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Epitaxial Hexagonal Ferrites for Millimeter Wave Tunable Filters

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liquid phase epitaxial growth of strontium hexaferrite layers on these substrates by means of a lead oxide - boron oxide flux, and the characterization of these materials. Techniques were devised for fairly reproducible growth of hexaferrites which had linewidths substantially less than 100 Oe and which required fields of only about 7 K0e for resonance at 60 GHz. The best sample had a linewidth of 60 Oe, a significant improvement over previous epitaxial hexaferrites.
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ABSTRACT

This program has consisted of an investigation of the liquid phase epitaxial growth of hexagonal ferrites. The objective has been to obtain high quality single crystal layers of hexagonal ferrite which would be suitable for use in millimeter-wave tunable filters. The specific objectives were to determine the conditions required for preparation of ferrites which would give ferromagnetic resonance at frequencies in the range of 50 to 70 GHz using magnetic bias fields available with present technology and having resonance linewidths no greater than 50 Oe. The work consisted of the growth and preparation of gallate spinel substrate crystals, the liquid phase epitaxial growth of strontium hexaferrite layers on these substrates by means of a lead oxide - boron oxide flux, and the characterization of these materials. Techniques were devised for fairly reproducible growth of hexaferrites which had linewidths substantially less than 100 Oe and which required fields of only about 7 K0e for resonance at 60 GHz. The best sample had a linewidth of 60 Oe, a significant improvement over previous epitaxial hexaferrites.
INTRODUCTION

Over the past several years, great progress has been made in developing new and improved millimeter-wave components. However, relatively little attention has been paid to the needs for nonreciprocal devices. Perhaps the most promising approach toward meeting these needs is to use hexagonal ferrites. These ferrites have high magnetocrystalline anisotropy fields which, in effect, provide built-in biasing. The result is that ferrite components, similar to those used in microwave systems, can operate at millimeter-wave frequencies without the need for large external bias magnets. The key to realizing such components is to be able to prepare high quality hexagonal ferrites. This is the basic goal of the work reported here.

Hexagonal ferrites\(^1,2\) have been studied intensively for about 30 years. They have become commercially important in a number of applications for which a polycrystalline ceramic format is suitable. However, single crystals of high homogeneity and low defect density have been difficult to grow and fabricate. Thus, the development of devices which require single crystals has languished. Moreover, the inability to prepare crystals of high quality reproducibly has impeded the study of fundamental magnetic and crystallographic phenomena in these materials.

The research conducted under this contract has built upon the recently demonstrated LPE (liquid phase epitaxy) method for growing hexagonal ferrites in the form of single crystal layers on non-magnetic, transparent substrates\(^3-6\). The LPE method circumvents most of the obstacles encountered when hexagonal ferrites are prepared by conventional single crystal technology. The single crystal layer format is well suited to many device applications and is compatible with planar circuit designs. This format is also useful for measurement of fundamental properties, including magnetic domain structures which can be observed directly by the Faraday effect.

The objective of this program was to prepare, by the LPE method, single crystal hexagonal ferrites which are superior in quality to those grown by conventional methods. In order to have a more specific goal, superior quality was defined in terms of the requirements for low-linewidth millimeter-wave
tunable filters. This goal was chosen not only to direct the research toward
defined Army needs, but also to provide an opportunity to study such basic
phenomena as the origins of magnetic anisotropy and dissipative processes in
the hexagonal ferrites. The results of the program also would permit evalua-
tion of the use of LPE hexagonal ferrites in a variety of other millimeter-
wave devices such as power limiters, resonance (power) isolators, circulators
and frequency doublers. A recent Navy study\(^7\) pointed out the unique capa-
bilities of hexagonal ferrites in such devices. Since many of the device
designs employ the ferrite in the form of thin films or slabs, the LPE format
should be particularly suitable. Another potential advantage of the LPE format
is that the insulating substrate can be used as a dielectric waveguide. More-
over, it may be possible to deposit epitaxial layers of III-V semiconductor
on the same substrate\(^8\) to make multi-material monolithic circuits.

The Statement of Work for this research contract was divided into three
parts:

a. Grow and prepare nonmagnetic single crystals for use as substrates
   for epitaxial growth of hexagonal ferrites;

b. Deposit on these substrates, by LPE methods, hexagonal ferrite
   layers;

c. Determine substrate preparation and LPE deposition conditions which
   permit reproducible growth of hexagonal ferrite layers suitable for
   use in millimeter-wave tunable filters having operating frequencies
   in the range of 50 GHz to 70 GHz.

Suitability was defined as operation in the defined frequency range using
existing bias magnet technology and operation at these frequencies with a
ferromagnetic resonance linewidth no greater than 50 Oe.

**SUBSTRATE PREPARATION & CHARACTERIZATION**

All substrate crystals were grown by the flux method, also called slow
cooling. Attention was focused on gallate spinels and indium substituted
gallate spinels. The specific compositions were zinc gallate (ZnGa\(_2\)O\(_4\)),
magnesium gallate (MgGa\(_2\)O\(_4\)) and magnesium indium gallate (Mg[In,Ga]\(_2\)O\(_4\)).
These compositions were chosen because they are good dielectrics, the arrange-
ment and spacing of atoms on their (111) planes closely resemble the arrangement
and spacing on hexagonal ferrite basal planes, and our earlier work showed that these crystals could be grown successfully and would function as substrates for LPE of hexagonal ferrites. In the case of the magnesium indium gallate spinel, the lattice parameter and, therefore, the atomic spacing on the (111) planes, could be varied in a controllable manner by selecting the ratio of indium to gallium oxides in the starting mixture.

The flux used for substrate growth was a mixture of lead oxide and boron oxide. Typically, the mole ratio PbO:B₂O₃ was 5.2:1.0. Dissolved in this flux were the oxide constituents of the desired spinel. For the case of magnesium gallate, this would be MgO and Ga₂O₃. Although the mole ratio is 1:1 in the spinel, we used a slight excess of MgO, about 1.1:1.0. This is reported to give a more homogeneous crystal since it avoids formation of gallia-rich solid solutions.

In order to optimize the growth procedure, we measured the solubility of magnesium gallate in the lead oxide - boron oxide flux. We did this by preparing several melts which were identical in all respects except for the total concentration of MgO + Ga₂O₃. After melting in platinum crucibles, these melts were cooled and a small magnesium gallate spinel crystal was added to each. The crucibles were covered, heated to an initial temperature, 1200 or 1000°C, held for 24 hours, and then cooled fairly rapidly to room temperature. Survival of the spinel crystals was an indication that at the holding temperature the solution was saturated. In this way we determined that the solubility of magnesium gallate at 1200°C in our melts is slightly greater than 16 mole percent. This is the upper limit on solute concentration for the starting mixture when 1200°C is the initial temperature.

In order to get efficient growth of large, good quality crystals, we used a solute concentration (MgO plus Ga₂O₃) close to the solubility limit, a large crucible (250 or 500 ml), an initial soak which is sufficient to give complete dissolution (24 hours at 1200°C), a slow rate of cooling (0.5°C/hr) to a low termination temperature (~600°C), and localized cooling at the crucible bottom (by welding a platinum rod to the bottom and having the rod extend out of the furnace). Similar procedures were followed for the indium substituted magnesium gallate and for the zinc gallate. Although the growth process is
long, about two months, it entails very little labor. Crystals which were large enough to provide substrates ≥1cm in diameter were obtained with fairly good reproducibility.

In addition to the slow cooling method, we grew crystals by the top seeded solution growth (TSSG) method. In this case, similar solution compositions were used; but solute concentrations were reduced so that saturation occurred at temperatures around 1000°C. This enabled us to grow crystals at lower temperatures where evaporation of lead oxide is not a severe problem. Thus, we could keep the crucibles open and easily introduce a spinel seed crystal onto the top surface of the solution. By confining growth to a seed, we were assured of growing a single, large crystal. We grew several crystals by this method; enough to demonstrate its feasibility. However, the crystals grown by slow cooling were more than sufficient to supply the needs of this program. TSSG may be needed in the future to supply even larger crystals; however, direct growth from the melt, particularly for the relatively non-volatile magnesium gallate, may be preferred.

We reported our results on gallate spinel crystal growth by both the slow cooling and TSSG methods at a crystal growth conference; but we are withholding publication until we have more data.

Crystals were cut into slices oriented close to (111). The natural {111} facets were used as guides. The cutting, with a diamond impregnated wire saw, was followed by lapping with alumina slurry and polishing with colloidal silica. The polishing process was very similar to that used for polishing GGG (gadolinium gallium garnet). In order to check the effects of substrate misorientation from (111), orientations of some wafers were checked by x-ray back-reflection Laue patterns.

One polished wafer of magnesium indium gallate spinel was sent to G. Simonis at Harry Diamond Laboratories for measurement of transmission coefficients in the 90 GHz to 600 GHz range. As expected, the material showed very low losses.

Our previous x-ray diffraction analysis had shown that the quality of the flux-grown gallate spinel crystals was quite good. This was confirmed
for one of the polished magnesium indium gallate spinel substrates by means of an x-ray double crystal diffractometer. The diffraction peak, usually called a rocking curve, had a full width at half maximum of 0.55 minutes of arc. This is an order of magnitude wider than expected for a perfect crystal. X-ray reflection topographs showed that this peak broadening was associated with long range strains in the crystal. Probably, these long range strains were produced by slight variations in composition; variations in the indium: gallium ratio or variations in impurity (lead) incorporation. Such variations are not unusual in flux-grown crystals when the growth process covers a large temperature range. Under this interpretation the rocking curve width indicates that the lattice parameter varies by about 100ppm or about 0.001Å between the center and the periphery of the crystal. The topographs also revealed a few long, linear defects. Most likely these were dislocations. The density was less than 10 per cm².

To put these x-ray results in perspective, we can say that the substrate crystal quality is almost as good as GGG (gadolinium gallium garnet) and better than sapphire. For GGG, dislocations are seldom seen and the lattice parameter variation and rocking curve width are about half as big as for the spinel. Sapphire substrates have dislocation densities about two orders of magnitude greater and have rocking curve widths a little less (when the sapphire is carefully prepared to avoid long range strain).

HEXAGONAL FERRITE PREPARATION & CHARACTERIZATION

The most common of the hexagonal ferrites is barium hexaferrite, Ba₀·₆Fe₂₀₃. The crystal structure is that of the mineral magnetoplumbite, which essentially is Pb₀·₆Fe₂₀₃. Strontium, which is chemically similar to barium, can also form hexagonal ferrite. Most commercial ceramic hexagonal ferrites are barium, strontium, or mixed barium-strontium hexaferrites. Most of the reported work on single crystal hexagonal ferrites has dealt with the barium compounds. For the specific goal of a low-linewidth millimeter-wave tunable filter, any of these hexaferrite compounds should be satisfactory if the crystal quality is good.

Prior to this program, we had investigated LPE growth of barium hexaferrite³-⁶ and lead hexaferrite¹¹. The barium compounds gave lower linewidths
and, since they have somewhat higher magnetocrystalline anisotropy, also required lower bias fields than the lead compounds. On the other hand, the lead compounds seemed easier to grow; the LPE melt drained more readily from the layer surface and the ferrite nucleated more easily so that the layer tended to cover the substrate more completely. In some of our earliest work, we had grown barium hexaferrite from an LPE melt which contained PbO. That was an attempt to obtain better drainage. For this program we decided to try to grow strontium hexaferrite from an LPE melt containing PbO.

For simplicity, we can describe the LPE process as the growth of strontium hexaferrite (solute) from lead oxide - boron oxide flux (solvent). In effect, this emulates the successful LPE garnet (YIG) technology which employs this flux. In contrast to garnets, Pb atoms can be readily taken up into hexagonal ferrite crystals resulting, in our case, in a mixed strontium-lead hexaferrite. However, since the LPE method entails isothermal growth from a very large solution, the lead content should be uniform and not troublesome.

There were two other factors which influenced our choice of strontium hexaferrite. There had been reports of epitaxial growth of aluminum substituted strontium hexaferrite by a solvent evaporation method; and, of the three simple hexagonal ferrites, strontium hexaferrite has the highest anisotropy field as well as a high saturation magnetization so it should be best suited to millimeter-wave devices.

Although barium hexaferrite can be grown by LPE without using lead oxide, in essence by using a barium oxide - boron oxide flux, this is not possible for strontium hexaferrite if the required temperatures are to be kept reasonable. Our task was to determine first of all whether strontium hexaferrite could be grown from a PbO flux and, if so, to try to optimize the process. To begin, we prepared an LPE melt similar to the one we used for growth of barium hexaferrite from lead oxide - boron oxide flux, but with strontium carbonate in place of barium carbonate. (The carbonates, which decompose at the temperatures employed, are used as the sources of the barium and strontium oxides). The very first experiments yielded epitaxial hexagonal ferrite deposits on magnesium gallate spinel substrates. At 35 GHz, ferromagnetic resonance
was observed at applied fields of a few hundred oersted. The lowest linewidth, 24 Oe, was slightly less than the lowest previous value for any epitaxial hexagonal ferrite at this frequency.

This early result was encouraging. However, it merely showed that we could prepare epitaxial strontium hexaferrite of a quality similar to the barium hexaferrites which we had prepared previously. We knew that a good linewidth at 35 GHz did not imply a good linewidth at 50 GHz and above, because the 35 GHz measurement tends to show only the best regions of the sample. Also, if the sample composition were close to that of pure (lead-free) strontium hexaferrite, then we should not have observed resonance at 35 GHz because the anisotropy field would have been too high. Therefore, the sample probably contained a fairly high concentration of lead. Lower lead content would be preferred, since it would reduce the magnitude of the required applied magnetic field.

We then began a series of LPE experiments in which we kept the molar ratio of strontium oxide to lead oxide constant at 1:1 and tried different values of boron oxide concentration. In each case we started out with a fairly low concentration of iron oxide so that, by subsequent stepwise additions, we could determine the value of iron oxide concentration required for hexaferrite to be the primary crystallizing phase. We found that the optimum boron oxide concentration (for the 1:1 ratio of strontium oxide to lead oxide) corresponds to a lead oxide to boron oxide mole ratio of about 1.6:1.0. If the boron oxide concentration is appreciably higher, strontium borate tends to crystallize. If the boron oxide concentration is lower, the melting point of the LPE solution increases so that ferrite deposition requires higher temperatures. This can lead to problems of PbO evaporation and interdiffusion between the ferrite deposit and the substrate. So the 1.6:1.0 ratio was used in all subsequent experiments.

For the strontium, lead and boron oxide concentrations given in the preceding paragraph, hexaferrite begins to crystallize when the LPE melt contains approximately 12 mole percent Fe$_2$O$_3$. The quality of the hexaferrite improves as the iron oxide concentration is increased. We have not yet determined either the optimum or maximum iron oxide concentrations for hexaferrite deposition. (Nor have we explored the effects of varying the ratio of strontium oxide to
lead oxide). However, we have been able to produce epitaxial deposits of strontium hexaferrite (with as yet undetermined lead content) which exhibit better morphology and substantially lower linewidth at frequencies above 50 GHz than any previously reported epitaxial hexagonal ferrites.

All epitaxial hexagonal ferrite deposits on (111) gallate spinel substrate exhibit an hexagonal island or scale morphology. In the past, the island diameter was on the order of 0.1mm. For the strontium hexaferrite deposits prepared from the LPE melt described in the preceding paragraph, the diameters are 1mm or more. This is shown in Figure 1. Each island or scale is like an individual single crystal. Generally, at least one hillock is observed on each island. Many of the hillocks have prominent growth spirals. These features show that the islands are not perfect crystals.

Figure 2 shows power absorption from a piece cut from the same sample. The horizontal axis covers the frequency range from 57 to 60 GHz. This resonance, centered at 58.5 GHz for a field of 6.7 KOe, has a half-power linewidth of 70 Oe. The lowest linewidth we have observed for these materials is 60 Oe. The relationship between applied field and center frequency shows that the zero-field resonance frequency would be 40 GHz. This is about 5 GHz higher than for barium hexaferrite and indicates a film composition close to pure strontium hexaferrite.
Figure 1. Optical micrograph showing surface of strontium hexaferrite epitaxial layer. Field of view 1.2 mm by 1.6 mm.

Figure 2. Resonance absorption of epitaxial strontium hexaferrite sample. Center frequency 58.5 GHz. Half power linewidth 70 Oe.
INTERACTIONS WITH THE SCIENTIFIC COMMUNITY

The principal investigator attended the 1981 and 1982 INTERMAG Conferences with part of the travel expenses paid from contract funds. At the 1981 conference he presented a paper coauthored with L. R. Adkins. The paper, "Liquid Phase Epitaxial Hexagonal and Spinel Ferrites" included results obtained during the contract effort. The principal investigator also served as a session chairman at the conference. At the 1982 INTERMAG he served as a panel member for a workshop entitled "Application of Garnet and Ferrite Thin Films to Microwave Devices."

The principal investigator also attended the 6th Conference on Crystal Growth in June 1982 and was coauthor of the paper presented by F. S. Stearns. That paper, "Growth of Large Gallate Spinel Crystals from Lead Oxide - Boron Oxide Flux," described the substrate growth portion of the contract effort. The principal investigator was a participant in the ARO Workshop on Short Millimeter Wave Nonreciprocal Materials and Devices held at ARO in November 1981. Contract funds were not used for participation in the crystal growth conference or the ARO workshop.

Although no articles have been submitted for publication, papers describing substrate growth and LPE growth of the strontium hexaferrite are planned.

Conference and workshop attendance provided opportunities to meet with other scientists and engineers working in fields related to the contract effort, including key technical people from Army laboratories. As has been mentioned already, a sample gallate spinel substrate was provided to G. Simonis of Harry Diamond Laboratories for evaluation of dielectric properties. In addition, several samples of epitaxial hexagonal ferrite were provided to A. Tauber of Fort Monmouth for evaluation of millimeter-wave properties. Extensive discussions were held with F. Rothwarf of the Army European Research Office, J. C. Sethares of the Air Force RADC, C. Vittoria of NRL.
PERSONNEL

The scientific personnel who contributed to this program were:

Howard L. Glass, who served as principal investigator and program manager and who performed the LPE ferrite growth experiments and x-ray and optical characterization.

Larry R. Adkins, who carried out the millimeter-wave characterization.

Frederick S. Stearns, who performed the substrate crystal growth experiments and the substrate cutting and polishing.

Daniel Medellin developed the substrate polishing procedures.
REFERENCES