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COLORADO UNIV BOULDER DEPT OF ELECTRICAL ENGINEERING
SINGLE CRYSTALS OF YTTRIUM AND RARE EARTH GALLIUM PEROVSKITES F--ETC(U)
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Final Report

Single Crystals of Yttrium and Rare Earth Gallium
Perovskites for Use as Substrates for Bubble Domain
Iron Perovskites.

~~Office of Naval Research Contract Numbers~~

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INTRODUCTION

The project had certain primary goals:

1. To determine whether the rare-earth gallium perovskites could be made at high temperature.
2. To determine whether crystals of rare earth gallium perovskites could be grown to serve as substrates for rare earth iron perovskites which could be useful for "bubble domain" devices.
3. To determine properties of hexagonal rare earth gallium compounds discovered in the course of the work.
4. To grow rare earth iron perovskite films for possible use in bubble domain devices.

RESULTS

1. A paper (S. Geller, P. J. Curlander and G. F. Ruse, "Perovskite-Like Rare Earth Gallium Oxides Prepared at Atmospheric Pressure", Mat. Res. Bull. 9, 637-644 (1974) has been published giving the results pertinent to the first goal. The abstract from that paper follows:

The rare earth gallium oxide perovskites, RGaO_3 , $\text{R}=\text{Sm-Er}$, have been synthesized at normal pressure, quenched from temperatures exceeding 1650°C . Lattice constants of these and of newly prepared LaGaO_3 , PrGaO_3 by solid state reaction have been measured. The c and a vs. atomic number plots are characteristic of the lanthanon contraction with cusps at gadolinium.

2. Crystals of the very high temperature RGaO_3 perovskites suitable as substrate crystals could not be grown. This was ascertained with very few experiments as briefly described in the publication under 1. We therefore decided to try to grow NdGaO_3 which is stable over a wide temperature range. At first, considerable trouble was encountered with twinning and cracking. However, the difficulties were overcome, and crystals suitable for substrates have been grown. A paper (G. F. Ruse and S. Geller, "Growth of Neodymium Gallium Oxide Crystals", J. Crystat. Growth, 29, 305-308 (1975)) has been published.
3. As indicated above, new hexagonal RGaO_3 compounds were found in the course of the high temperature experiments.

Crystals large enough for a crystal structure determination were obtained and the structure was determined (S. Geller, J. B. Jeffries and P. J. Curlander, "The Crystal Structure of a New High-Temperature Modification of YGaO_3 ", Acta Cryst. B31, 2770-2774 (1975)). Attempts were made to switch the polarization of a crystal, but either the material is not ferroelectric or the crystal was too small for reliable conclusions. Crystals large enough for such reliable measurements have not been obtained, though some attempts were made.

4. Much of the work was aimed toward accomplishing the fourth goal which is the most important one. At least part of the reason for not attaining this goal to date is inadequate funding both for equipment and for manpower.

Inasmuch as we have not written anything for publication on this subject, we give a brief final report on it now.

Experiments are carried out in a vertical tube resistance-heated furnace which gives a nearly constant temperature zone where the crucible containing the film ingredients and flux is situated.

The starting material in the crucible consists of

0.0275 moles Sm_2O_3

0.0225 moles Tb_2O_3

0.05 moles Fe_2O_3

0.0807 moles B_2O_3

1.259 moles PbO

Several fillings and "melt-downs" are required to get this material

into the crucible which, after all the "melt-downs", is three-fourths full.

The NdGaO_3 substrate crystals are cut with a diamond saw and polishing is done with $1\mu \text{Al}_2\text{O}_3$, followed by Syton polishing.

The substrate is mounted horizontally on a Pt wire holder designed so that there is minimum contact with the substrate crystal. The Pt holder is also used as a stirrer; it can be rotated at speeds up to 100 rpm.

Prior to a run, the crucible and contents are heated to 1100°C and held at this temperature for about 8 hr. The furnace is then cooled slowly to the run temperature and held there for approximately 2 hr. before the substrate is dipped into it.

When the desired temperature is attained by the crucible and contents, the substrate is slowly lowered to a position approximately 2 cm. above the melt surface to preheat it. Preheating times from 15 sec to 15 min have been tried. The longer the preheating period, the more the crystal is attacked by the PbO vapors. Preheating periods that are too short can result in thermal shock of the substrate crystal and spontaneous spurious growth. The preheating temperature is close to that of the crucible contents. Following the preheating of the substrate, it is quickly immersed in the melt while rotating at 100 rpm. The run is terminated by raising the crystal to the region just above the crucible and spinning off the adhering flux. The sample is then raised to a cooler region. Excess flux is removed in 50% HNO_3 .

Thus far, reproducibility has not been attained because of PbO loss. Most films are single crystal as ascertained by Laue X-ray photography and have the sought composition $\text{Sm}_{0.55}\text{Tb}_{0.45}\text{FeO}_3$, as ascertained by X-ray powder diffraction photography of the stripped films. Growth temperatures must be changed with the increasing age of the melt because the saturation temperature increases as PbO is lost by evaporation. The range of growth temperatures has been 950 to 1100° C. A method for making up the PbO loss would certainly be advantageous, but this is virtually impossible with our present equipment.

The quality of the epitaxial layer of the orthoferrite is strongly dependent on the preheating step. For the shorter preheating periods, the crystals are first etched in H_3PO_4 at 350° C for 5 min. This results in a chemically polished surface.

Most experiments have given films which are too thin to support bubble domains. The short "lifetime" of the melt makes it difficult to determine growth parameters, but this must eventually be done for this system.