

Figure 2 Average growth rates for short growths.

results of previous workers because growth rates are extremely sensitive to the vapour pressures in the apparatus [5]. The order of magnitude seems reasonable, however. Seki *et al.* [3], for instance, quote a mean rate of $27 \mu\text{m h}^{-1}$ for (111) Ga slices at 760°C and Hollan and Schiller [6] give $80 \mu\text{m h}^{-1}$ for a temperature of 755°C . A curve giving the average growth rate for different growth times is given in Fig. 2. It can be seen that the very short growths show a greater average rate. The effect is partly masked in a plot such as Fig. 2, however, because of the averaging effect. It is a simple matter to use the graph of Fig. 2 to calculate a curve of true growth rate against time. This is presented in Fig. 3 which also shows, dotted, the long-term growth rate of $27 \mu\text{m h}^{-1}$.

Fig. 3 indicates that the true growth rate settles down to its long-term value after about 2 min. Observation of the grown layers by optical and scanning-electron microscopy indicated that this time corresponded approximately to the time taken to form a complete layer on the substrate. The likely explanation for the effect is therefore that

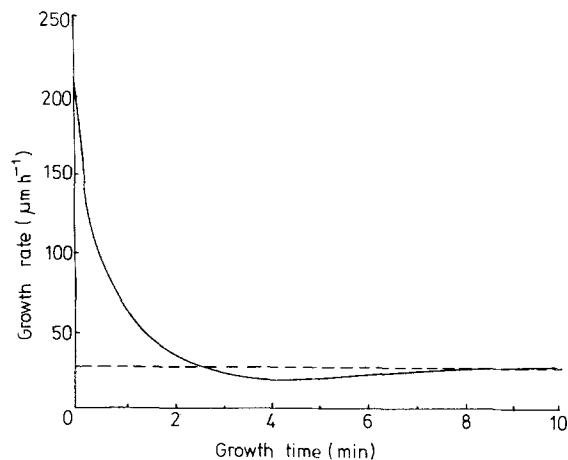


Figure 3 Growth rate versus time for GaAs on a (111) Ga face. The dotted line represents the long-term rate.

growth is much more rapid on the chemically polished surface of the substrate than on a completed layer. The two types of surface would be expected to be quite different on the atomic scale, so it is perhaps not surprising that they gave rise to different growth rates.

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The growth and characterization of strontium fluoro chloride crystals

A variation of the normal flux method, in which growth is accomplished as a result of a chemical reaction taking place in the molten state and subsequent cooling of the molten mass, has been

successfully used over the past few years to grow crystals of specific interest [1–4]. This method, sometimes referred to as the reacted flux technique, has been employed by us to grow single crystals of SrFCl and an account of the growth and related studies made on them is reported here.

The production of SrFCl can be materialized by

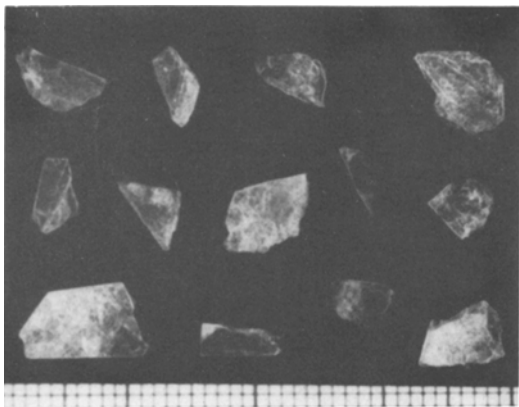


Figure 1 Synthetic strontium fluorochloride crystals (mm scale).

the reaction of SrCl_2 and NaF in accordance with the following chemical reaction:



To carry out the reaction in the molten state a stoichiometric mixture of analytical grade SrCl_2 and NaF in a platinum crucible with a loosely fitting lid was heated to a temperature of 880°C in a horizontal electric furnace. The melt was maintained at that temperature for about 2 h so that it became homogeneous. The temperature was then cooled to 700°C at a rate of 10°C h^{-1} after which the furnace was switched off and the crucible cooled over night. The crystals which

were in the upper region of the crucible were removed mechanically and used for further studies.

The synthetic crystals were of the platy habit perpendicular to the tetragonal axis and of an average size $6\text{ mm} \times 3\text{ mm} \times 0.2\text{ mm}$. An appreciable increase in the crystal size could be achieved by increasing the temperature of the furnace, and cooling at a rate of 20°C h^{-1} to 810°C and then cooling as usual. This temperature cycling causes the dissolution of the smaller crystals, the larger growing further on subsequent cooling. Fig. 1 shows some typical crystals of SrFCl grown in the laboratory. The microscopic examination of the habit faces revealed the presence of dendritic growth patterns on them indicating the attainment of high degree of supersaturation in the last stages of growth as is often the case with flux growth. Fig. 2 shows a typical dendritic pattern. Further, the crystals exhibited a profound cleavage along (001) .

The space group and unit cell dimensions of the crystal were determined from oscillation and Weissenberg photographs taken about the crystallographic axes using nickel filtered copper radiation. The crystal belongs to the tetragonal space group $P4/nmm$ (conditions limiting possible reflections- hkl : no condition; $hk0$: $h+k=2n$; $0kl$: no condition; hhl : no condition) with the following unit cell dimensions: $a = 4.079 \pm 0.008 \text{ \AA}$, $c = 6.914 \pm 0.01 \text{ \AA}$. The crystal is likely



Figure 2 A typical dendritic pattern on the habit face of the synthetic crystal, $\times 200$.



Figure 3 An etch pattern on the (001) cleavage face of SrFCl, $\times 200$.

to be isostructural with BaFCl and PbFCl which crystallize into layer-like structures with the same space group. The calculated density for SrFCl with two molecules in its unit cell (4.102 g cm^{-3}) agrees with the reported value (4.18 g cm^{-3}).

The impurity content of the synthetic crystals has been determined by the mass spectrometric method. The result of the typical analysis is shown in Table I.

TABLE I Mass spectrographic analysis

Element	Concentration (atomic ppm)
Sulphur S	400
Silicon Si	3300
Iron Fe	400
Barium Ba	100
Bromine Br	400
Yttrium Y	30
Sodium Na	4000

The fact that no trace of platinum is observed suggests that the crucible material does not contaminate the crystals. The elements S, Si, Fe, Ba, Br were present in the starting materials in relatively higher concentrations and hence have been incorporated in the crystal during growth. Starting materials of higher purity should naturally yield better results. The incorporation of the flux may be either as impurities on the lattice sites or in the form of gross inclusions. The existence of inclusions in crystals has actually been observed

with the help of the optical microscope. The relatively high concentration of Na as an impurity can, therefore, be accounted for.

Nicklaus and Fischer [5] have observed a strong OH absorption band at 3520 cm^{-1} in the infra-red spectrum of BaFCl grown in air and have attributed it to the reaction of water vapour in the atmosphere with the growing crystals. However, the infra-red spectrum of synthetic SrFCl did not show any indication for the presence of OH in it. This is understandable, because in the case of flux growth wherein the crucibles are usually closed, it is most unlikely that contamination from an external source will arise.

Finally, an assessment of the dislocation density in these crystals was made by the usual etching technique. Concentrated nitric acid at about 80°C was found to etch the (001) cleavages of these crystals selectively at dislocation sites. An etch pattern on one such cleavage plane is as shown in the Fig. 3. The average dislocation density of the crystals was found to be of the order of 10^4 cm^{-2} .

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Additives causing internal bias in TGS crystals

The recent interest in triglycine sulphate for infra-red detectors has re-stimulated work on this material and has led to the interesting and useful discovery that doping with alanine can cause permanent polarisation in one direction [1]. This effect has been explained in terms of modification of the hydrogen bonding by the substitution of small amounts of the larger alanine molecule for certain of the glycine units. Similar but less useful effects have been obtained by doping with sarcosine and other amino acids [2].

Numerous other dopants have been used in TGS growth in attempts to modify the Curie temperature, resistivity, dielectric constant and loss of the material. Generally the only effective additives are those which form isostructural compounds and complete solid solution ranges, such as selenates and fluoberyllates or the equivalent deuterated compounds. Many other additives cause habit modification, but do not give any significant changes in properties. However, this failure to cause property modification may partly be due to the fact that TGS substantially rejects most impurities and very high concentrations in solution are necessary before significant quantities are incorporated in the crystals.

In the present work we report on the effect of incorporation of Ru³⁺, Fe³⁺ and Cr³⁺ in TGS; in the last two cases, much higher concentrations of additives have been used than have hitherto been reported [3].

Ruthenium red (Johnson Matthey Chemicals Ltd) was used as one of the very few water soluble ruthenium salts available. FeCl₃·6H₂O and KCr(SO₄)₂·12H₂O (both Hopkin and Williams Ltd) were used for the other dopants.

In most cases the crystals were grown in 1 litre

beakers suspended in a temperature-controlled silicone oil bath similar to that described by Moravec and Novotny [3]. Seed crystals were mounted in silicone rubber on perspex platforms which rotated at 70 rpm; the latter also served to stir the solutions. The direction of rotation was reversed every 30 sec to promote uniformity of growth. In some cases crystals for preliminary studies were grown by evaporation in beakers using similar seed mounting and stirring arrangements.

The compositions of the solutions grown were:

“standard” solution: 1 M TGS in water (saturated approximately at room temperature)

Dopants added: Ru red 2 to 5 g l⁻¹.

FeCl₃·6H₂O, 0.08, 0.27, 0.64, 1.32, 2.64 and 5.28 M

KCr(SO₄)₂·12H₂O, 0.2 M

HCl, 0.24 M.

The addition of HCl was made for control purposes to determine the effect of Cl⁻ alone.

The Ru-doped crystals from several runs showed a consistent habit modification compared with undoped TGS [3]. However, on different occasions some degree of decomposition was noted in the solutions during growth with the production of a brown precipitate. The crystal products were slightly brown-green in colour and showed an internal bias which varied in different specimens, to a maximum of ~ 2 kV cm⁻¹, which is comparable with that obtained for TGS grown from 20% L-alanine doped solutions. Analysis indicated that the crystals showing the highest bias contained 10 ppm of Ru.

The reasons for the variable results obtained are thought to be due to the very complex and not well understood chemistry of Ru compounds. Commercial ruthenium red is not a simple substance and evidently degrades when added to TGS solutions. The reaction products vary —