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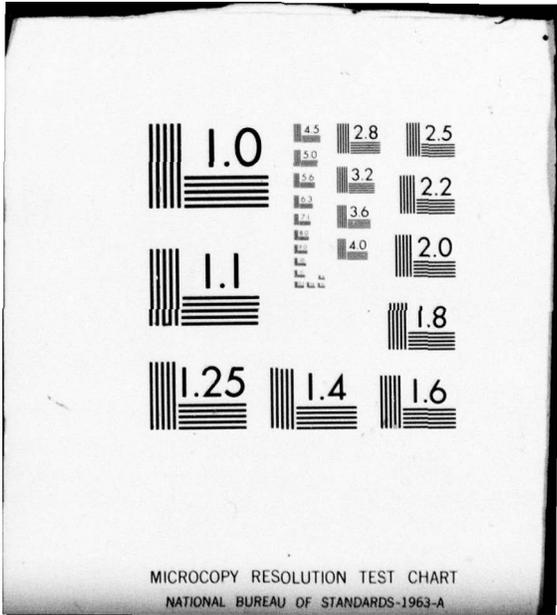
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Specular reflection of infrared bands of pure, pressed crystal powders is compared with that of crystal cuts (published data) and faces of monocrystals. Samples are shown for NaClO ₃ , CaCO ₃ , and NaNO ₂ .		

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Derivation of IR Optical Constants of Aerosols
and Polycrystalline Surfaces
[Specular Reflection by Pressed Crystal Powders]

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Introduction

The specular reflectance of cold pressed crystal powders has obtained very little attention in IR spectroscopy and crystallography, in contrast to the use of loose powders in diffuse reflectance spectroscopy for chemical analysis (Kubelka-Munk - theory) and in reflectance and emission studies of minerals for IR remote sensing applications. This method was earlier proposed by the author¹ for calculation of the optical constants of dry aerosol substance, but was solely based on the identity of spectra of $(\text{NH}_4)_2\text{SO}_4$ both in crystal form and as pressed powder (PP). However, this may not generally be true. Reinkober² probably was the first to use - for lack of crystals - PPs to measure Reststrahlen bands. Sanderson's³ comparison of such results with reflectance (R) of crystals indicated generally reduced R and some shifts. Working in the far IR, Barnes⁴ reported considerable change of R of crushed pressed marble with particle size and pressure. Though some crystal powders can be pressed into glassy, transparent pellets (KBr, $(\text{NH}_4)_2\text{SO}_4$), harder substances will visually be opaque with no trace of gloss and therefore might have insufficient specular R in the IR, too. Most crystals exhibit a vibration band only in certain orientation and beam polarization, and their pressed powders may at best show some averaged band intensity. For better insight into the problem, some measurements with pure crystal powders were performed and compared with published spectra, and where possible, with our own measurements of reflection off crystal faces.

Experimental

Pellets of pressed powders were generally prepared from moderately to extensively ground powders by pressing under vacuum at 120,000 PSI = 8200 kg/cm² = 820 MPa between polished rams of a standard KBr die, and usually inspected for visual surface gloss and bulk appearance. In a few cases, 2 to 5 times higher densification was obtained by repressing (under vacuum) parts of such pellets between old rams which became slightly indented in the process. To investigate reflection of fused materials, the salt - where possible - was molten and pressed between cold glass plates, or a layer (0.5 - 1 mm

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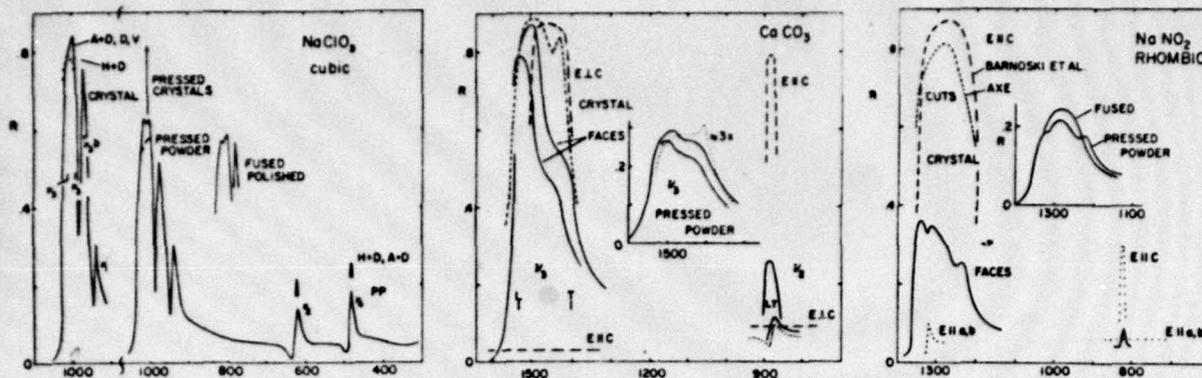
thick) of melt was allowed to cool on black anodized brass. Crystals for comparative measurements were either borrowed (quartz, gypsum, cleaved calcite) or attempts were made to grow them from solution. Only the latter were, when necessary, polished. All work was done at outside temperature of less than -5°C , eliminating any problems with moisture.

Optical measurements were made with the micro reflectance attachment (sample area less than 1 mm^2) of the Perkin Elmer Model 180 spectrometer and usually restricted to the spectral range of bands. Measurements below 300 cm^{-1} have not yet been made. Beam angle on the sample is about $20^{\circ}\times 20^{\circ}$ (reduced from $20^{\circ}\times 35^{\circ}$) with one side of the cone only 2° from normal incidence. Though beam polarization changes from about 12 to 67% in each of the grating ranges (500 to 250 cm^{-1} and multiples), a polarizer was normally not used. At those small incidence angles the errors are small (Simon⁵): reflectance (without polarizer) in a plane \perp to the optic axis of a quartz crystal face (which produces both the ordinary (o) and extraordinary (e) spectra with polarizer) shows only traces of the strong e-band at 540 cm^{-1} . No polarization effects are expected (and were not observed) of PP reflectance. This makes the method attractive to aerosol optics which cannot generally handle anisotropic scattering.

Results

1. Isometric (or nearly so). As already mentioned, crystallographic cuts, crystal faces (Toon et al.⁶) and PP of $(\text{NH}_4)_2\text{SO}_4$ (rhombohedral, but only slightly trichroitic in the spectral range considered) gave the same R - spectra, with maximum of 42% at 1100 cm^{-1} . Instead, we discuss NaClO_3 (cubic structure, with the same R spectrum from all faces, Anderman and Dows⁷) in Figure 1. The branches of the ν_3 band of crystals appear again in PP spectra, but reduced in amplitude by about 30% as in fused samples. In a pellet prepared from not previously crushed crystals, R could be maximized to 85% at certain locations of the pellet. That the R peak of the main band exhibited varying details in different PP samples was an experience with other salts, too. In the case of SrTiO_3 (also cubic) with very high crystal reflectance below 800 cm^{-1} apart from a deep minimum at 480 cm^{-1} , the reduction of the PP reflectance is 50% for a very fine powder (the surface showed visually high gloss, but no specular reflectance).

2. Pressed powders in strongly anisotropic conditions. The IR bands of CaCO_3 (hexagonal) are strongly polarized (Hellwege et al.⁸), that is reflection in the ν_3 -band from a principal section (cut \parallel to the C axis) approaches 90% for $E\perp C$ while no band is seen in $E\parallel C$; the opposite is true of the ν_2 vibration (Figure 2). In calcite, this cut is oblique to the faces and cleavage planes, but R from faces obviously is more important in the powder problem. While the crystallographic cut



Figures 1-3. Reflectance Spectra of Crystals (cuts and faces) and of Pressed Powders. Wave numbers in cm^{-1} .

produces (at least at small incidence angles) a rather symmetric ν_3 band (dotted in Figure 2), cleavage faces mostly give asymmetric bands (solid lines). In the rather weak PP reflectance, this asymmetry feature is not as much preserved as one might expect from the crystal face spectra. In the ν_2 band, all faces give (for both polarizations) about 42% R in most situations, as compared to the strongly different polarization effects in the C-cut. The PP band is very weak, even in relation to the ν_3 band. The same band shape and cut situation is observed with NaNO_3 (Hellwege et al.⁸) since it is isomorphous with calcite. However, the PP reflection in the ν_3 band is much less reduced. Though the chlorate pellets have specular R to the eye, the high gloss of the calcite pellet should have made it a perfect reflector in the IR, too. A further sample (NaNO_2 , Axe⁹, Fig. 3) involving a rhombic crystal for which polarized R spectra may be different for all 3 axes shows in the 1300 cm^{-1} band low face reflections (possibly because of inferior quality of the tiny specimen) and even lower PP reflection than calcite. More difficult to discuss are the results from biaxial materials like SrSO_4 and BaSO_4 . Polarized spectra indicate strong, but well separated bands in the three principal axes, but the peak of the weak PP spectra seems to be just outside of the crystal band area.— If a simple mixture rule for peak reflectance of the main bands of biaxial crystals, $\bar{R} = \sqrt[3]{R_a R_b R_c}$ ($R_a = R_b = R_o$, $R_3 = R_e$ for uniaxial crystals) is applicable to the PP problem, one would expect $\bar{R} = 0.32$ for calcite and NaClO_3 while measured values are 0.28 and 0.60. In the case of SiO_2 , the broad, largely overlapping bands at $\approx 1100 \text{ cm}^{-1}$ ($R_o = R_e = 0.9$) would be expected to yield $\bar{R} = 0.9$, but measured is 0.33 — an indication that the extraordinary ray may play a minor role.— So far, the influences of pressure and powder size have hardly been mentioned. Indeed, the effects are mostly within the range of reproducibility. Although smaller pressure than our standard pressure was found to reduce R, even 3 times higher densification had only the effect to enhance features on

the low frequency side of the main band (also observed with SiO_2) without increasing R as such. However, normally white, brittle pellets (CaCO_3 , SiO_2) became hard and glassy but not really transparent because of cracks and inclusions (of air, according to appearance of Christiansen bands in transmittance measurements).

3. Amorphous and polycrystalline powders. Pellets of finely ground glass, sandstone and basalt showed 30 to 45% of the parent materials reflection. However, smoothness of the pressed surface (and of the polished sandstone and basalt) may have been insufficient.

Conclusions

Measurements of Reststrahlen bands of pressed powders of crystals with no or small orientation effects show in general only 50 to 70% of the crystals specular reflectance though some pressed substances ($(\text{NH}_4)_2\text{SO}_4$, KBr) reflect like the crystal or nearly so (SiO_2). Strongly polarized bands of calcite produce the expected powder reflectance, but NaNO_3 and NaNO_2 seem to reflect twice as strong. Powder spectra (even without pressing) of BaSO_4 differ considerably from crystallographic spectra. Surface roughness and particles size have little influence. The results indicate that interpretation (and extraction of optical constants) of reflectance spectra of pressed powders of unknown composition will be difficult. The difference between crystallographic polarized reflectance and surface reflectance certainly also applies to emission and mineral spectroscopy (remote sensing).

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