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PROCESS FOR THE GROWTH OF ORDERED LITHIUM FERRITE

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The present invention relates to a technique for the growth of single crystal ordered lithium ferrite in a flux comprising lead oxide and boron oxide.

In recent years, lithium ferrite, $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ has received considerable attention since in the single crystal form it manifests the lowest line width of any of the spinel ferrites, approximately five oersteds, coupled with a large theoretical magnetic moment, of the order of 2.5 Bohr magnetons. This compares with yttrium iron garnet, so causing this material to be of particular interest for use in devices utilizing such properties.

It is now well known to those skilled in the art that lithium ferrite, as ordinarily formed, suffers from an inherent defect, namely, the crystals manifest a disordered state; that is, the relative positions of the lithium and iron atoms in the octahedral sites are random. It is further known that in the so-called "ordered" state the positions of the octahedral lithium and iron atoms are fixed in such manner that a single lithium ion is followed by three iron ions, and so forth. Commonly, this ordered state is approached by producing a crystal in any ordinary manner, characteristically by flux growth, nucleation generally commencing at temperatures of the order of 1300°C . to 1200°C ., followed by removal from the flux, washing, and heat treatment at temperatures of the order of 750°C . and below for several hours. Unfortunately, such techniques are generally not reproducible and typically result in a degree of order less than desired.

In accordance with the present invention, crystals of ordered lithium ferrite are grown directly from a flux comprising boron oxide and lead oxide utilizing nutrient to flux ratios such that nucleation initially occurs at temperatures of 800°C . or below. Crystals, so produced, do not require the prior art heat treatment, are reproducible and evidence a higher degree of order than has heretofore been attained, in addition to an unusually low spin wave line width.

In growing crystals of the type described, it is essential to employ a flux composition which will assure initial nucleation at temperatures of 800°C . or lower. It has been determined that boron oxide-lead oxide fluxes, in which the weight ratio of these ingredients is within the range of 1:5.8 to 1:6.6 in that order, are suitable for this purpose. The ratio considered optimum is 1:6.25. The minimum limit of the broad range is determined by the minimum solubility which will effect crystallization above the solidification temperature of the entire mass. The maximum limit in the broad range is determined by the formation of borates of iron and lithium.

The general procedure for crystallization processes involving the lithium ferrite, described herein, employs 800°C . as the upper limit of temperature. The lower temperature limit of the system during crystallization is determined by increasing viscosity of the melt and the eventual solidification thereof at temperatures substantially lower than 500°C .

Optimum cooling rates over the crystallization range of from about 800°C . to 500°C . are determined by the usual criteria, the faster the rate of cooling, the greater the number of nucleation centers with a con-

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sequent decrease in crystal size and vice versa. Cooling rates may vary from as low as $\frac{1}{2}^\circ\text{C}$. per hour or lower to as high as 10°C . per hour. It is generally desired to cool as slowly as possible to secure the largest possible crystal size.

Ideal nutrient concentration increases with increased boron. It is desirable for a 1:6.25 flux to operate at the approximate nutrient to flux weight ratio of 1:3.9. However, variations over the range of ratio may be used from 1:3.7 to 1:4.0. Operation with the lesser nutrient concentration (1:4.0) results in the initiation of nucleation at a somewhat lower temperature and results in an overall decrease in the temperature range of crystallization with a resultant decrease in yield. Operation below the more concentrated ratio (1:3.7) results in an increase in the number of nucleation centers for a given cooling rate with a consequent loss in control.

The formula for lithium ferrite described herein is $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, so indicating a molecular ratio of one part lithium oxide to five parts of iron oxide (weight ratio of 1:20.5). The optimum observed weight ratio of starting ingredients, however, on which the above figures are based, is 1:3.2. This excess of lithium oxide is necessary to avoid the formation of magnetoplumbites and iron oxides. The preferred range is of the order of from 1:2.8 to 1:3.7.

Examples of the application of the present inventive concept 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:

Each of the examples set forth below has been described in terms of lithium carbonate and iron oxide (Fe_2O_3) as initial materials. However, it will be appreciated by those skilled in the art that obvious alternatives are suitable. They include lithium hydroxide, lithium oxalate, iron carbonate, iron oxalate, etc.

The starting ingredients, including lithium carbonate, iron oxide, boron oxide and lead oxide are weighed into a platinum crucible and covered with a platinum lid. Next, the crucible is placed in a horizontal global furnace with a silicon carbide muffle and mullite floor plate and the crucible, together with its contents, heated to a temperature within the range of 1000 – 1200°C . and maintained at this level for a time period within the range of 1 to 3 hours, so facilitating solution of the ingredients. The furnace may then be cooled rapidly to 850°C . and maintained at this temperature for approximately one hour in order to attain thermal equilibrium. Controlled cooling at a rate within the range of $\frac{1}{2}$ to 5°C . per hour is then initiated by a controlled energization of the furnace. This program is continued until a temperature of approximately 500°C . has been reached at which point crystallization is essentially complete. The crucible may then be removed from the furnace and permitted to cool to room temperature or in the alternative it may be left in the furnace with the power turned off. After cooling, the crucible is then immersed in a vessel containing a hot solution of dilute nitric acid and water (1 part acid to 3 parts water). The acid cleaning procedure is continued until all flux residue has been removed from the crystals. Subsequently, the acid solution is poured off, the crucible removed from the container, and the crystals washed in distilled water. Following the crystals are dried by air drying at room temperature and their properties studied.

TABLE I

Example	Ingredient Composition	Gms.	Flux Composition		Product	Properties
			PbO, gms.	B ₂ O ₃ , gms.		
1-----	{Li ₂ CO ₃ ----- Fe ₂ O ₃ -----	{7.00} 22.60}	100.00	16.00	Li _{0.5} Fe _{2.5} O ₄ --	X-ray analysis revealed crystals to be of a high degree of order and evidencing spin wave line widths of 0.5 at room temperature.
2-----	{Li ₂ CO ₃ ----- Fe ₂ O ₃ -----	{7.20} 23.40}	100.00	16.00	Li _{0.5} Fe _{2.5} O ₄ --	
3-----	{Li ₂ CO ₃ ----- Fe ₂ O ₃ -----	{6.00} 19.50}	100.00	16.00	Li _{0.5} Fe _{2.5} O ₄ --	
4-----	{Li ₂ CO ₃ ----- Fe ₂ O ₃ -----	{8.00} 26.00}	100.00	16.00	Li _{0.5} Fe _{2.5} O ₄ --	

Each of the samples prepared, as described above, was compared with Li_{0.5}Fe_{2.5}O₄ prepared as described in The Journal of Applied Physics, Supplement to vol. 33, No. 3, March 1962, pages 1379-1380, by J. W. Nielsen et al. The crystals, prepared in accordance with the inventive technique, were more ordered than those prepared by the prior art method, the latter evidencing spin wave line widths of 2.0 at room temperature.

It is to be appreciated that the examples set forth above are intended merely as illustrative, and not by way of limitation. Variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. The method of growing single crystal ordered lithium ferrite which comprises the steps of heating a nutrient comprising a mixture of (a) an excess of at least one member selected from the group consisting of lithium oxalate, lithium hydroxide, and lithium carbonate, and (b) at least one member selected from the group consisting of iron oxalate, iron carbonate, and iron oxide together with a flux comprising a mixture of boron oxide and lead oxide, the weight ratio of boron oxide to lead oxide being in the range of 1:5.8 to 1:6.6, the gross nutrient to flux ratio being in the range of 1:3.7 to 1:4.0, to a temperature sufficient to dissolve the said nutrient and cooling the resultant melt to a temperature of the order of 500° C. whereby said ordered lithium ferrite precipitates from the melt in crystals.

2. The method in accordance with claim 1 wherein said melt comprises Li₂CO₃, Fe₂O₃, B₂O₃ and PbO.

3. The method in accordance with claim 1 wherein the weight ratio of B₂O₃ to PbO is approximately 1:6.25.

4. The method in accordance with claim 1 wherein the gross nutrient to flux ratio is approximately 1:3.9.

5. The method in accordance with claim 2 wherein said heating is conducted to a temperature of approximately 1200° C.

6. The method in accordance with claim 2 wherein the weight ratio of Li₂CO₃ to Fe₂O₃ is within the range of 1:2.8 to 1:3.7.

7. The method in accordance with claim 5 wherein the weight ratio of B₂O₃ to PbO is 1:6.25, the weight ratio of Li₂CO₃ to Fe₂O₃ is 1:3.2 and the gross nutrient to flux ratio is 1:3.9.

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