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QUARTERLY REPORT NO. 3

ON

INFRARED STUDIES OF CRYSTALS

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INFRARED STUDIES OF CRYSTALS

I. PURPOSE OF THE RESEARCH

The objectives within this period are essentially the same as those given in Quarterly Report No. 2 and need not be repeated.

II. ACCOUNT OF WORK DONE

A. Diamond (Mr. W. G. Simeral)

The examination of single diamonds as regards transmission of ultra violet radiation has been resumed. A particularly suitable stone (M4) belonging to the department has been investigated. Its transmission was quite variable and in particular one corner appeared to be much more transparent to the λ 2536 A line of the mercury arc. In conjunction with these observations, the transmission at various selected points on the infra-red has been determined using the micro-spectrometer. There is considerable qualitative agreement between the regions which transmit λ 2536 and appear to have weak type I bands in the infra-red. This stone is being studied in more detail to see whether these qualitative resemblances can be made more precise. This is the first occasion in which a single stone has been shown to consist partly of type I and partly of type II by both infra-red and ultra violet transmission.

Arrangements are in hand to submit certain selected diamonds to bombardment by deuterons in the cyclotron to see if this treatment can affect the spectroscopic properties of the diamond in the infra-red. Such treatment is known to alter the colour of the diamond.

In order to explore a more suitable technique for the study of the far infra-red spectrum of diamond five carats of diamond dust have been obtained from Arthur A. Craft of Detroit. The maximum particle size is presumably two microns although the material has a tendency to form aggregates of considerably larger size. Spectra were run on this powder using just the powder (precipitated from isopropyl alcohol) and then in a Nujol mull. Both methods revealed a band structure not in agreement with the crystal spectrum of diamond. Similarities to past spectra were noted and examination made it clear that one of the three following materials is present as an impurity: Si, SiC, SiO₂. The absorption coefficient at 8.5 microns is of the order of 75 in the dust whereas the highest coefficient Blackwell records is about 25 for the 7.81 micron band. In none of the dust

spectra is the 4.6 - 5.0 micron region of greater intensity than 2 to 4% if it is present at all. Consequently, it was decided to try to remove whatever impurities were present. The following density table indicates that bromoform should separate Si and SiO₂ from diamond in sedimentation.

| <u>Substance</u> | <u>Density</u> |
|------------------|----------------|
| Diamond | 3.51 |
| SiC | 3.17 |
| Bromoform | 2.89 |
| SiO ₂ | 2.2-2.8 |
| Si | 2.34 |

Four separations were performed. The bromoform was removed by use of isopropyl alcohol. The spectrum of the purified dust was not appreciably altered except that the relative intensity of the band at 12μ seemed to decrease with respect to that of the band at 9μ. At present there seem to be two methods of attack open. (1) On the chance that the SiO₂ is too heavy to be effectively removed in bromoform and that SiC may be present a separation can be attempted with methylene iodide (density is 3.33). (2) A chemical separation employing hydrofluoric acid will separate Si and SiO₂ from the mixture.

Scattering remains a problem even when the impurities are removed. High index media are indicated as a means for employing this diamond dust. One could imbed the dust in a molten mass of Thallium iodide or chloride or KRS and then polish the solidified mass. Methylene iodide also has a high index and presumably also has a spectrum which is not too complex. The information on indices of refraction is summarized below.

| <u>Substance</u> | <u>Index of Refraction</u> |
|-------------------------------|----------------------------|
| Thallium monoiodide | 2.78 |
| Diamond | 2.42 |
| Thallium monochloride..... | 2.25 |
| Methylene iodide | 1.74 |
| Bromoform | 1.58 |
| AgCl | 2.07 |
| AgBr | 2.25 |

The near infra-red spectrum of the dust indicates that it contains one or more of silicon, silica, or silicon carbide as impurity. Separations by means of sedimentation in heavy liquids were not sufficient to remove the impurity.

The spectra of two different samples of silicon carbide show that the relative intensity of the two principal bands is not constant. This indicates that one of the bands must be due to an impurity. The source of the SiC was a grinding compound.

B. Barium Titanate (Mr. R. T. Mara)

In order to see whether the method of preparing the BaTiO₃ powder samples for spectroscopic examination (as described in Quarterly Report No. 2) might be causing a preferential concentration of BaCO₃ in the layers deposited on rock salt, a run was made with the BaTiO₃ from the National Lead Company in which the material was not put through the preparative process but put directly on the rock salt plate. The spectrum obtained was exactly the same as that previously recorded (Fig. XII, 2nd Quarterly Report) showing the presumed BaCO₃ bands at 6.9 μ and 11.65 μ with the same intensity. It therefore seems unlikely that the preparation process causes any concentration of trace impurities.

Pursuing the examination of various specimens of BaTiO₃ now available it was noted that hexagonal crystals (L128-40-7-1) and tetragonal (L128-40-74-1) each exhibit two different colours. The hexagonal form contains clear amber and also cloudy brown crystals. The tetragonal sample contains white and pinkish crystals. The two types are easily separated in each case by hand. The spectra of all four forms were obtained.

The preparation of the film is done in each case in the following manner. The crystal is ground in a mortar and shaken with a few milliliters of isopropyl alcohol. The suspension is then poured into a 50ml graduated cylinder and the cylinder filled with clean isopropyl alcohol. The suspension is again mixed and then allowed to stand for one hour. The top 25ml are removed, and the particles separated by centrifuging. All but about one ml of the alcohol is poured off. The particles are then stirred into the remaining alcohol and placed on a NaCl plate with a dropper. The alcohol is allowed to evaporate, and a film of BaTiO₃ particles forms on the plate. The film may be built up to the desired thickness.

The spectra will be given in the next report. Here it may be reported that in general the spectra of the two hexagonal forms were very similar but differed markedly from the spectra of the tetragonal forms which again were very similar.

The hexagonal crystals yield a spectrum very similar to that found for the BaTiO₃ of the National Lead Company (Quarterly Report No. 2, Fig. XII). However the clear amber form shows a broad weak band in the region of 9 - 10 μ which is not found in the cloudy brown form.

The two tetragonal forms yield a richer spectrum in which all the bands found in the hexagonal forms are present (except the weak 9.3 μ band) but in addition new bands appear at 11.05 μ , 11.4 μ , 11.85 μ and 12.85 μ . The pink form also has bands at 9.45 μ (sharp) and near 10.4 μ (shoulder). These results are summarised in Table I.

Table I

Absorption Bands of Various Forms of BaTiO₃

| <u>HEXAGONAL</u> | | <u>TETRAGONAL</u> | |
|-------------------------------|---------------------|---------------------|---------------------------|
| <u>Clear Amber</u> | <u>Cloudy Brown</u> | <u>Cloudy White</u> | <u>Cloudy Pink</u> |
| 6.9 μ | 6.9 μ | 6.9 μ | 6.9 μ (strong) |
| 7.1 (shoulder) | 7.1 (shoulder) | 7.1 (shoulder) | 7.1 (shoulder) |
| 9.3 - 9.4 (broad, shallow) | - | - | - |
| - | - | - | 9.45 (sharp) |
| - | - | - | 10.3 - 10.4 (shoulder) |
| - | - | 11.05 | 11.05 |
| - | - | 11.4 | 11.4 (shoulder) |
| 11.65 | 11.65 | 11.65 | 11.65 (strong) |
| - | - | 11.85 | 11.85 |
| - | - | 12.85 | 12.85 |
| 15 (or beyond) | 15 (or beyond) | 15 (or beyond) | 15 (or beyond) |

With regard to the suggestion that the bands at 6.9 μ and 11.65 μ are due to BaCO₃ it is very significant that the specimen which exhibited these bands most intensely (tetragonal pink) also showed a weak band at 9.45 μ . This is where BaCO₃ also exhibits a weak band.

It is encouraging to note that the tetragonal and hexagonal forms do yield different spectra seeing that the tetragonal form is the only one which has ferroelectric properties.

III. FUTURE PROGRAM

This is essentially the same as that given in the 2nd Quarterly Report.

