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Observations on the growth of thallium vanadium sulphide single crystals

The preparation and properties of single crystals of thallium vanadium sulphide for use in acoustic surface wave devices has been described by several groups of workers [1–3]. The crystals were grown by the Bridgman–Stockbarger technique in sealed silica glass ampoules at growth rates of 5 mm day^{-1}. This work records some observations made on the growth of crystals under similar conditions.

The starting material was received from the manufacturers* in three forms: First in the form of polycrystalline lumps prepared by sealed tube reaction of the elements, second, this same material which had been subjected to zone-refining at a refining rate of $2.0\,\text{cm}\,\text{h}^{-1}$ in a sealed silica glass ampoule, which produced a polycrystalline bar and finally the same starting material which had been subjected to Bridgman–Stockbarger growth at a rate of $1\,\text{cm}\,\text{day}^{-1}$. This material contained large single-crystal pieces.

All of these materials were subjected to Bridgman-growth in which only a single furnace was used and the ampoules were lowered out of this furnace by means of a rack and pinion lowering mechanism situated beneath the furnace. This was driven by a multi-speed motor and this provided lowering rates of 1.0 to $30.0\,\text{mm}\,\text{day}^{-1}$. The temperature gradient used was $10^\circ\,\text{C}\,\text{mm}^{-1}$ and the temperature was controlled by a Variac a.c. voltage controller only. The ampoules were cleaned prior to loading by immersion in aqua regia for at least 1 h followed by washing in distilled water and then iso-propyl alcohol. They were dried in an air oven at 80° C for at least 4 h. When dry they were loaded with the appropriate starting material, evacuated to 10^{-3} Torr, filled with pure argon to 0.3 atm pressure and sealed. The principal ampoule size was 20 mm diameter by 100 mm long sealed. This produced crystals of this diameter and about 50 mm long. Two seeding tips were used, first a 60° cone and second a bulb, 5 mm diameter connected to the main tube cone of about 90°, by a 10 mm long, 1.0 mm internal diameter capillary. Attempts to use seeds were not successful.

Table I lists a selection of results. From these it can be seen that most of the crystals started as a polycrystalline mass and the grain size gradually increased as growth proceeded. Occasionally a complete single crystal was obtained. This effect was not changed by the nature of the tip, the growth rate or the type of starting material. However, the extent of a second phase which appeared as particles made visible in the crystals by transmitted light, was markedly affected by the latter and zone refining or pre-growth of the starting material reduced the extent of this second phase. It was considered that the difficulty of obtaining complete single crystals every time might be a result of changes in stoichometry as growth proceeded. As a result sections along a boule were analysed. The mean of several analyses is given in Table II. It proved possible to obtain reproducible results for sulphur content, but the results for the thallium and vanadium showed a wide spread which did not allow meaningful conclusions to be drawn. Assuming the thallium is in a monovalent state and vanadium is in a pentavalent state a fomula for the samples is given in the table. These results indicate that if there is any change in composition as growth proceeds it is not extensive, but

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*BDH Chemicals Ltd, Poole, Dorset, UK.

TABLE I

Crystal code	Starting material	Tube diameter (mm)	Type of tip	Growth rate (mm d^{-1})	Crystal characteristics
R1	Polycrystalline lumps	12	Bulb plus neck	5.0	Lower half very small grain polycrystalline. Upper half larger grain polycrystalline. Inclusions present.
R2	Zone-refined polycrystalline Finishing third of bar	20	Bulb plus neck	5.0	Lower two-thirds single. Inclusions present.
R3	Zone-refined polycrystalline. Starting third of bar	20	Bulb plus neck	5.0	Very large grain polycrystalline throughout. Few inclusions present.
R4	Zone-refined polycrystalline. Middle third of bar	20	Bulb plus neck	5.0	Large grain polycrystalline throughout. Cracks at crystal periphery. Few inclusions present.
R5	Rear pieces cut from crystals R1 to R4	18	60° cone	5.0	Lower half small grain polycrystalline. Few inclusions present.
R8	Zone-refined polycrystalline. Starting half of bar	20	Bulb plus neck	1.7	Lower three-quarters single crystal. No inclusions present.
R9	Zone-refined polycrystalline. Finishing half of bar	20	Bulb plus neck	1.7	Lower two-thirds small grain polycrystalline. Upper third single. Inclusions present.
R10	Polycrystalline lump	20	Bulb plus neck	5.0	Polycrystalline grain size increasing towards top. Inclusions, cracks, voids in crystal.
R11	Clear pieces selected from previous crystals	20	Bulb plus neck	1.7	Polycrystalline grain size increasing towards top. Few inclusions present.
R15	As above	22	60° cone	17.3	Polycrystalline grain size increasing towards top. Few inclusions, crystal cracked.
R17	As above	22	60° cone	5.0	As above.
R18	As above	18	Bulb plus neck	1.7	Lower third-polycrystalline, upper two-thirds single. Few inclusions present.
R19	Single-crystal material from manufacturer with inclusions.	18	60° cone	5.0	Completely single 30 mm long. Few inclusions present.
R20	Grown by manufacturer.	20	60° cone	4.0	Boule length 210 mm. Grain size increasing towards top. 80 mm single. Inclusions present.

growth takes place on the thallium sulphide-rich side of the binary phase diagram of the two sulphides involved.

The results indicate that although large pieces of single-crystal thallium vanadium sulphide can be obtained by the growth process used complete single crystals are difficult to obtain. This probably arises from a large degree of supercooling of the liquid at the container tip which suddenly solidifies giving rapid initial growth much higher than the applied growth rate. Thereafter growth proceeds at the applied growth rate and the grain size increases. Under these circumstances the best method of growth is the growth of very long crystals of 100 mm length at least from pre-grown starting material, which provides the best quality,

TABLE II

Samples from R20 Table I	Sulphur content (wt%)	Formula
Crystal tip	15.4–16.0	$3.2Tl_2S:V_2S_5$
40.0 mm from tip, polycrystalline	15.3–15.4	$3.4Tl_2S:V_2S_5$
130 mm from tip, single crystal	16.1–16.3	$3Tl_2S:V_2S_5$
200 mm from tip, single crystal	14.0:15.4	$3.3Tl_2:V_2S_5$

at a rate not greater than 1 cm day^{-1}. Under these circumstances the upper half of the crystal will usually be single crystal of good quality.

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Relaxation time and molar free energy of activation for some rare-earth complexes of kaolinite

Vankeymeulen [1] and Vankeymeulen and Dekeyser [2] studied the dielectric loss and defects in kaolinite with frequency and temperature variations. They took two specific clay minerals, namely kaolinite and dickite, from different locations for their studies and established their activation energies. Bhattacharjee [3] studied the dielectric properties of kaolinite with temperature at two frequencies: 500×10^3 and 1×10^6 cycle sec^{-1} and correlated his results with X-ray measurements. Ghosh [4] studied the dielectric behaviour of some bentonites of different origins and established that their relaxation times depend on their origin. The literature records little work done on the dielectric properties of clay minerals and the dielectric properties of the rare-earth complexes of kaolinite has not been studied so far. The main purpose of this communication is to report the variation of relaxation time and molar free energy of activation for dipole relaxation for different rare-earth complexes of kaolinite. These rare-earth complexes were prepared by cation exchange processes.

The measurements included the determination of dielectric loss (ϵ'') within the range of frequency 120 to 10^5 cycle sec^{-1} and relaxation time

TABLE I Chemical composition of kaolinite

Components	%
SiO_2	45.80
TiO_2	Trace
Al_2O_3	37.59
Fe_2O_3	00.65
MgO	00.21
CaO	00.39
Na_2O	00.11
K_2O	00.81
H_2O^+ H_2O^-	12.77

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