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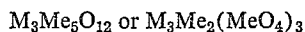
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PROCESS OF GROWING SINGLE CRYSTALS

Joseph P. Remeika, Berkeley Heights, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York
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This invention relates to a method of growing single crystals of synthetic garnet, orthoferrites and ferrites in a flux comprising lead oxide and boron oxide.

The synthetic garnet materials considered here can be represented by the formulas



where O is oxygen, Me is a trivalent metal and M is yttrium or one of the rare earth elements of atomic number between 62 and 71 or a mixture of these rare earth elements with each other or with yttrium. Me may be trivalent iron or trivalent iron mixed in part with at least one of the elements of gallium, aluminum, scandium, chromium or cobalt.

The orthoferrites considered can be represented by the formula $XFeO_3$ where Fe is iron, O is oxygen and X may be yttrium, lanthanum, praseodymium, neodymium, or one of the rare earth elements of atomic number between 62 and 71.

The ferrites considered here are mainly magnetic spinels. However, other materials of the spinel structure may also be prepared according to the present invention. Magnetic spinels prepared from the combined lead oxide-boron oxide flux include: magnesium, nickel, cobalt, aluminum, zinc and cadmium ferrites. Non-magnetic spinels prepared include magnesium aluminum and magnesium gallium.

In recent years considerable work has been done in the production of spinel ferrites and many processes are now well known in the art. Generally, ferrites are produced by mixing oxides of selected metals and heating the mixture to a given temperature at which a reaction between the oxides takes place. The mixture is then cooled, ground, and pressed into a suitable shaped and sintered.

Single crystalline magnetic ferrites have been crystallized in the prior art from a lead oxide flux as described in U.S. Patent No. 2,848,310, granted to J. P. Remeika on August 19, 1958.

The synthetic garnets described above are termed "garnets," because they possess the cubic structure of the mineral garnets such as grossularite, $Ca_3Al_2(SiO_4)_3$.

As is well known in the art, single crystals of ferrimagnetic material show enhancement of certain magnetic properties associated with the polycrystalline material. In particular, the resonance lines of single crystal materials are much narrower than those found in the polycrystalline material, this property forming the basis for the types of microwave devices described in copending application Serial Number 778,352, filed December 5, 1958, now U.S. Patent No. 3,016,495, and Serial Number 774,172, filed November 17, 1958, now U.S. Patent No. 3,013,229. A convenient prior art method of producing such single crystals consisted of combining the reactants in proper proportions with a flux consisting of lead oxide, heating the mixture to form a homogeneous liquid, and forming the single crystals from a molten bath by standard crystallization procedures. This technique is discussed in detail in copending application Serial Number 655,955, filed April 30, 1957, now U.S. Patent No. 2,957,827.

The present invention embodies the same general procedures as the aforementioned crystal growing methods with the exception of the flux employed. The present in-

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ventive method utilizes a flux initially comprising lead oxide and boron oxide. The use of such a flux is advantageous in several respects, the most important being the increased solubility of constituent materials which permits the process to be operated at lower temperatures than the prior art. Further advantages include increase in yield and crystal size.

An important aspect of applicant's invention lies in the use of specific flux ratios, i.e., critical ratios of lead oxide to boron oxide. In the growth of the garnet structures discussed above, it is essential that the weight ratio of boron oxide to lead oxide be within the range of 1:9 to 1:14 whereas in preparing orthoferrites and spinel ferrites the range of 1:18 to 1:22 is required.

The general operating procedures vary for growth of the materials falling within the scope of the three categories discussed above. Accordingly, each procedure is considered individually.

GARNETS

In growing the crystals of the garnet structure, it is desirable to include as much boron oxide as possible in the combined flux and so secure the greatest possible solubility. In the growth of the garnet structure discussed herein, borate formation is the most important consideration in determining a maximum boron content. It has been found that use of a ratio of boron oxide to lead oxide of greater than about 1 to 9 results in formation of borates resulting in increased difficulty of separation of this material from the desired crystal. Studies on the growth of yttrium iron garnet with various ratios have extended down to 1 to 14, at which there is a noticeable decrease of solubility of yttrium iron garnet in the flux. There is no objection to further decreasing the boron content in the flux, although this results in decreased solubility. The preferred range is from 1:9 to 1:11. An optimum range has been found to correspond to the approximate ratio of 1 to 10.

The general procedure for crystallization processes involving the garnet systems employs 1300° C. as the upper limit of temperature. This limitation is set by reason of considerations pertaining to volatility of ingredients in solution, changing composition of the flux, as well as by reactions with crucible materials, such as platinum, at temperatures substantially in excess of this limit and for various practical reasons such as apparatus limitations. The lower temperature limit of the system during crystallization in the yttrium iron garnet and gadolinium iron garnet systems is determined by the observed re-solution of these materials in the solvent at temperatures substantially lower than about 1000° C., although this limit is determined by a most favorable flux composition and is somewhat increased by varying from this optimum. So, for example, use of a boron to lead ratio substantially different from 1 to 10 results in an increase of this minimum figure to as high as of the order of 1050° C. Due to this re-solution observed at temperatures below this minimum it is necessary in the growth of garnet structures in this system to remove all the liquid portion of the flux at about this temperature. It is possible to avoid re-solution by rapid quench of the flux from this minimum temperature to a complete solidification, so permitting acid separation where desirable. This re-solution phenomenon is common to the use of the orthodox lead oxide flux.

Optimum cooling rates over the crystallization range of from about 1300° C. to 1000° C. are determined by the usual criteria, the faster the rate of cooling, the greater the number of nucleation centers with a consequent decrease in crystal size, and vice versa. Cooling rates may vary from as low as 2° C. per hour or lower to as high as 10° C. per hour. It is generally desirable to cool as slowly as possible to secure the largest possible crystal

size and consequently a cooling rate of as low as $\frac{1}{2}^{\circ}\text{C.}$ per hour is most desirable. Particularly, where lower cooling rates are used, it is desirable from an economic standpoint to more rapidly cool from the initial high temperature of 1300°C. down to the temperature at which nucleation is first observed. For the usual situation, using the preferred 1 to 10 flux and a nutrient concentration close to the preferred value, this initial nucleation occurs at 1215°C.

Ideal nutrient concentration increases with increased boron. It is desirable for a 1 to 10 flux to operate at the approximate nutrient flux weight ratio of 1 to 2. However, variations over the range of ratio may be used from 1:1.8 to 1:2.2. Operation with the lesser nutrient concentration (1:2.2) results in the initiation of nucleation at a somewhat lower temperature, and since it has little effect on the minimum (dependent on re-solution temperature) results in an overall decrease in the temperature range of crystallization, with a resultant decrease in yield. Operation at a more concentrated ratio (1:1.8) results in an increase in the number of nucleation centers for a given cooling rate, with a consequent loss in control, and since it increases the resolution minimum (to the order of 1050°C.) may not result in a yield commensurate with the increased concentration of starting ingredients. A further danger of operating at a higher nutrient concentration is the observed increase in the number of crystal clusters which are separated only with difficulty and with attendant further loss in material.

The formula for yttrium iron garnet is $\text{Y}_3\text{Fe}_5\text{O}_{12}$, so indicating a molecular ratio of three parts of yttrium oxide to five parts of iron oxide (weight ratio of 6.8:8.0). The optimum observed weight ratio of starting ingredients, however, on which the above figures are based, is 8.0:11.0. This excess of iron oxide is necessary to keep the yttrium iron garnet in equilibrium over the crystallization range. Operation with the ratio indicated by the stoichiometric materials results in a decrease of yield of the order of 30 percent. The use of an excess of yttrium oxide results in the formation of yttrium orthoferrite and yttrium borates as the stable phase and virtually no yttrium iron garnet is produced. The absolute limit at one end of the range corresponds with the stoichiometric ratio of yttrium orthoferrite, i.e., 11.0 yttrium to 8.0 iron. The preferred range is of the order of from 7.9 yttrium to 11.1 iron, to 8.1 yttrium to 10.9 iron.

For the usual microwave application, where one is interested in adding small amounts, up to 1 percent, of one or more rare earths, all of the above considerations apply. Since a certain amount of the additive remains in the flux after removal of the product it is necessary to include an excess of the order of 100 percent. So, where it is desired to produce an yttrium iron garnet crystal containing $\frac{1}{100}$ percent of gadolinium it has been found desirable to include $\frac{2}{100}$ percent in the flux based on the given amounts of starting ingredients. Reasons for making such substitution are to obtain variations in line width and magnetic resonance, etc. The preparation of crystalline compositions of the entire range intermediate the two materials, yttrium iron garnet and gadolinium iron garnet, are feasible. Where the additive material is to be included in large amounts, substantially above the order of 10 percent, flux ratio and nutrient to flux ratio will vary slightly. Such variations are predictable on the basis of the difference in optimum conditions that apply to the growth of the end compositions.

In the growth of gadolinium iron garnet the considerations discussed relative to yttrium iron garnet apply. Accordingly, the boron to lead ratio in the flux and also the preferred ranges discussed are suitable. The maximum temperature of 1300°C. is the same for the various reasons described. The gross nutrient to flux ratio is approximately the same as the for yttrium iron garnet. The preferred range is of the order of from 0.5:1.1 to

0.7:1.1. The main difference in the two systems results from the increased solubility of gadolinium iron garnet in the flux, so resulting in initial nucleation at a lower temperature for the same starting amounts as for the yttrium iron garnet system. However, there is a further advantage in the gadolinium system in that re-solution is not a significant factor until about 925°C. for the ideal flux ratio (as compared with 1000°C. for yttrium iron garnet), so resulting in an extension of the range of crystallization at the lower temperature end. This increase in temperature range of crystallization favors larger yield and larger crystal size.

Other garnet materials which have been prepared by this method include; yttrium gallium garnet, gadolinium gallium garnet, erbium iron garnet, ytterbium, and all of the rare earth iron garnets from samarium to lutecium. Other substitutions including partial substitution of up to 50 percent gallium for iron have been made in the yttrium iron garnet system. All conditions discussed above are suitably used in the growth of any of the rare earth garnets.

It is also possible to introduce aluminum into a garnet system. Such substitutions are suitably carried out by the method as set forth herein since aluminum oxide is soluble in the boron-containing flux. Yttrium iron garnet containing aluminum has been prepared as discussed below.

Examples of the application of the present invention are set forth below. They are intended merely as illustrations and it is to be appreciated that the processes 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 set of data in Table I is to be considered as a separate example, since each set of data was obtained in a separate process. The procedure followed in each of the examples is as follows:

A mixture of the starting materials is weighed into a 100 cubic centimeter platinum crucible and sealed with a platinum lid. The crucible is next placed into a horizontal globar furnace with a silicon carbide muffle and a mullite floor plate. For expediency, the furnace may be preheated to 1300°C. The crucible, together with its contents, is then permitted to attain a temperature of 1300°C. and is maintained at this temperature for a period of eight hours. For charges of the order of 500 grams it has been found helpful to stir the mixture and so assure complete solution. Without stirring, in a charge of this size, it is observed that stratification of the nutrient materials occurs at the top of the melt which is caused by the large differences in densities of nutrient and flux.

Controlled cooling at the rate of 2° per hour from the maximum of 1300°C. is then commenced by a controlled energization of the furnace. This program is continued until the re-solution temperature is reached. At this point, the crucible is removed from the furnace and the still liquid portion is poured off. After pouring off the liquid, the crystals still in the crucible are permitted to cool. This is tantamount to an air quench, cooling taking of the order of one hour to reach the ambient temperature.

The crucible is then immersed in a vessel containing a dilute solution of nitric acid and water, of the order of 50 percent by volume. The acid cleaning procedure is continued until all flux residue has been removed from the crystals. Under ordinary circumstances, acid cleaning at room temperature takes of the order of three hours, although this is variable, being dependent on the amount of residue, the size of the charge and the number of clusters. It is found expeditious to carry out the acid cleaning at temperatures approximating the boiling point of the acid solution. Subsequent to this, the acid solution is poured off, the crucible removed from the container and the crystals washed in three successive rinses of boiling distilled water. Following the water washing, the crystals

are dried by air-drying at room temperature. The resultant crystals were chemically analyzed and magnetic measurements were made on the washed product. These measurements, not considered to be within the scope of this disclosure, were in conformity with observed magnetic properties on other specimens of these compositions.

Table I

Ex.	Starting ingredients (gms.)		Flux composition		Product	Yield (gms.)	Crystal size maximum dimensions (cms.)
			PbO (gms.)	B ₂ O ₃ (gms.)			
1	Fe ₂ O ₃	22	80	8	Yttrium iron garnet..... (Y ₃ Fe ₂ O ₁₂)	9.3	½
	Y ₂ O ₃	16					
2	Fe ₂ O ₃	26	80	8	Gadolinium iron garnet..... (Gd ₃ Fe ₂ O ₁₂)	13.0	1
	Gd ₂ O ₃	21.7					
3	Ga ₂ O ₃	18.76	80	8	Gadolinium gallium garnet..... (Gd ₃ Ga ₂ O ₁₂)	13.0	¾
	Gd ₂ O ₃	15.20					
4	Fe ₂ O ₃	26	80	8	Ytterbium iron garnet..... (Yb ₃ Fe ₂ O ₁₂)	12.2	¾
	Yb ₂ O ₃	28					
5	Fe ₂ O ₃	20.0	80	8	Yttrium erbium iron garnet..... (Y ₁ Er) ₂ Fe ₂ O ₁₂	10.2	¾
	Y ₂ O ₃	8					
	Er ₂ O ₃	8					
6	Ga ₂ O ₃	13.0	80	8	Yttrium gallium iron garnet..... Y ₃ (Ga _{4.95} Fe _{0.05})O ₁₂	10.1	¾
	Y ₂ O ₃	10.0					
	Fe ₂ O ₃	0.5					

RARE EARTH ORTHOFERRITES

The prior art work on spontaneous nucleation with rare earth orthoferrites was carried out in a lead oxide flux. As in yttrium iron garnet, an advantage is realized in using a combined lead oxide-boron oxide flux from the standpoint of yield, typical improvement being of the order of at least two to one. A striking feature realized by the use of the combined flux is the increase in crystal size, which is a result of the decreased viscosity of the system, resulting, at least in part, from the fact that the mixed flux is a liquid glass. Typically, the increase in crystal size, by weight, is of the order of five times, crystals of yttrium orthoferrite of rectangular configuration, 1 x 1 x 2 centimeters being obtained in the combined flux, as compared with ½ x ½ x 1 centimeter in the PbO₂ flux. As in the lead oxide flux, orthoferrites based on lanthanum, praseodymium, and neodymium are somewhat smaller than the other orthoferrites, the same increase in crystal size being realized, however, by use of the combined flux. Orthoferrites which have been produced in the combined flux are: yttrium, lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium. All of these materials are transparent with the exception of praseodymium and neodymium.

These materials may be modified by inclusion of small amounts of additional ingredients, such as in the yttrium iron garnet system. By analogy again, the combined flux is uniquely suitable for addition of aluminum as a modifying ingredient. Such modification may be carried out, for example, for the purpose of improving light transmission. These materials evidence interesting magnetic properties.

The domain boundaries move for applied fields of less than 1 oersted, however, approximately 50 oersteds are required to magnetize the crystals to saturation. When saturated, crystals as large as 0.2 x 0.2 x 0.1 inch remain single domains. Fields of approximately 2500 oersteds are then required to reverse the first magnetization on the single domain crystals.

The preferred flux composition for the orthoferrites and also the spinels is at the ratio of 1 to 20. The range of 1:18 to 1:22 is considered to define the exclusive useful operating flux compositional range for this system. Use of appreciably greater ratios results in borate formation with the attendant difficulty of separation of final product, as discussed above in connection with the garnet system. Use of appreciably lesser ratios simply results in decreased solubility and so puts a further limit on yield. It is esti-

ated that a change in the ratio of from 1:20 to 1:22 decreases the yield by about 30 percent.

The orthoferrite system has a much greater temperature range of stability than does the garnet system. It has, therefore, been found unnecessary to use other than stoichiometric amounts of starting ingredients, so indicat-

ing equal molecular amounts of rare earth oxide and Fe₂O₃. The preferred gross nutrient to flux ratio is 1 to 3, with a preferred range encompassed by the ratio limits of 1:2.8 to 1:3.2. As in the discussion relative to the garnets, this range consideration is based on the temperature limits there used, i.e., an upper temperature limit of the order of 1300° C. Use of higher temperatures is again disadvantageous resulting in loss of boron oxide from the flux, and also by reason of apparatus and other practical limitations.

Since the orthoferrite materials do not manifest the resolution phenomenon, there is no critical lower temperature limit on the process. It is convenient here to continue cooling until all of the material has been crystallized and then to separate the product from the flux by use of nitric acid. Cooling rates are desirably as slow as possible, commensurate with economic requirements. As in the garnet system, it has been found suitable to use a rate of the order of 2° C. per hour with a practical upper limit again of the order of 10° C. per hour. It is desirable again to operate at still lower cooling rates, of the order of ½° C. per hour. As in the garnet and other related systems, lower cooling rates result in larger crystal size. For the preferred limits set forth, crystallization is likely to begin at about 1250° C., so that controlled cooling is of the essence only from this temperature down.

In general, the procedure employed for growth of orthoferrite crystals is similar to that discussed above for the garnet system. However, there are slight variations as follows: after mixing the starting ingredients in a platinum crucible the procedure for garnet growth is repeated until the cooling step is reached. At this point, cooling is continued until complete crystallization of the entire contents of the crucible, which generally occurs at 850° C. for the orthoferrites. When attaining this temperature the input to the furnace is cut off and cooling continued at a rate determined by the specific apparatus employed, for example, 50° C. per hour. When entire contents reach the ambient temperature it is necessary to separate nutrient from flux. This is done by immersing the crucible in a dilute solution of nitric acid and water, approximately one to one by volume although the concentration of the acid may be varied in a manner well known to those skilled in the art. In the alternative the garnet procedure may be followed for separation of nutrient from flux. Following the acid treatment, the crystals are washed in three successive rinses of hot distilled water,

rinsed in acetone and air dried. Examples of the application of the present invention to orthoferrites are set forth below in Table II.

As will be evident to those skilled in the art, many variations and modifications can be practiced within the spirit and scope of the disclosure and claims to this in-

Table II

Ex.	Starting ingredients (gms.)		Flux composition		Product	Yield (gms.)	Crystal size	Identifying characteristics
			PbO (gms.)	B ₂ O ₃ (gms.)				
7	Y ₂ O ₃ Fe ₂ O ₃	6.78 4.80	80.0	80.0	Yttrium orthoferrite, YFeO ₃	4.5	½ cm. square by 1½ cm. long.	Transparent, slightly reddish in color.
8	La ₂ O ₃ Fe ₂ O ₃	6.52 3.20	80.0	4.0	Lanthanum orthoferrite, LaFeO ₃ ...	3.8	0.1 cm. square by ½ cm. long...	
9	Ho ₂ O ₃ Fe ₂ O ₃	7.54 3.20	80.0	4.0	Holmium orthoferrite, HoFeO ₃	4.8	½ cm. square by 1½ cm. long...	Transparent, reddish yellow.

Other materials of the structure XZO₃ have also been produced according to this procedure wherein X may be yttrium, lanthanum, praseodymium, neodymium or one of the rare earth elements of atomic number between 62 and 71 and O is oxygen. These include those in which Z 20 was cobalt, chromium, gallium or aluminum. These materials are known as rare earth cobaltates, rare earth orthochromites, rare earth gallates and rare earth aluminates. With the exception of cobaltates, the other XZO₃ compounds are transparent, generally evidencing no 25 coloration whatsoever except for the orthochromates which are greenish.

SPINEL FERRITES

Single crystalline magnetic spinel ferrites have been 30 crystallized in the prior art from a lead oxide flux. The advantage of using a lead oxide-boron oxide flux here is the same as for the orthoferrites. Solubility is increased by the order of a factor of three, so resulting in a concomitant increase in yield.

Commercially, ceramic ferrites are in widespread use in microwave devices, due primarily to economic reasons. It has been suggested that for many uses single crystal 35 garnets will replace ferrites in certain special applications, this by reason of their considerably narrower line width and lower loss properties.

In general, all considerations for the orthoferrites apply to the spinels also. The chief exception is in the ratio of nutrient to flux. This ratio may vary appreciably from one spinel to the other, this variation being due to appreciable differences in solubilities. Accordingly, although 40 a 1 to 4 ratio is suitable for nickel spinel, decreased solubility for magnesium ferrites dictates a preferred ratio of 1 to 5. The most soluble of the spinels is cobalt, which, accordingly may be used in the higher ratio in the order of 1 to 2. Zinc and cadmium are of intermediate 45 solubility and fall in the general range of nickel (1 to 4). Since, both magnesium garnet and magnesium aluminum spinels having appreciably less solubility than magnesium iron, a ratio of the order of 1 to 7 is employed.

Examples of the application of the present invention to spinel ferrites are set forth below in Table III. The procedure for preparing the orthoferrites as in Examples 7-9 was followed with the exception of the ratio of nutrient to flux.

vention.

What is claimed is:

1. The method of growing single crystals of a material selected from the group consisting of synthetic garnets, spinel ferrites and orthoferrites which comprises heating the constituent components of said material together with a mixture of lead oxide and boron oxide, the weight ratio of PbO to B₂O₃ being in the range of 9:1 to 14:1 for garnet growth and in the range of 18:1 to 22:1 for orthoferrite and spinel ferrite growth, the gross nutrient to flux ratio being in the range of 1:1.8 to 1:2.2 for garnet growth, 1:2.8 to 1:3.2 for orthoferrites, and 1:2 to 1:5 for spinel ferrites, and slowly cooling the resultant melt whereby said material precipitates from the melt in crystals.

2. The method of claim 1 in which said crystal is a synthetic garnet and said melt comprises Y₂O₃, PbO, B₂O₃ and Fe₂O₃.

3. The method of claim 1 in which said crystal is a synthetic garnet and said melt comprises Fe₂O₃, Gd₂O₃, PbO and B₂O₃.

4. The method of claim 1 in which said crystal is a synthetic garnet and said melt comprises Ga₂O₃, Gd₂O₃, PbO and B₂O₃.

5. The method of claim 1 in which said crystal is a synthetic garnet and said melt comprises Yb₂O₃, Fe₂O₃, PbO and B₂O₃.

6. The method of claim 1 in which said crystal is a synthetic garnet and said melt comprises Y₂O₃, Er₂O₃, Fe₂O₃, PbO, and B₂O₃.

7. The method of claim 2 in which the weight ratio of lead oxide to boron oxide in the melt is 10 to 1.

8. The method of claim 7 in which the weight ratio of Fe₂O₃ to Y₂O₃ is approximately 8 to 11.

9. The method of claim 1 in which said crystal is an orthoferrite and said melt comprises Y₂O₃, Fe₂O₃, PbO and B₂O₃.

10. The method of claim 9 in which the weight ratio of lead oxide to boron oxide in the melt is 20 to 1 and the gross nutrient to flux ratio is in the range of 1:2.8 to 1:3.2.

11. The method of claim 1 in which said crystal is an orthoferrite and said melt comprises Fe₂O₃, La₂O₃, PbO and B₂O₃.

Table III

Ex.	Starting ingredients (gms.)		Flux composition		Product	Yield (gms.)	Crystal size	Identifying characteristics
			PbO (gms.)	B ₂ O ₃ (gms.)				
10	Ni..... Fe ₂ O ₃	7.7 15.97	100	5.0	NiFe ₂ O ₄	8	½ cm. on an octahedral edge..	Opaque; shiny black.
11	MgO..... Fe ₂ O ₃	4.03 15.97	100	5.0	MgFe ₂ O ₄	7	½ cm. on an octahedral edge...	Opaque; transparent in thin section (up to 4 mils); red by transmitted light.
12	MgO..... FeO..... Al ₂ O ₃	4.03 7.88 5.09	100	5.0	MgAlFeO ₄	6	¼ cm. on an octahedral edge..	

12. The method of claim 1 in which said crystal is an orthoferrite and said melt comprises Ho_2O_3 , Fe_2O_3 , PbO and B_2O_3 .

13. The method of claim 1 in which said crystal is a spinel ferrite and said melt comprises PbO , B_2O_3 , NiO and Fe_2O_3 .

14. The method of claim 1 in which said crystal is a spinel ferrite and said melt comprises MgO , Fe_2O_3 , Al_2O_3 , PbO and B_2O_3 .

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