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BORON OXIDE-LEAD OXIDE ETCHANT AND ETCHING PROCESS

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9 Claims. (Cl. 156—17)

This invention relates to a method for etching single crystals of garnet, spinels, orthoferrites and corundum and to the novel etchant employed.

More specifically, this invention is directed to the use of a boron oxide-lead oxide mixture as an etchant to supplement the usual mechanical polishing procedures for the materials discussed above.

The resonance lines of single crystal material are much narrower than those found in the polycrystalline material, this property forming the basis for the types of microwave devices described in copending applications Serial Number 778,352, filed December 5, 1958, now United States Patent 3,016,495, and Serial Number 774,172, filed November 17, 1958, now United States Patent 3,013,229. The practice of this invention results in substantial narrowing of line width in these materials as well as removal of strain, thus, permitting observance of strain-free domain patterns. Removal of strained surface from non magnetic crystalline material may achieve other desiderata. In corundum, of interest as a host lattice material for maser use, the purpose may be primarily improvement of energy transmission or reflection at the surface. Other objectives are known to those skilled in the art.

Recognizing the obvious advantages of etching a polished surface, the prior art has done extensive research with a view to finding a suitable etchant for these materials. In general, strong acids, such as sulphuric acid have been used. However, this type of treatment has produced pitting of the surface to such an extent that it produces a crystalline surface, generally inferior to that prepared by careful mechanical polishing.

It has been discovered that a mixture of boron oxide and lead oxide in critical proportions can be used effectively as an etchant for single crystals of garnet, spinel ferrites, orthoferrites and corundum without the attendant problems discussed above.

The novel etching procedure is carried out by using a boron oxide-lead oxide etchant in which the weight ratio of these ingredients is within the range of 0.9:10 to 1.1:10 in that order. The preferred ratio is 1:10. Appreciably increasing the boron oxide content results in the formation of crystalline material of the formula $4PbO \cdot B_2O_3$ and decreasing the boron oxide content results in increasing the viscosity and so narrowing the feasible temperature range.

Etching is generally conducted at a temperature in the range of 500–800° C., the higher temperatures in the range being feasible for thicker sections of the order of 10 mils and up, whereas etching with a view to ultimately producing a section of the order of 2 mils in thickness is carried out at temperatures approaching 500° C. Due to the differences in solubility the materials etched have slightly varied preferred etching ranges. However, such variations do not cause pitting over the temeprature range of 500–800° C. Temperature ranges within the 500–800° C. limits are desirably employed depending on the solubility of the material being etched. Thus, for example, yttrium iron garnet is desirably etched within the range of 550–700° C. whereas gadolinium iron garnet is etched effectively at temperatures of the order of 500–700° C. The orthoferrites are generally etched over the temperature range of 525–700° C. and the ferrites from 550–700° C.

With regard to the etching of corundum, the same general considerations apply as discussed above for etching garnets, spinels and orthoferrites. However, for economically feasible etching rates the temperatures employed are generally within the range of 700–800° C.

Applicant's etchant is generally used for the purpose of obtaining thin plate specimens, however the utility of the etchant is not so limited and it may be used to produce smooth unstrained surfaces of any configuration. It has long been recognized that measured line width of yttrium iron garnet and other magnetic materials decreases as surface uniformity is improved, so resulting in the practice of finer and finer mechanical polishing. The use of the etchant described herein removes strained surfaces resulting even from such refined techniques and, accordingly, decreases line width. The measurement of line width in magnesium ferrite in spherical configurations has resulted in a measured line width appreciably less than any previously recorded for this material, namely, of the order of 4 to 5 oersteds as compared to about 14 oersteds previously.

The etchants of this invention are also useful for obtaining rectangular hysteresis loops. The squareness ratio in the hysteresis loop is known to be a function of configuration, being commensurate with a hollow configuration such as toroids or rectangular picture frame structures. The etchants are useful, not only in producing these configurations but also in assuring absence or removal of strained surfaces which otherwise impair the squareness ratio.

Examples of the application of the present invention are set forth below. They are intended merely as illustration and it is to be appreciated that the methods described may be varied by one skilled in the art without departing from the spirit and scope of the present invention.

The examples are in tabular form for convenience and brevity. Each example in the table is to be considered separately since each set of data was obtained in a separate process. The procedure followed in each of these examples is as follows:

The starting ingredients are weighed into a platinum crucible and heated to complete solution, generally 450° C. It is desirable to include the crystal to be etched with the powder before melting so as to minimize thermal shock and this practice has been followed in the examples set forth below. When the material has become molten an agitating means is employed to assure uniform etching of all surfaces and so avoid concentration gradients due to the otherwise diffusion limited process. Agitating may be brought about by use of an inserted stirrer, or the entire crucible and contents may be agitated as by a vibrating or rotating platform. Following the agitation the melt temperature is increased to the desired eching temperature, 600–700° C., and is maintained at this temperature for the desired time. This desired time period is determined empirically by freezing content and flux and by visual observation of the plate thickness. The etching rate may then be calculated on the basis of this observation.

The crucible is then removed from the source of heat and the melt allowed to cool. A clear, transparent yellow glass with the crystal imbedded therein results. The resultant crystal may be examined without removing it from the crucible in order to determine if the desired amount of etching has occurred. If not, the glass may be remelted and etching continued.

When the desired state has been reached, the entire crucible may be placed in a solution of, for example, concentrated nitric acid and water in the proportion of 1:4 by volume. This dissolves the glass and allows the crystal to fall free. The nitric acid-water solution may also be

heated in order to accelerate the solution of the glass. Alternate procedures, as removal of molten etchant prior to freezing, or substitution of other solvents, are suitable.

Table

Example	Etchant	Crystal	Temperature of Etching, Degree Centigrade	Domain Pattern
1	H_2SO_4	Yttrium iron garnet ($Y_3Fe_5O_{12}$)	675	Pitting observed. Domain pattern not observed due to strain.
2	None—Crystal was Mechanically Polished.	do		Obscure due to strain.
3	B_2O_3—PbO, 1:10	do	675	Strain free domain pattern observed.
4	B_2O_3—PbO, 1:10	Gadolinium iron garnet ($Gd_3Fe_5O_{12}$)	600	Do.
5	B_2O_3—PbO, 1:10	Holmium Orthoferrite ($HoFeO_3$)	675	Do.
6	B_2O_3—PbO, 1:10	Magnesium Ferrite ($MgFe_2O_4$)	675	Do.
7	B_2O_3—PbO, 1:10	Corundum (Al_2O_3)	750	Non-magnetic so no domain pattern; however, surface perfection observed visibly.

While the invention has been described in detail in the foregoing description, the aforesaid is by way of illustration only and is not restrictive in character. The several modifications which will readily suggest themselves to persons skilled in the art, are all considered within the broad scope of this invention, reference being had to the appended claims.

What is claimed is:

1. The method of etching single crystals of a material consisting essentially of at least one member selected from the group consisting of synthetic garnets, ferrites, corundum and orthoferrites which comprises heating said material together with a mixture of lead oxide and boron oxide to a temperature in the range of 500–800° C., thereby forming a melt, cooling the said melt until the said mixture solidifies with the crystal imbedded therein and dissolving the solidified mixture.

2. The method of claim 1 wherein the weight ratio of boron oxide to lead oxide is within the range of 0.9:10 to 1.1:10.

3. The method of claim 1 wherein the weight ratio of boron oxide to lead oxide is approximately 1:10.

4. The method of etching a single crystal of yttrium iron garnet which comprises heating said material together with a mixture of lead oxide and boron oxide to a temperature in the range of 550–700° C., thereby forming a melt, cooling the said melt until the said mixture solidifies with the crystal imbedded therein and dissolving the solidified mixture.

5. The method of etching a single crystal of gadolinium iron garnet which comprises heating said material together with a mixture of lead oxide and boron oxide to a temperature in the range of 500–700° C., thereby forming a melt, cooling the said melt until the said mixture solidifies with the crystal imbedded therein and dissolving the solidified mixture.

6. The method of etching a single crystal of holmium orthoferrite which comprises heating said material together with a mixture of lead oxide and boron oxide to a temperature in the range of 600–700° C., thereby forming a melt, cooling the said melt until the said mixture solidifies with the crystal imbedded therein and dissolving the solidified mixture.

7. The method of etching a single crystal of magnesium ferrite which comprises heating said material together with a mixture of lead oxide and boron oxide to a temperature in the range of 600–700° C., thereby forming a melt, cooling the said melt until the said mixture solidifies with the crystal imbedded therein and dissolving the solidified mixture.

8. The method of etching a single crystal of corundum which comprises heating said material together with a mixture of lead oxide and boron oxide to a temperature in the range of 700–800° C., thereby forming a melt, cooling the said melt until the said mixture solidifies with the crystal imbedded therein and dissolving the solidified mixture.

9. The method according to the procedure of claim 1, wherein the said solidified mixture is dissolved by a mixture of nitric acid and water.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,063,886 November 13, 1962

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 3 and 4, in the table, fourth column, line 1 thereof, for "675" read -- 275 --.

Signed and sealed this 14th day of May 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents