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METHOD OF MAKING SINGLE CRYSTAL GARNETS

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FIG. 1

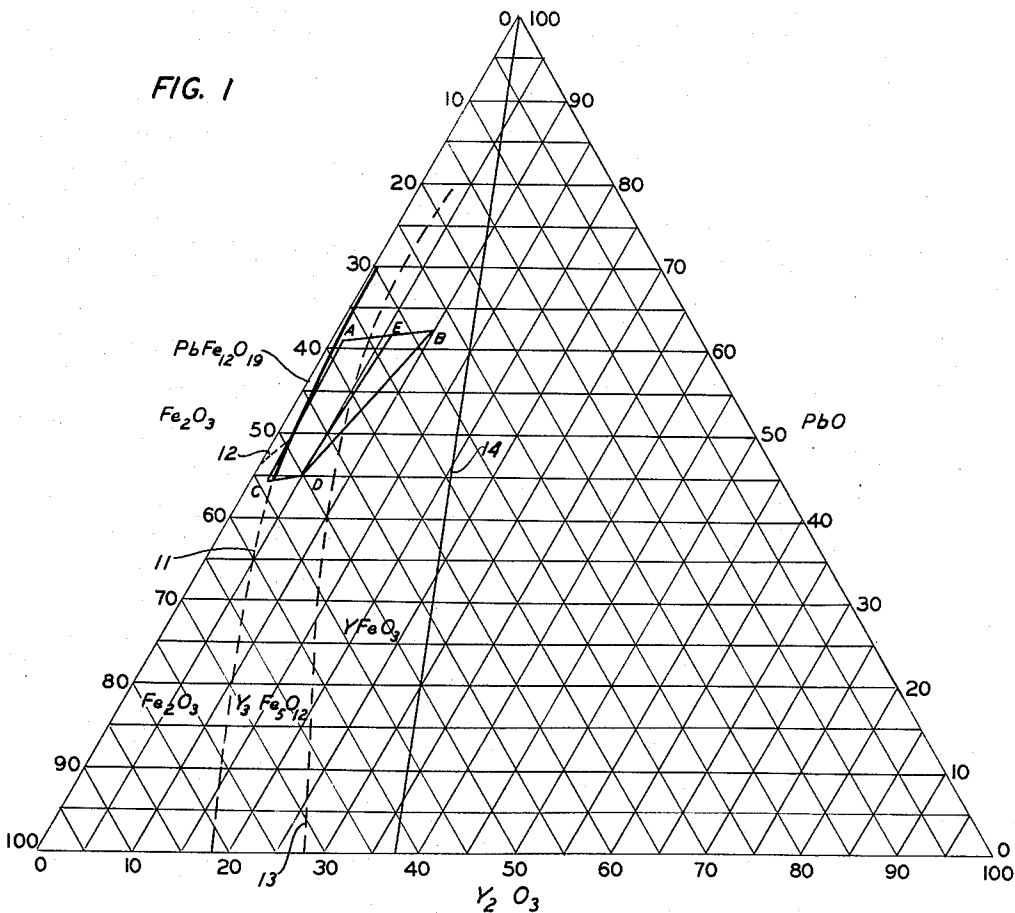
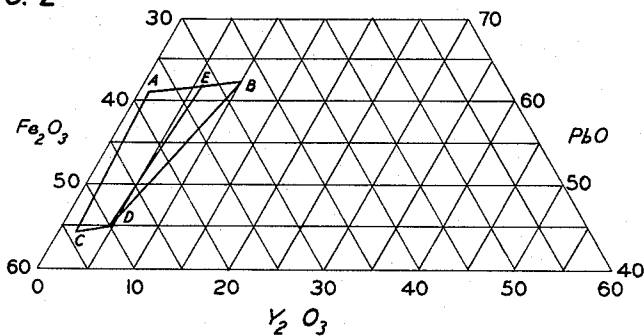


FIG. 2



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METHOD OF MAKING SINGLE CRYSTAL GARNETS

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2 Claims. (Cl. 252—62.5)

This invention relates to methods of making single crystals of synthetic garnets, and to the garnet materials so produced.

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



where O is oxygen, and M and Me are trivalent metals.

In particular, M may be yttrium or one of the rare earth elements of atomic number between 62 and 71, or mixtures 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 gallium, aluminum, or scandium. Where M is yttrium, these materials have been described as "yttrium-iron garnets" where M is one of the rare earths herein specified the materials are termed "rare earth iron garnets."

The synthetic materials described above are "garnets," because they have the same complicated cubic structure as the mineral garnets, such as, for example, grossularite, $Ca_3Al_2(SiO_4)_3$. The synthetic garnets differ from this naturally-occurring form in lacking the divalent and quadrivalent metal ions of the latter, with trivalent atoms replacing them in the lattice.

The synthetic garnets containing a substantial iron content are ferrimagnetic and can be used in the construction of inductive devices as cores therefor. The garnets show the property of Faraday rotation for microwaves, and in transparent section can also be used to rotate visible light. Because of their magnetic properties, the coefficient of specific rotation in the garnets is larger than in other transparent materials, making them especially useful. Where non-magnetic ions have been in part substituted for iron in these garnets, the mole ratio of iron to the substituent is preferably at least 3 to 2 for substantial magnetic properties to be retained.

The lattice structure of the synthetic garnets will accommodate trivalent ions of two sizes. Ions of yttrium and the rare earths between atomic numbers 62 and 71 all have radii of approximately the same size and can interchangeably occupy the same lattice sites. Mixtures of two or more of these materials can be substituted in the lattice of the garnets. Iron has a smaller ionic radius, and occupies a different set of lattice sites in the garnet crystal. Certain other trivalent metal ions, namely aluminum, gallium, and scandium may be substituted in part for the iron in these synthetic garnets. The ions of Fe, Ga, Al and Sc all have spherical electronic configurations, are all chemically similar, yield isostructural garnets, and are comparable in size.

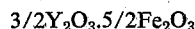
The synthetic garnet materials mentioned above are produced in single crystal form by crystallization from a bath of molten lead oxide, PbO. Such baths of lead oxide have been used heretofore in growing single crystal of other materials, namely ferrites, XFe_2O_4 , where X is a divalent metal.

However, in such techniques, the presence, in the PbO bath, of stoichiometric amounts of the metal oxide XO

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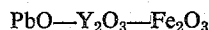
and ferric oxide Fe_2O_3 is sufficient to promote formation of the crystalline product. Such a technique is inapplicable, and fails, if used in an attempt to grow garnets in the more complex system now under consideration.

- 5 Taking yttrium iron garnet, $Y_3Fe_5O_{12}$, as a convenient example, the material stoichiometrically contains 5 moles of Fe_2O_3 to each 3 moles of yttrium oxide Y_2O_3 , that is, $Y_3Fe_5O_{12}$ may be written as

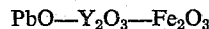


- 10 However, when the garnet is sought to be grown from a lead oxide bath, the maintenance of a stoichiometric mole ratio of 5 to 3 between iron oxide and yttrium oxide respectively does not lead to the crystallization of $Y_3Fe_5O_{12}$.

A phase diagram of the system



- is useful in understanding the present method of growing synthetic garnet single crystals. Because of the identity of the behavior of the rare earth oxides with that of yttrium oxide, and the fact that mixtures of iron oxide with the oxides of gallium, scandium, or aluminum behave as does pure iron oxide alone, the phase diagram for



may be taken as representative of the system

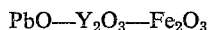


- 30 where M and Me have the significance given earlier herein. The identity of behavior noted is due, as earlier mentioned, to the similarity of the ionic radii in yttrium and the rare earths on one hand, and iron and its substitutes on the other.

- 35 Fig. 1 is a triaxial diagram showing that part of the system $PbO-Y_2O_3-Fe_2O_3$ of particular interest in growing yttrium-iron garnet; and

- Fig. 2 is a portion of the triaxial diagram of Fig. 1 delimiting a range of compositions of particular interest in growing yttrium-iron garnet and, in general, synthetic garnets of the formula $M_3Me_5O_{12}$.

- In Fig. 1 the three axes or base lines of the diagram define mole percentages of each of the three components, Y_2O_3 , Fe_2O_3 and PbO, present in the three component system. The area defines the limits of the relative proportions of the three components in the system



- Each point within the area corresponds with a composition within this system. Line 11, shown in part as a heavy line and in part as a broken line, and broken lines 12 and 13 divide the area into four regions marked Fe_2O_3 , $Y_3Fe_5O_{12}$, $PbFe_{12}O_{19}$ and $YFeO_3$ respectively. If points within the areas of Fig. 1 defined by lines 11, 12 and 13 represent the compositions of homogeneous melts consisting of Fe_2O_3 , Y_2O_3 and PbO in the mole percentages determined from the coordinates, then the formula associated with each area indicates that compound which will first crystallize from the melt on cooling.

- Lines 12 and 13, and line 11, in part, are broken to indicate that they are proximate only. One or more points on the lines have been determined, and the lines are considered fairly representative of phase relationships in the system. But portions of the phase diagram cannot be precisely ascertained experimentally for reasons which will become later apparent, and must be deduced theoretically. The heavy portion of line 11 has been thoroughly examined, however, by chemical analysis of melts of a composition such as to lay on the line. It is apparent that line 11 does not extend to the Fe_2O_3 base-line, nor does line 13 separate completely the areas marked $Y_3Fe_5O_{12}$ and $YFeO_3$. To this extent the di-

agram is also not comprehensive. For purposes of this specification however, such discrepancies are not material.

Line 14 defines all those melt compositions within the three component systems in which ferric oxide and yttrium oxide are present in the molar ratio 5 to 3: the stoichiometric ratio present in the compound $Y_3Fe_5O_{12}$. It is apparent from the diagram that the initial crystalline material which would precipitate on cooling melts of these compositions is not $Y_3Fe_5O_{12}$, but $YFeO_3$. While such does not preclude, in theory, the later crystallization of $Y_3Fe_5O_{12}$ from the melt as its composition changes because of removal of solid matter therefrom, in practice the production of garnet crystals from such melts is not feasible. For most of the points defined by line 14, the temperatures required to produce melts of such composition are so high as to preclude containment of the melts in vessels made of known materials suitable for holding the melts. For the limited range of compositions in which such melts can be produced and handled, the large amounts of $YFeO_3$ first needed to be precipitated from the melt before the melt composition moves into the $Y_3Fe_5O_{12}$ region preclude the precipitation of significant amounts of the latter compound.

On Fig. 1, and reproduced in Fig. 2, are rectangular areas ABDC and ACDE which define those compositions of most interest in producing synthetic garnet materials by the method of the present invention. Points A, B, C, D, and E correspond with the following compositions in mole percentages:

	PbO	Fe ₂ O ₃	Y ₂ O ₃
A-----	61	37.5	1.5
B-----	62.5	27.5	10
C-----	44	54	2
D-----	45	50	5
E-----	61.5	32.5	6

Those compositions within the rectangle ABDC of Figs. 1 and 2 are suitable for the production of single crystal garnet by crystallization from a melt. Those compositions falling within the area ACDE give particularly high yields of single crystal garnet materials. An optimum composition for crystal growth has been observed when the composition of the three component system is as follows: 52.5 mole percent PbO, 44 mole percent Fe_2O_3 , and 3.5 mole percent Y_2O_3 .

Lines 11, 12, 13 and 14 are to be read as relating to melt compositions in defining the phase relationships within the system depicted in Fig. 1. The points, lines and areas related to the rectangles ABDC and ACDE are to be interpreted not only as referring to melt compositions, but also as referring to the mole percentages of unfused starting materials used in the preparation of the melts in question. In most cases, the compositions of the melts and of the unfused ingredients will be identical. However, in some cases, kinetic failure of the system to reach equilibrium under the time and temperature limitations of a particular crystal-growing experiment may result in an incomplete solution of all the starting materials into the liquid PbO produced on heating. Although substantially complete solution of the more refractory components occurs, it is desirable to define areas ABDC and ACDE in terms of the composition of starting mixtures, rather than solely as equilibrium melt compositions.

Before proceeding, it is again emphasized that Figs. 1 and 2, though drawn with particular reference to the system $PbO-Fe_2O_3-Y_2O_3$ are applicable, especially areas ABDC and ACDE, to systems in which one or more of the rare earth elements having atomic numbers between 62 and 71 are substituted in whole or in part for yttrium and for those systems in which aluminum, gallium, or scandium are substituted in part for iron.

In preparing the melts, mixtures of starting compositions as above defined are weighed out. Reagent grade materials are used. Though the systems have heretofore

been described in terms of the oxides, it is understood that other compounds may be used which can be converted to oxides on heating. Carbonates, oxalates, acetates and so forth may be used in preparing the melts, as long as the molar proportions set forth above in terms of the oxides are retained. Such non-oxidic compounds are preferably first converted to oxides before being mixed with PbO. Thus reduction of the PbO to metallic lead, which tends to attack crucible materials, is avoided.

The reactants are put in platinum crucibles and covered. The covers preferably are crimped onto the crucibles to avoid evaporation of the crucible contents. The crucibles are then placed in a muffle furnace in which an oxygen-enriched atmosphere is maintained. Two liters of oxygen passed per minute through a small furnace are sufficient for this purpose. The maintenance of an oxygen-enriched atmosphere decreases the tendency of molten PbO to reduce and attack the platinum crucibles in which it is retained.

The crucible is then heated to fuse the PbO, in which the remaining components are soluble. Though PbO liquefies at $888^\circ C.$, solution of the other components therein, in the proportions indicated, takes place at temperatures above $1250^\circ C.$ As the rate of fusion of the components may be slow at this temperature, still higher temperatures are preferred. A practical limitation on maximum temperature appears at $1400^\circ C.$ Above this point, the melts too actively attack the platinum crucibles in which they are prepared. Since other materials commonly used in crucible manufacture, such as ceramics, are attacked even more readily than is platinum by the melts, no evasion of this practical limitation as yet appears feasible. It is to be understood, however, that temperatures greater than $1400^\circ C.$ can be used in preparing the garnets herein, if such can be obtained with other than conventional apparatus. It is this practical temperature limitation which prevents the exploration of the entire phase diagram of Fig. 1, and precludes the attainment of most compositions lying on line 14 of Fig. 1.

Heating at an elevated temperature is continued till a substantially homogeneous melt is produced from the starting composition. At temperatures near $1250^\circ C.$, which is the lower limit of the feasible temperature range, heating periods between an hour and 24 hours may be required for the compositions. When the temperature is kept at around $1350^\circ C.$ to $1400^\circ C.$, fusion can be completed in between 1 hour and 10 hours, and usually in less than five.

After fusion is complete, or substantially so, the melts are permitted to cool at a slow rate. Since equilibrium cooling is preferred, cooling should be as slow as is practically possible. Cooling rates between $1^\circ C.$ per hour and $10^\circ C.$ per hour are usually used, though crystals may be grown by cooling as rapidly as $20^\circ C.$ per hour. A cooling rate of $1^\circ C.$ per hour has given particularly good results.

The material which first crystallizes from the melt on cooling may be Fe_2O_3 , $Y_3Fe_5O_{12}$, $YFeO_3$ or $PbFe_{12}O_{19}$ depending on the melt composition. If the composition corresponds with a point lying on lines 11 or 12, crystallization of more than one component may result. Along line 11 the melt and precipitated solids will be in equilibrium, with Fe_2O_3 and $Y_3Fe_5O_{12}$ crystallizing simultaneously below the intersection of line 12 with line 11. Above this point of intersection, $Y_3Fe_5O_{12}$ and $PbFe_{12}O_{19}$ crystallize simultaneously. Along line 13, $Y_3Fe_5O_{12}$ and $YFeO_3$ will precipitate at the same time on cooling, with the solids and melt in equilibrium.

For melt compositions not on lines 11 and 12, the first appearing solid will be that indicated in the area in which the point lies. The composition of the melt will change as solid is removed therefrom in a manner predictable from the triaxial diagram of Fig. 1. By joining the point corresponding with the composition of the cooling melt with a point on a base line corresponding with the com-

position of the crystallizing material, a line is defined which will give the changing composition of the cooling melt. At an intersection of this line with line 11 or 12, an equilibrium system can be established, and the cooling melt composition thereafter may follow the equilibrium line 11 or 12.

After the crucibles have cooled preferably to a temperature below 1050° C., to ensure high yields, they are removed from the furnace and air cooled to room temperature. The solidified matrix of lead oxide is next dissolved in 2N-8N nitric acid, leaving crystalline phases unaffected. Crystalline Fe_2O_3 , an orthoferrite phase MFeO_3 , and magnetoplumbite- $\text{PbFe}_{12}\text{O}_{19}$ may be present as crystals in addition to garnet. In many cases, the garnet can be distinguished from other crystals present by visual inspection. The crystals have a shiny surface and crystallize in a dodecahedral habit with (110) planes exposed or in an icositetrahedral habit with (211) planes exposed. The crystals are distinguishable from the rectangular rods of the orthoferrites, the hexagonal plates of magnetoplumbite, and the squarish plates of Fe_2O_3 which may be formed.

Magnetic separation may also be effected. The orthoferrites, magnetoplumbite and the garnets are all magnetic, but have Curie points at different temperatures. By screening the crystals magnetically at different temperatures all the phases can be separated. In the yttrium-iron system for example, an initial magnetic treatment will separate magnetic materials from crystalline non-magnetic iron oxide. Because yttrium orthoferrite has a Curie point below the Curie point of yttrium-iron garnet at 270° C., heating to a temperature of about 260° C. will render the orthoferrite phase non-magnetic, and hence separable from the garnet and magnetoplumbite. By next heating above 270° C., the Curie point of the garnet, but below 360° C., the Curie point of magnetoplumbite, an isolation of the garnet phase is possible.

An alternative "continuous" method of crystallizing the garnet materials uses a crucible in which a thermal gradient is established, and only a portion of the melt is cooled to effect crystallization. A deep platinum crucible containing the constituents of the garnets, dissolved in molten PbO , is heated more strongly in its upper portions than in its lower portions. The main body of the solution is a melt of a composition from which garnet may be crystallized. At the melt surface, where the melt temperature is greatest, undissolved garnet constituents float on the surface of the dense molten PbO . At the bottom of the crucible, where the melt temperature is lower than in the main body of the melt, seed crystals of garnet are suspended. Because of the thermal gradient, garnet tends to leave the melt, depositing on the seeds. As the melt is thus depleted of the garnet constituents by precipitation, more of these same constituents dissolve in the warmer surface portions of the melt, maintaining a fairly constant melt composition. The whole melt is stirred gently to prevent too large local variations in melt composition. A thermal gradient between 1° C. per centimeter and 0.25° C. per centimeter is preferably used. In a platinum crucible 20 centimeters deep, in which a surface temperature of between 1230° C. to 1250° C. is kept, for example, the corresponding temperature in the coolest portion of the crucible then varies between 1210° C. and 1245° C.

Examples of the preparation of several synthetic garnet materials are given below.

Example 1

One hundred grams of lead oxide (PbO), 60 grams of iron oxide (Fe_2O_3), and 10.4 grams of samarium oxide (Sm_2O_3) were heated in a covered platinum crucible at a temperature of 1350° C. for five hours in an oxygen-enriched atmosphere. The crucible was cooled at a rate of 1° C. per hour to a temperature of 920° C., when it was removed from the furnace and cooled to room tem-

perature. The lead oxide in the crucible was dissolved in an aqueous solution of nitric acid. Single crystals of $\text{Sm}_2\text{Fe}_5\text{O}_{12}$ were separated from crystals of $\text{PbFe}_{12}\text{O}_{19}$ and SmFeO_3 by inspection. The crystals varied between about one millimeter and 10 millimeters in average size.

Example 2

Crystals of $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ were prepared by heating a mixture of 100 grams PbO , 60 grams of Fe_2O_3 and 10.75 grams of gadolinium oxide (Gd_2O_3) in a covered platinum crucible for five hours at 1370° C. in an oxygen-enriched atmosphere. The crucible was cooled to 910° C. at a rate of 1° C. per hour, then removed from the furnace and cooled to room temperature. Crystals of $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ were separated from crystals of $\text{PbFe}_{12}\text{O}_{19}$ after removal of PbO by solution thereof in nitric acid.

Example 3

$\text{Y}_3\text{Fe}_5\text{O}_{12}$ single crystals were produced by preparing melts consisting of 80 grams PbO , 70 grams Fe_2O_3 , and 3.5 grams of yttrium oxide (Y_2O_3) from a temperature of 1350°. After 5 hours at this temperature, the melts were cooled to temperatures ranging between 1235° C. and 780° C., at rates varying between 5° C. per hour and 1° C. per hour, before removal from the furnace and cooling to room temperature. In each case, crystals of yttrium-iron garnet were recovered by magnetic separation from $\text{PbFe}_{12}\text{O}_{19}$ and Fe_2O_3 after solution of the PbO matrix in nitric acid.

Example 4

Crystals of an yttrium iron garnet containing gallium substituted in part for the iron were prepared from a melt heated for five hours at 1370° C. The melt consisted of 100 grams PbO , 54 grams Fe_2O_3 , 7.0 grams Y_2O_3 and 7.0 grams of gallium oxide, Ga_2O_3 . The melt was cooled to a temperature of 910° C. at a rate of 5° C. per hour, then removed from the furnace and cooled to room temperature. Crystals of the iron-substituted garnets were separated by inspection from crystals of magnetoplumbite, $\text{PbFe}_{12}\text{O}_{19}$. The presence of gallium in the crystals was detected by measurement of their magnetic properties and comparison with the same properties of $\text{Y}_3\text{Fe}_5\text{O}_{12}$ in which the magnetic iron is undiluted by non-magnetic materials.

Example 5

Erbium-iron garnet, $\text{Er}_3\text{Fe}_5\text{O}_{12}$, was prepared by heating 100 grams of PbO , 60 grams of Fe_2O_3 and 11.5 grams of Er_2O_3 in a covered platinum crucible at 1350° C. for 5 hours. The melt was then cooled to solidification at a rate of 1° C. per hour. The garnet and magnetoplumbite remained as crystals after solution of PbO in nitric acid, and were separable by inspection.

What is claimed is:

1. The method of growing single crystals of synthetic garnet materials of the formula



where O is oxygen, M is at least one element selected from the group consisting of yttrium and the rare earth elements with atomic number between 62 and 71 inclusive, and Me is an element selected from the group consisting of trivalent iron and trivalent iron mixed with at least one non-ferrous element selected from the group consisting of aluminum, gallium, and scandium in such proportions that the ratio of moles of iron to moles of said non-ferrous elements is at least 3 to 2, which method comprises fusing a composition consisting of lead oxide and the oxides of the elements M and Me, as defined above, to form a substantially homogeneous melt, said compositions being defined within an area on a ternary diagram having as its coordinates mole percent PbO , mole percent M_2O_3 and mole percent Me_2O_3 , said area being defined by a quadrilateral having at its corners the four points defined by

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- (1) 61 percent PbO, 1.5 percent M_2O_3 , 37.5 percent Me_2O_3 ,
 (2) 44 percent PbO, 2 percent M_2O_3 , 54 percent Me_2O_3 ,
 (3) 45 percent PbO, 5 percent M_2O_3 , 50 percent Me_2O_3 ,
 (4) 62.5 percent PbO, 10 percent M_2O_3 , 27.5 percent Me_2O_3 ,

and then cooling at least a portion of said melt, whereby crystals of $M_3Me_5O_{12}$ are formed.

2. The method of growing single crystals of synthetic garnet materials of the formula



where O is oxygen, M is at least one element selected from the group consisting of yttrium and the rare earth elements with atomic number between 62 and 71 inclusive, and Me is an element selected from the group consisting of trivalent iron and trivalent iron mixed with at least one non-ferrous element selected from the group consisting of aluminum, gallium, and scandium in such proportions that the ratio of moles of iron to moles of said non-ferrous elements is at least 3 to 2, which method comprises fusing a composition consisting of lead oxide and the oxides of the elements M and Me, as defined above, to form a substantially homogeneous melt, said compositions being defined within an area on a ternary diagram having as its coordinates mole percent PbO, mole percent M_2O_3 and mole percent Me_2O_3 , said area being defined by a quadrilateral having at its corners the four points defined by

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- (1) 61 percent PbO, 1.5 percent M_2O_3 , 37.5 percent Me_2O_3 ,
 (2) 44 percent PbO, 2 percent M_2O_3 , 54 percent Me_2O_3 ,
 (3) 45 percent PbO, 5 percent M_2O_3 , 50 percent Me_2O_3 ,
 (4) 61.5 percent PbO, 6 percent M_2O_3 , 32.5 percent Me_2O_3 ,

and then cooling at least a portion of said melt, whereby crystals of $M_3Me_5O_{12}$ are formed.

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