SHORT COMMUNICATIONS

Hydrothermal growth of single-crystal scheelite.

SCHEELITE, calcium tungstate, $CaWO_4$, is currently of interest as a material for maser applications, since it provides a suitable host lattice for a wide range of paramagnetic ions. Single crystal material has hitherto been obtained by pulling from the melt or by flame fusion methods [1, 7], and by crystallization from solution in a molten salt [2, 3]. The hydrothermal method of growth often offers advantages in the production of relatively strain-free crystals with low dislocation densities, because of the low temperatures and slow growth rates commonly used. Russian workers have reported the hydrothermal formation of spontaneously nucleated calcium tungstate crystals [4], but no satisfactory method of growing the material on seed crystals has so far been described.

It has now been found that hydrothermal growth on seed crystals is possible with a temperature gradient method. Initial studies under isothermal conditions showed that calcium tungstate was formed from calcium oxide and tungsten oxide, and some recrystallization occurred, in aqueous alkaline media between 300° and 400° C and at a pressure of 500 atmospheres. Attempts to obtain growth on seed crystals were made with techniques similar to those used for the growth of single crystal quartz [5]. Unlined 1 in. diameter mild or stainless steel autoclaves were heated on a hotplate, and the temperature gradient over the length of the autoclave was varied by alteration of the amount of insulation used. The seed crystals, grown by flame fusion, were suspended at the top of the autoclave by platinum wire, and a baffle with a small central hole was placed between them and the source material. This was either pressed and sintered powder, or crushed crystals from the flame fusion process. The degree of filling of the autoclave with solution was estimated for a given temperature and pressure from Kennedy's data for water [6]. Growth on the seed crystals was found to occur over a range of conditions, both in sodium carbonate and sodium hydroxide solutions. The optimum conditions were N sodium hydroxide solution at 500 atmospheres, a base temperature of 350° C and a top temperature of 250° C, and an 8–10 % baffle opening; and under these conditions seed crystals increased in weight by 15–20 % per week. Studies with a spherical seed showed that all orientations

had similar growth rates, and a complex polyhedral habit developed. Among faces developed were the {001} and {011}. Lower growth rates were obtained in sodium carbonate solutions, while in stronger sodium hydroxide solutions precipitation of calcium hydroxide occurred. The use of a pressure of 1000 atmospheres did not have a marked influence on growth rates.

Contrary to the experience with silicate systems, corrosion proved a serious problem in unlined autoclaves. The quality of new growth was poor, and microscopic examination revealed particles of magnetite, Fe_3O_4, associated with the grown crystal. Experiments in a silver-plated autoclave were unsuccessful, as corrosion of this lining also took place in the alkaline solutions. However, when crystals were grown in a platinum tube contained in a 2 in. diameter autoclave, corrosion products were excluded, and good quality growth was obtained.

In separate isothermal experiments in gold tubes inside the autoclaves, small, slighly coloured crystals of calcium tungstate were spontaneously nucleated in the presence of trivalent chromium or of divalent manganese, showing that the introduction of suitable paramagnetic ions into hydrothermally grown crystals is possible.

The General Electric Co. Ltd.,
Central Research Laboratories,
Hirst Research Centre,
Wembley,
England.

P. B. HART
F. W. WEBSTER

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Ages of some Tertiary intrusive rocks in Arran.

THE first results of an attempt to unravel the sequence of igneous rocks in Arran (Scotland) by radioactive age determination are presented (Table I). The ages so far obtained are grouped closely enough to suggest that the whole range of later igneous activity took place within