Annual Technical Report
on
RESEARCH AND CRYSTAL GROWTH ON HIGH DIELECTRIC
CONSTANT MATERIALS FOR MM WAVE APPLICATIONS
ONR Contract #N00014-82-K-0266
ONR Work Unit #NR651-007
(Dr. R. Pohanka)
Submitted to
Office of Naval Research
CMR-84-4
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I. INTRODUCTION

This program has as its major aim the growth of single crystals of ferroelectric materials for mm wave device applications. The material requirements for this application are a high dielectric constant and low losses. Large non-linear effects are associated with ferroelectric materials operated in the temperature range just above or just below the Curie point $T_c$, and materials such as BaTiO$_3$ and KTN have been evaluated for possible applications in phase shifters and other devices in the mm waveband.

The materials initially selected for this investigation were (a) ferroelectric fluorides with the tetragonal SrAlF$_5$ structure, (b) Ba$_{1-x}$Sr$_x$TiO$_3$ solid solutions (c) CdIn$_2$Te$_4$. Our contacts with Hughes Research Laboratories suggested a declining interest in the latter material so we have concentrated on (a) and (b). This report summarizes recent work on these materials, and discusses some very recent work on a new family of ferroelectric materials based on ScTaO$_4$.

II. EXPERIMENTAL RESULTS

A. PbAlF$_5$

The SrAlF$_5$ family contains a number of interesting materials with ferroelectric transition temperatures around 300°C. There appears to be a one-to-one correlation between ferroelectricity and the occurrence of the tetragonal structure with space group I4. The nature of the ferroelectric transition is discussed by Abrahams et al. (1). SrAlF$_5$ is relatively difficult to grow as a single crystal, but is easier than other members in the series since it melts congruently. We were able to grow SrAlF$_5$ boules from which a single crystal almost 1 cm in size could be cut, but the relative permittivity is rather low, peaking at 22 according to (1).

The analogous lead compound, reported to have the PbAlF$_5$ stoichiometry (1), is of greater interest for mm wave applications since the maximum value of the relative permittivity is around 7000 (2). There is in fact controversy over whether this compound really has that composition, or should be Pb$_3$Al$_2$F$_{12}$, as suggested by Shore.
and Wanklyn (3). It is to be expected that Pb$_3$Al$_2$F$_{12}$ would be ferroelectric also since ferroelectricity has been observed in the Pb$_3$M$_2$F$_{12}$ family (including M = Ga) as reported recently (4). The phase diagram is also confused since Ravez and Dumora (5) report PbAl$_2$F$_8$, PbAlF$_5$ and Pb$_9$Al$_2$F$_{24}$ in addition to PbAlF$_5$, while Shore and Wanklyn (3) find Pb$_3$Al$_2$F$_{12}$ as the only compound in the system.

Our own attempts to resolve these anomalies have not been wholly conclusive. DTA experiments, even though performed rapidly, are subject to weight losses of about 10%. The results, however, are consistent with the phase diagram shown by Shore and Wanklyn, although we have found evidence for the Pb$_9$Al$_2$F$_{24}$ phase reported by Ravez. In long term annealing experiments, we have found evidence for the existence of the PbAlF$_5$ phase and in crystal growth experiments where non equilibrium conditions may prevail, the results suggest that the Pb$_3$Al$_2$F$_{12}$ incongruently melting phase perseveres.

The main focus of our work has been on attempts to grow high quality crystals of either phase for mm wave measurements, to check the permittivity data previously published (2) and to see whether the losses are low, as in SrAlF$_5$.

A summary of the crystal growth experiments performed to date is given in Table 1 (Code numbers omitted from this list refer to experiments in which only the synthesis from PbF$_2$ and AlF$_3$ was studied and a subsequent Bridgman growth experiment was not performed). A significant improvement in crystal quality was achieved by raising the Bridgman furnace temperature well above the DTA liquidus temperature to ensure complete melting prior to crucible lowering. Sample 15, grown from a composition 0.4 AlF$_3$ + 0.6 PbF$_2$, was fairly clear and transparent over most of its length, showing only traces of the solidification of eutectic liquid in the center of the crystal, a peculiar phenomenon. Cracking is the most severe problem encountered in our crystals to date, and is the major factor preventing the realization of at least 5x5x5 mm crystals. The boules are generally large grain polycrystalline, so the achievement of a single crystal at least during the earlier stages of growth would probably lead to a relative freedom from cracks. Reducing the temperature gradient
Table 1: Experiments on PbAlF₅ Crystal Growth by the Bridgman Method

<table>
<thead>
<tr>
<th>Code</th>
<th>Composition</th>
<th>Conditions</th>
<th>Appearance</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AlF₃ m/δ</td>
<td>PbF₂ m/δ</td>
<td>Tmax (°C)</td>
<td>dT/dy deg/cm</td>
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<tr>
<td>2</td>
<td>50</td>
<td>50</td>
<td>700</td>
<td>25</td>
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<td>850</td>
<td>45</td>
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during growth by the addition of an after-heater was found to lead to a deterioration in crystal quality.

A small crystal was cut from one of the better boules and is shown in Fig. 1(a). This crystal was initially twice as large as that shown but new cracks developed during cutting. Fig. 1(b) is a conoscopic figure which shows that the grain from which this crystal was cut grew with an orientation close to the c-axis. Dielectric constant measurements on this crystal gave a value of around 1800, changing only slowly with temperature.

The crystals contain inclusions in the form of small-diameter pipes which have been found to be metallic lead. These pipes are presumably caused by graphite inclusions in the melt which can result in reduction to the metal, with the evolution of fluorine gas. Use of a boron nitride crucible should eliminate this type of inclusion. Fig. 2a shows a section through a crystal which has been sliced to remove a crack-free region. Extensive cracking and lead 'pipes'. Fig. 2b shows eutectic inclusions.

The most serious defects in our crystals, however, are probably oxide and OH inclusions which are a general problem in fluorides. Our starting materials were found to contain 4.6 wt% oxygen in the case of AlF$_3$ and 0.6 wt% in the PbF$_2$. Reaction under HF has, in most of our past experience, been effective in removing oxide impurities and in yielding transparent, crack-free crystals, but it appears that stronger measures are necessary for this material. Vacuum fusion analysis revealed that sample #12 contained 0.31 wt% oxygen, and #15 contained 0.34 wt%.

Thermodynamic calculations indicate that heating in HF should be effective in removing PbO from PbF$_2$ but will not transform Al$_2$O$_3$ to AlF$_3$. We have therefore attempted to purify the AlF$_3$ by distillation, and oxygen analysis suggests that a single stage distillation removes about 80% of the oxygen from AlF$_3$. However, heating in HF was not found to be effective for removing oxygen from PbF$_2$. Our present strategy is therefore based on multiple distillation of AlF$_3$ in vacuum, and distillation of PbF$_2$ in HF.
Fig. 1(a) Single crystal of PbAlF$_5$ cut from a boule 1 cm in diameter (scale in mm).

(b) Conoscopic figure taken in the direction perpendicular to the face shown in (a).
Fig. 2 Defects in PbAlF$_5$ crystals
(a) cracks and metallic lead inclusions in a slice 1 cm in diameter (b) eutectic inclusions, also in a cracked region (100x).
Preliminary experiments have also been performed using COF₂ for purification. Thermodynamic calculations and discussions with M. Robinson of Hughes Research suggest that this is much more likely than HF to remove oxide and hydroxide from AlF₃. COF₂ is extremely expensive to buy as a cylinder gas and so we are generating it in-situ by the reaction between CO₂ and heated Teflon. A gas analyzer is being connected to the system so that the removal of anionic impurities can be optimized.

Some combination of these purification procedures under investigation should result in a purer material which appears to be necessary for the growth of larger, crack-free crystals.

The composition of the ferroelectric phase is still in doubt. Our own phase diagram studies support the Pb₃Al₂F₁₂ formula, but on the other hand, as indicated previously, solid state synthesis in sealed tubes produced samples which appeared more clearly single phase in the 1 PbF₂:1 AlF₃ sample. Microprobe analysis of grown crystals is strongly in favor of Pb₃Al₂F₁₂, in fact the Pb:Al ratio is closer to 2:1. This method is somewhat suspect because of the large difference in atomic number between Pb and Al, but we presently believe that the weight of evidence is in support of Pb₃Al₂F₁₂, analogous to Pb₃GaF₁₂ (4). We recently attempted to resolve this question conclusively using wet chemical analysis using the difference in solubility between PbSO₄ (42 mg/l) and Al₂(SO₄)₃ (313 g/l) in water at room temperature. Trial samples of PbF₂AlF₃ were dissolved in nitric acid and the lead sulphate precipitated with sulfuric acid, but the errors involved in collecting and drying the precipitate were too great for definitive answers to be obtained from this method for small samples. It is possible that both PbAlF₅ and Pb₃AlF₁₂ do exist, and that the stability is influenced by oxygen or OH concentration. Purification of the fluorides may favor a more definitive answer to this apparently simple but practically troublesome question. It will also permit us to develop the true binary phase diagram of the PbF₂-AlF₃ system in the region of these two compositions.
B. **BaTiO$_3$**

A number of BaTiO$_3$ crystals have been grown, mostly clusters of crystals on polycrystalline seeds. These experiments have led to a number of improvements to the furnace, to increase the vertical temperature gradient and to improve the monitoring and control of temperatures in the chamber. Four thermocouples are now used, measuring respectively the axial temperature just below the crucible, inside the seed crystal, on the melt surface about 3 cm from the axis and in the furnace wall close to the elements. The rate of cooling air flow through the seed holder can be regulated fairly well, but an improved arrangement utilizing a Mass flow controller is being installed to improve the precision and reproducibility of the rate of flow control, and hence of temperature control in this critical region near the seed crystal. Single crystal seeds will be used for future experiments.

C. **ScTaO$_4$**

Scandium tantalate ScTaO$_4$ was recently found to be ferroelectric (5) with a Curie point of 70°C and a maximum relative permittivity $\varepsilon_{22}$ of about 7500. These properties make it particularly interesting for a device operating at room temperature. It is monoclinic at room temperature, with the wolframite structure (space group P2/C). The original study (5) was made on small crystals grown by the flux method, but no information was available in the literature on whether ScTaO$_4$ can be grown from the melt.

We therefore attempted to grow a crystal in the form of a fiber using the laser-heated pedestal growth method. A source rod was fabricated from hot-pressed material and a clear fiber (Fig. 3) was grown after a few trial experiments. The melting point was found to be about 2300°C, and the material appeared to melt congruently. The crystal structure of this fiber was, however, found to be a new phase having the tetragonal zircon structure, with $a = 6.713$ Å and $c = 6.305$ Å. The unit cell volume is 1% greater than that of ScVO$_4$, which also has the zircon structure with $a = 6.78$ Å and $c = 6.12$ Å. ScVO$_4$ has been reported to be ferroelectric (6) with a Curie
Fig. 2. Single crystal fiber of ScTaO$_4$. 
point of 24°C and a peak relative permittivity of 680. It is therefore expected that the tetragonal form of ScTaO₄ will also be ferroelectric, and fibers will be grown for electrical measurements. A hot pressed sample of the wolframite phase had a relative permittivity of around 2200 at the published Curie temperature. We repeated the original flux growth experiment (5) and obtained somewhat larger crystals than those reported. Fairly large crystals could probably be obtained by scaling up, but the high cost of Sc₂O₃ is a handicap.

The zircon phase of ScTaO₄ transforms back to the wolframite structure on heating above 1400°C. The exact transition temperature has not yet been determined.

Scandium niobate ScNbO₄ also has the wolframite structure (7) with similar unit cell size to the tantalate, but its dielectric properties have not been reported. Samples of this material have been hot pressed and a single crystal was grown for the first time in fiber form. Unlike the tantalate, this material melts without a phase transformation and the fiber crystal was found to have the same wolframite structure as the source rod. By analogy with lithium niobate and tantalate, ScNbO₄ may have similar properties to ScTaO₄, and we believe that this whole family of materials is particularly exciting for future study.

Summary

A small clear crystal of PbAlF₅ was grown for dielectric constant measurement, and gave a value of ~ 1800, not changing substantially on passing through the expected Curie temperature. The main problem in preventing the growth of larger crystals is cracking, generally associated with polycrystallinity. Purification of the fluoride source materials to remove oxide and hydroxide contaminants is expected to result in larger crystals with fewer cracks. The weight of evidence favors the formula Pb₃Al₂F₁₂ rather than PbAlF₅ under conditions where O or OH contamination is present and non equilibrium conditions prevail.
The temperature distribution in the furnace used to grow barium titanate crystals now appears to be close to optimum, and satisfactory results have been obtained with polycrystalline seeds.

A new tetragonal phase of ScTaO$_4$ has been obtained by growing a single crystal fiber by the laser-heated pedestal method. A single crystal of ScNbO$_4$ has also been grown in the form of a fiber, possibly the first single crystal growth of this material. The ScTaO$_4$ family of materials appears very promising for ferroelectric studies.

References


