovebag. The die is then removed from the bag and evacuated with a small vacuum pump for 5 min. For KBr, the mixture is pressed with ~9 metric tons for 10 minutes. For PE, the mixture is pressed with ~ 8.4 metric tons while heating with a heat gun to ~ 120C (PE melts ~ 138C). After 4 minutes, the heat is turned off and pressure is applied for an additional 6 minutes while the die cools. The pellet will still be somewhat soft until the die cools to ~50C, at which point it can

be removed and stored. Because KBr is hygroscopic, KBr pellets will adsorb surficial water and cloud up if exposed to humidity. Newly-formed KBr pellets are immediately placed in N₂-purged vials with desiccant, sealed with parafilm, and stored under vacuum. PE pellets are less susceptible to the atmosphere and are stored in vials with lint-free wipes.

Blank (no sample) PE pellets should be translucent. Blank KBr pellets should be transparent. Sample-bearing pellets should be uniformly tinted. Pellets that show excessive contamination, non-uniformity, defects, or cloudiness are discarded.

Results: Infrared spectra are taken using an N₂-purged Bruker Vertex-70 FTIR spectrometer at 1 cm⁻¹ resolution for KBr and 2 cm⁻¹ resolution for PE pellets (Figures 1 and 2). Pellets are mounted at an angle of 15 degrees from nadir. This greatly reduces fringing in the spectra due to interference from multiple internal reflections off the pellets' smooth surfaces.

Using our sample preparation procedure, there is little evidence of oxidation in the below spectra of pyrrhotite, though pyrite may have oxidized somewhat as indicated by the presence of a strong absorption band at 24 μm (Figure 1).

The PE and KBr spectra overlap from ~ 20 to 24 μm. Agreement is good in both figures, after a single multiplicative scaling of the far-IR spectrum to the mid-IR spectrum to account for the different amounts of sample used in the two pellets. A small multiplicative offset may remain which is currently attributed to error in our mass measurements from balance artifacts and transfer loss of powders. However, there is concern that scattering may be present due to the significant mismatch between the real index of refraction of the sulfides (~ 4-6) and KBr or PE (~ 1.5), that would increase the apparent absorption. We will characterize this potential effect by comparison to results from transmission spectra at mid-IR wavelengths of thin (~ 1-5 micron) sections of sulfide minerals.

Conclusions: We have demonstrated a potentially effective procedure for obtaining mid-IR through far-IR spectra of sulfides relevant to comets. Procedural improvements such as sample preparation under an N₂ purge were instrumental in improving the quality of the resulting spectra. Strong spectral features occur from the mid-IR to ~40 μm in sulfides and may be important for interpreting Spitzer, Herschel [5], and other longwave IR measurements of comets, dust clouds, and other astronomical objects.

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References:

- [1] A'Hearn et al. (2005) *Science*, 310, 258-264. [2] Lisse et al. (2006) *Science*, 313, 635-640. [3] Jauhari et al. (2008), *DPS XL*. [4] Hibbitts et al. (2009), *LPS XL*. [5] Brusentova et al. (2008), *IEEE*, 10.1109.

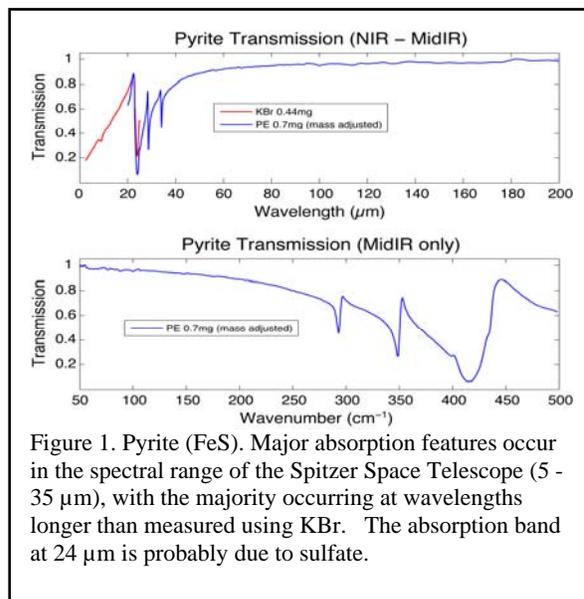


Figure 1. Pyrite (FeS). Major absorption features occur in the spectral range of the Spitzer Space Telescope (5 - 35 μm), with the majority occurring at wavelengths longer than measured using KBr. The absorption band at 24 μm is probably due to sulfate.

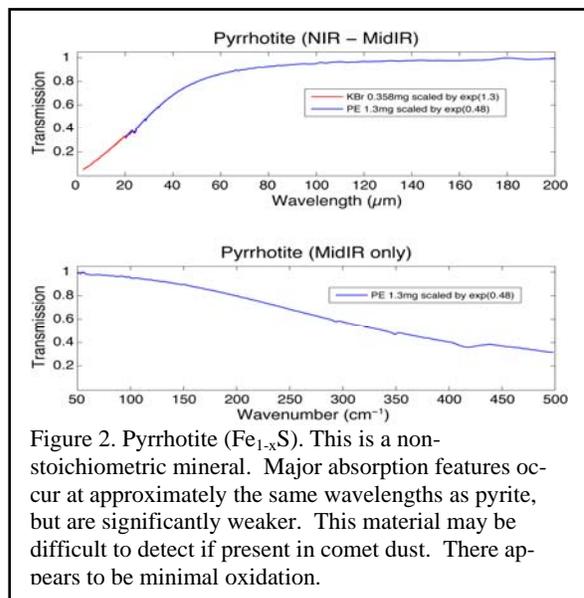


Figure 2. Pyrrhotite (Fe_{1-x}S). This is a non-stoichiometric mineral. Major absorption features occur at approximately the same wavelengths as pyrite, but are significantly weaker. This material may be difficult to detect if present in comet dust. There appears to be minimal oxidation.