The spectral reflectivity of synthetic calcium monoferrite

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Summary. The principal reflectivities of orthorhombic calcium monoferrite have been determined at 500 Å intervals from 4500 to 6500 Å. A small amount of calcium hexaferrite was shown to be present by electron probe examination.

CALCIUM–iron oxides of varying composition, and often containing small amounts of other elements, occur in a variety of industrial materials such as iron-ore sinters, cements, and catalysts used in the Haber ammonia synthesis process. The single term 'calcium ferrite' is commonly used for such oxides, despite the wide variation in composition.

Dicalcium ferrite, $2CaO.Fe_2O_3$, seems to have the greatest thermal stability range amongst the pure compounds and is formed under a wide range of conditions. The more iron-rich compositions such as $CaO.2Fe_2O_3$, $4CaO.FeO.8Fe_2O_3$, etc., have been reported as occurring in iron-ore sinters. They seem to have a lower thermal stability range, unless stabilized by small quantities of other elements such as aluminium, titanium, manganese. The relative amounts of FeO and Fe_2O_3 in such compounds have not in many cases been determined and there is, therefore, a lack of reliable data that would allow the recognition of particular compositions from the measurement of physical properties. Etch tests have been suggested as a means of identification, but these are notoriously unreliable and can give only a broad indication of variations in composition.

The measurement of reflectivity offers a quantitative method of identification that may readily be combined with the normal optical examination of these materials in polished specimen. The present account gives the results of measurements on synthetic calcium monoferrite, $CaO.Fe_2O_3$, and it is intended to give data for other pure synthetic compounds in future papers.

Calcium monoferrite was prepared from Analar grade calcium carbonate and Griffin reagent ferric oxide (195-61HZ). Accurately weighed amounts of these materials were mixed in a mixer mill and melted in a nickel crucible at 1250° C. The melt was slowly cooled to 1200° C over five hours and large needle-shaped crystals 3 or 4 mm in length were formed. An examination of polished specimens showed that at least 95 % of the preparation consisted of monoferrite and its X-ray diffraction pattern agreed precisely with the A.S.T.M. card index file No. 8–100.

There were, however, small amounts of three other phases—wispy crystals of dicalcium ferrite, an iron-rich calcium ferrite, and hexagonal crystals, pinkish in colour, up to 30 μ in size. Examination with the electron microprobe analyser shows that the approximate composition of this phase is $CaO.6Fe_2O_3$. So far as we are aware, calcium hexaferrite has not previously been described, but our investigation of it is not yet complete. The compositions of the dicalcium ferrite and the calcium monoferrite were also checked with the probe, and nickel contamination from the container was shown to be undetectable at distances greater than 50 μ from the crucible wall. Permanganate titration showed 0·38 wt. % FeO in the bulk sample, believed to be mainly in the iron-rich calcium ferrite phase.

Reflectivity measurements were obtained using an 11-stage photomultiplier (Nichol and Phillips, 1965) fitted to the photometer ocular of a Vickers ore microscope. A ×40 objective was used, but the lamp iris was closed down so that only a small central part of the aperture was illuminated, thus eliminating errors due to convergence.

Calcium monoferrite is orthorhombic and will therefore show three principal reflectivities which may be designated R_α, R_β, R_γ, by analogy with the designation of refractive indices in biaxial crystals. Any random section will in general have for its principal reflectivities a value between R_α and R_β in one direction and between R_β and R_γ at right angles to this. Measurements taken on a series of randomly oriented grains should enable an estimate to be made of all three principal values for the crystal. The method has recently been used by Cameron (1963) to determine the values at a single wavelength for certain opaque minerals of lower symmetry. In the present study the measurements were carried out at wavelength intervals of 500 Å from 4500 to 6500 Å using a sliding variable wavelength interference filter as monochromator. The spectral reflectivity obtained in this way should be of more value for identification purposes than measurements at a single wavelength. Pyrite was used as a comparison standard, taking the appropriate values from the measurements of Nichol and

Phillips (1965). Eight areas of monoferrite were chosen at random and a further two were selected for their small bireflectance. The maximum and minimum reflectivities for each grain were determined and it was confirmed that these directions were the extinction positions between crossed polars. The results are shown in the figure, from which the method of assessing R_β is obvious. The reflectivity and the bireflectance increase from the red to the blue end of the spectrum, with a maximum bireflectance at 5000 Å.

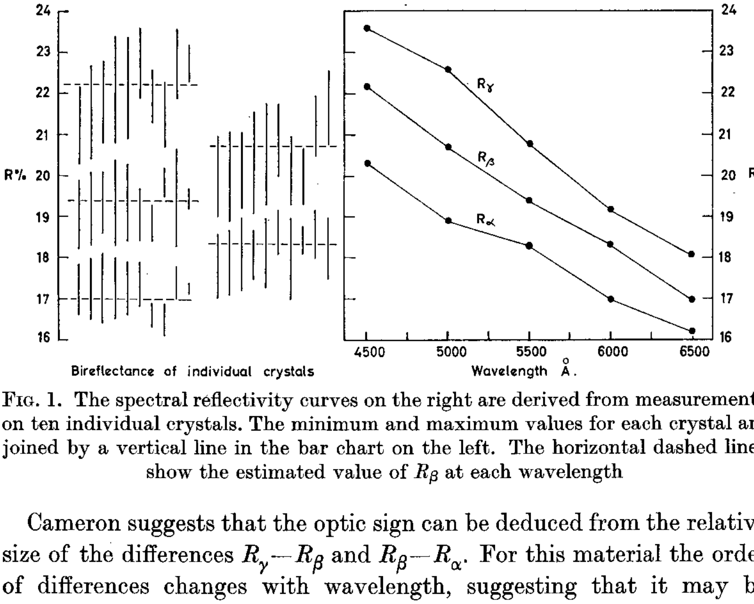

FIG. 1. The spectral reflectivity curves on the right are derived from measurements on ten individual crystals. The minimum and maximum values for each crystal are joined by a vertical line in the bar chart on the left. The horizontal dashed lines show the estimated value of R_β at each wavelength

Cameron suggests that the optic sign can be deduced from the relative size of the differences $R_\gamma - R_\beta$ and $R_\beta - R_\alpha$. For this material the order of differences changes with wavelength, suggesting that it may be optically positive or negative in different parts of the spectrum. By analogy with transparent biaxial crystals, this means that the optic axial angle, 2V, is large.

The diagnostic value of these measurements can only be fully assessed by comparison with measurements on the other calcium–iron oxides, but it is thought to be useful to place on record the results for the various pure compounds as they are obtained.

References

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