Letter

Absorption Spectrum of $NdNbO_4$ Crystals

A study of the compounds formed by sintering rare-earth oxides with niobia and tantala has disclosed a number of interesting compounds occurring in these systems [1]. A programme has been initiated for the preparation and study of the properties of single crystals of some of these compounds, starting with compounds occurring in the system Nd_2O_3-Nb_2O_5. Results are presented here for the composition $NdNbO_4$ which adopts the monoclinical fergusonite structure at low temperatures, and which becomes tetragonal on heating to 800° C [2].

The crystals were grown by the flux technique from solution in lead fluoride contained in a 20 ml platinum crucible. The starting mixture consisted of Nd_2O_3:Nb_2O_5:PbF_2 in the molar ratio of 1:1:8. This was cooled from 1200 to 800° C at a rate of 5° C/h.

The crystals grew as mauve, tetragonal bipyramids, often truncated, up to about 5 mm in length. A few, thin, plate-like crystals found on the walls of the crucible were of suitable size and thickness for optical investigations. Since the crystals grew above the monoclinic-tetragonal transition temperature, their morphology conformed to that of the tetragonal structure, and the deformation to the monoclinic form was accommodated by a type of polysynthetic twinning of complex lamellar form. When viewed under crossed polaroids, the appearance was reminiscent of a perovskite, ferroelectric, domain structure. The twin configurations could be altered by the mechanical application of pressure, and were alternately removed or regenerated by cycling the crystals between 700 and 800° C in a hot-stage microscope.

The broad features of the absorption spectrum of $NdNbO_4$ in the visible region is shown in fig. 1. The sample chosen for examination was a crystal plate of 1 cm length and 0.05 mm thickness. A dc Pointolite source was used, and the spectrum was recorded on a Hilger medium-glass spectrograph which had an inverse dispersion of 17.2 Å/mm at 4358° C.

The strongest transitions from the ground state are labelled in the figure with the excited states at which the transitions terminate. The identification of the terms is based on the extensive studies made by Carlson and Dieke [3] in establishing the energy levels of this rare earth ion. They have interpreted the Nd^{3+} levels in $NdCl_3$ diluted by $LaCl_3$ by comparing the empirical levels with the calculated levels.

Although the investigations by Carlson and Dieke were made on comparatively dilute concentrations of Nd^{3+} in a different host crystal, $LaCl_3$, it is not expected that the energy level positions will differ considerably in other host crystals, since the levels of the rare earth ions in solids are dependent on electrostatic and spin-orbit interactions, and are essentially independent of the crystal field.

There are several, strong absorption regions. The strongest of these groups is the transition from the $^4I_{9/2}$ ground state to the $^2G_{7/2}$ multiplet. This transition group comprises a broad band of lines centred at 5850 Å, approximately 300 Å wide. These lines appear broadened because the absorption in the undiluted crystal is very strong. Other strong transitions are to $^4G_{7/2}$ (centred at 5310 Å) and to $^4F_{7/2}$ (centred at 7500 Å).

Work on the effect of diluting the Nd^{3+} by growing solid-solution crystals with other suitable rare-earth niobates is in progress.

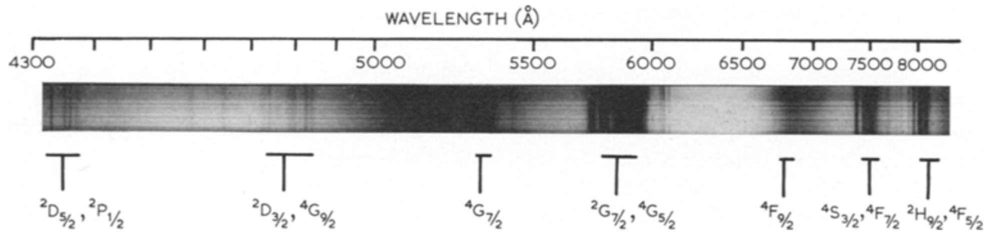

Figure 1 Absorption spectrum of $NdNbO_4$ at 300° K.

Acknowledgements
The authors wish to thank Professor W. R. S. Garton for the use of his spectroscopic facilities and Dr D. W. G. Ballentyne for his useful comments. One of us (F. H. Lou) is grateful to the International Research and Development Co Ltd (Newcastle) for financial support.

References
1. H. P. ROOKSBY and E. A. D. WHITE, *Acta Cryst.* **16** (1963) 888.
2. A. J. DYER and E. A. D. WHITE, *Trans. Brit. Ceram. Soc.* **63** (1964) 301.
3. E. H. CARLSON and G. H. DIEKE, *J. Chem. Phys.* **34** (1961) 1602.

2 November 1966

F. H. LOU
E. A. D. WHITE
Electrical Engineering Department
Imperial College
London, SW7, UK

Book Reviews

Boron

Volume 2: Preparation, Properties and Applications

G. K. Gaulé (editor)

Pp XV + 345 (Plenum Press, New York, 1965) $12.50

This collection of papers is based on the second symposium on boron held in Paris in 1964, following the first symposium in 1959. It is divided into four groups: concerned with synthesis, crystal structure, electronic and mechanical behaviour, and some electronic applications.

The complex allotropy and intricate directional bonding of boron in its various structures is still not entirely unravelled, though the complete structure determination of beta-rhombohedral boron with 105 atoms per unit cell is a major achievement. One paper, on a new form of boron produced by subjecting ordinary boron to high pressure, has an indicative opening sentence. "Elemental boron can be prepared at low pressures in something like four different crystalline modifications."

Most of the papers on properties are concerned with band structure, optical absorption, birefringence, resistivity and semiconducting parameters, and thermal conductivity. Two very interesting papers in this section deal with the strength of bulk boron and of boron filaments, especially with the influence of surface polishing. Boron appears to show no trace of plastic flow, and if the surface is properly treated, filaments of the metal, vapour-deposited on a tungsten core, have very promising characteristics which have recently set in motion a large, American, research effort directed to the production of fibre-reinforced metal composites. These have properties comparable to the carbon-fibre-reinforced composites recently announced in Britain; carbon fibres, however, have the advantage of being much cheaper.

The final section includes a detailed account of thermistor pairs based on two isotopes of boron. These thermistors are used as neutron dose-rate meters, since one isotope has a much larger neutron capture cross-section than the other, and this electrode therefore becomes warmer than the other. This must be the most ingenious dose-rate meter invented to date! The other paper describes the use of a simple boron semiconductor device (not requiring any doping) as a switch, which can be activated either by a current surge or by a temperature change. The use of such a device for various circuit functions such as overload protection and rectification is exemplified. The volume spans a wide range of topics and should offer stimulation to a number of readers, ranging from crystallographers to electrical engineers.

R. W. CAHN