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YTTRIUM AND RARE EARTH BORATES

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This invention relates to a novel series of borates and to methods for producing such borates in a flux comprising a molybdenum oxide and a potassium salt.

The materials considered here can be represented by the general formula $RX_3B_4O_{12}$ where R is yttrium or one of the rare earth elements of atomic number between 62 and 68, and X is aluminum, gallium, or chromium, but when X is chromium R must be a rare earth element.

The entire series of single crystalline compositions of the present invention is piezoelectric as indicated by the Giebe-Scheibe test, thus indicating the suitability of these materials for device applications.

The rare earth borates herein manifest ultraviolet excited fluorescence. The rare earth aluminum borates, in particular, manifest a bright, sharp line fluorescence with the most intense line evidencing a width of about 1 wave number (approximately 0.8 A.) for the terbium compound and slightly less than 1 wave number (approximately 0.7 A.) for the europium compound. Therefore, these compositions are of interest as optical maser materials.

In accordance with the methods of the present invention, a flux is utilized which initially comprises molybdic oxide or molybdic anhydride and a potassium salt, such as the sulfate, oxide or carbonate. The use of such a flux is advantageous in several respects, the most important being the good solubility of constituent materials which permits the process to be operated at temperatures substantially below that at which crystal decomposition occurs.

An important aspect of the present invention lies in the use of specific flux ratios, i.e., critical ratios of potassium composition to molybdenum oxide. In growing the crystals of the borate structure discussed above it is desirable to include as much potassium salt, such as the sulfate, in the combined flux and so secure the greatest possible solubility. However, it is essential that the mole ratio of potassium salt to molybdic oxide be within the range of 1:2 to 1:3. It has been found that use of a ratio of potassium sulfate to molybdic oxide of greater than about 1:2 fails to produce an appreciable number of crystals and those that are produced are of small magnitude. Studies of the growth of borate structures have extended down to 1:3, at which the volatility of the flux increases considerably, so occasioning a practical limit. At ratios appreciably beyond 1:3, such as 1:4, none of the borates are produced. An optimum range has been found to correspond to the approximate ratio of 1:2.7.

The general procedure for crystallization processes involving the borate systems employ 1200° C. as the upper limit of temperature, hereinafter referred to as soaking temperature. This limitation is set by reason of compositions pertaining to volatility of ingredients in solution, changing composition of the flux, decomposition of the borate structures as evidenced by opacity in the crystal, and for various practical reasons such as apparatus limitations. The lower temperature limit of the system during crystallization is determined by the solubility of the added oxides, i.e., yttrium oxide, boron oxide, aluminum oxide, etc. It is essential that the nutrient reach saturation and it has been determined that 700° C. is a practical lower limit. There is no objection to further decreasing the soaking temperature and cooling may be programmed until the flux becomes solid.

Optimum cooling rates over the crystallization range of from about 1200° C. to 700° 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 1° 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. Consequently, a cooling rate of as low as ½° C. per hour is most desirable where large crystals are preferred.

Typically, for a 1:2 to 1:3 flux a nutrient to flux weight ratio of 1:2.3 or 43 mole percent is employed. However, variations over the range of ratio may be used from 1 to 1.8 to 1:3.0 or 53 to 33 mole percent. Operation with lesser nutrient concentration (1:3.0) results in the initiation of nucleation at a somewhat lower temperature and in an overall decrease in the temperature range of crystallization, so causing a 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 may not result in a yield commensurate with the increased concentration of starting ingredients.

The general formula for the structures prepared in accordance with this invention is $RX_3B_4O_{12}$, so indicating a molecular ratio of 1 part of "R" oxide to 3 parts of "X" oxide to 4 parts of boron oxide. Operation with the ratio indicated by the stoichiometric material results in a satisfactory yield. However, a preferred mixture is one having a 1:2.4 molecular ratio (R:X:B). This preference may be attributed to the solubility of aluminum or chromium which may exceed the solubility of the nutrient composition.

The borates of this invention fall into two major categories, namely aluminum-containing and chromium-containing. Concerning the former, it is possible to prepare yttrium aluminum borate and rare earth aluminum borates of atomic number 62 through 68. However, in the preparation of the chromium borates attempts to prepare the yttrium chromium borates have been unsuccessful. Thus, in the general formula $RX_3B_4O_{12}$, when X is chromium, R must be a rare earth element.

Borates containing all of the designated rare earths as well as yttrium have been prepared and are reported in the examples herein.

The borates discussed herein crystallize as doubly-terminated hexagonal rods elongated in the C direction. Crystals are colorless except in those instances where the rare earth ion imparts its characteristic color, such colors being pastel in nature.

The crystal system of the novel compositions is trigonal with a rhombohedral lattice and the point group based on stereographic projection studies using the 2-circle reflection goniometer is D_3–32 corresponding to a space group of 32 with the rare earth or yttrium in the site symmetry 32.

The borates prepared herein are insoluble in potassium hydroxide, hydrochloric acid and nitric acid and do not melt at temperatures less than 1400° C. although at this temperature an opaqueness develops in the crystals which may be attributed to the decomposition of the borate groups.

Examples of the present invention are set forth below. They are intended merely as illustrative 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 Tables 1 and 3 is to be considered as a separate example, since each set of data was

obtained in a separate process. The procedure employed in each of the examples is as follows:

A mixture of a potassium compound, such as potassium sulfate, potassium oxide or potassium carbonate and a molybdenum oxide, such as molybdic oxide or molybdic anhydride is weighed into a 100 milliliter platinum crucible and heated until the mixture is melted. Next, the boron oxide is added. It is essential to follow this sequence of steps as a practical expedient in order to avoid frothing and provide a more intimate mixture. The yttrium or rare earth oxide and the aluminum or chromium oxide is added and the crucible sealed with a platinum lid. The crucible is next placed in a muffle furnace and soaked at a temperature within the range of 700° C. to 1200° C. for a time period within the range of 1 to 6 hours.

Controlled cooling at a rate within the range of 1 to 10° C. per hour from the maximum temperature is then commenced. The cooling rate, however, is critical only over the range from initial to complete crystallization. The grown crystals are recovered by dissolving the matrix in a mixture of hot potassium hydroxide and hydrochloric acid.

EXAMPLE 1

Table I

Starting ingredients (grams)	Flux Composition		Soaking temp. (° C.)	Cooling rate (° C. per hour)	Cooled to (° C.)	Product
	MoO_3 (grams)	K_2SO_4 (grams)				
Y_2O_3—17.9 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,100	3	900	Yttrium aluminum borate ($YAl_3B_4O_{12}$)

The resultant crystal is colorless and crystallized in a doubly-terminated hexagonal rod elongated in the C direction. Optical examination of the crystal shows it to be uniaxial negative with the indices of refraction of $n\omega$ 1.775±0.05 and $n\epsilon$ 1.715±0.05. The crystal hardness is approximately 7.5 on the Moh scale and the pycnometric density is 3.751. The theoretical density based on X-ray measurements is 3.75. The hexagonal lattice constants are a_H 9.287 A. and c_H 7.256 A. and for the rhombohedral lattice a_R=5.883 A. and α=104.26°.

The chemical composition of the yttrium aluminum borate was determined both by wet analysis and quantitative spectrochemical analysis and the presence of yttrium was also confirmed by the X-ray fluorescent technique. Table 2 shows the results of these analyses with the standard deviations.

Table II

Oxide	Theoretical $YAl_3B_4O_{12}$, percent	Wet analysis	Quantitative spectro chemical analysis	X-ray fluorescence
Y_2O_3	27.9	32.96±0.12	26 ±2	29.8±0.0
Al_2O_3	37.7	42.08±0.41	32 ±5	----------
B_2O_3	34.4	35.85±0.78	40 ±4	----------
	100.0	111.1 ±1.2	98.6±9.9	----------

The formula indicated by the above analysis is $YAl_3B_4O_{12}$. This corresponds to a theoretical percentage of the component oxides as indicated above. The agreement between the theoretical and the found composition is reasonable and further confirmation was obtained by calculating the formula weight of the unit cell from the volume of the unit cell and the density. This calculation confirms the formula arrived at by analytical means and shows there to be one formula weight in the rhombohedral unit cell.

Application of the Giebe-Scheibe test showed the yttrium aluminum borate to be piezoelectric in nature.

Table 3 indicates the various properties of the yttrium and rare earth aluminum borates and rare earth chromium borates prepared according to the present inventive techniques.

Table III

Ex.	Starting ingredients (gms.)	Flux composition		Soaking temp. and time	Cooling rate	Cooled to ° C.	Product	Identifying characteristics
		MoO_3 (gms.)	K_2SO_4 (gms.)					
----	Gd_2O_3—28.9 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,150° C----------	4° C./hr----	920	Gadolinium aluminum borate ($GdAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Colorless. (c) Hexagonal-rodlike crystal. (d) Trigonal crystal system with a rhombohedral lattice.
3----	ErO_3—30.5 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,200° C. for 5 hrs---	3.7° C./hr---	990	Erbium aluminum borate ($ErAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Pale blue color. (c) Hexagonal-rodlike crystal. (d) Trigonal crystal system with a rhombohedral lattice.
4 ---	Sm_2O_3—28.0 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,200° C. for 5 hrs---	3.7° C./hr---	990	Samarium aluminum borate ($SmAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Pale yellow color. (c) Hexagonal-rodlike crystal. (d) Trigonal crystal system with a rhombohedral lattice.
5----	Nd_2O_3—26.8 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,150° C. for 5 hrs---	3.5° C./hr---	900	Neodymium aluminum borate ($NdAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Pink in natural light, blue in artificial light. (c) Weakly fluorescent. (d) Hexagonal-rodlike crystal. (e) Trigonal crystal system with a rhombohedral lattice.
6----	Dy_2O_3—29.8 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,150° C. for 5 hrs---	3.5° C. hr---	900	Dysprosium aluminum borate ($DyAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Colorless. (c) White luminescence. (d) Hexagonal-rodlike crystal. (e) Trigonal crystal system with a rhombohedral lattice.

Table III—Continued

Ex.	Starting ingredients (gms.)	Flux composition		Soaking temp. and time	Cooling rate	Cooled to ° C.	Product	Identifying characteristics
		MoO_3 (gms.)	K_2SO_4 (gms.)					
7	Tb_2O_3—29.2 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,120° C. for 6 hrs.	3.2° C./hr.	850	Terbium aluminum borate ($TbAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Luminescent. (c) Sharp lines, approximately 0.8 A. (d) Colorless. (e) Hexagonal-rodlike crystal. (f) Trigonal crystal system with a rhombohedral lattice.
8	Y_2O_3—17.9 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8 152 mg. of Cr_2O_3 added to flux.	1,100° C. for 6 hrs.	3.0° C./hr.	900	Yttrium aluminum borate doped with chromium ($YAl_3B_4O_{12}$) (Cr^{+++} doped).	(a) Piezoelectric. (b) Luminescent. (c) Line width, approximately 0.9 A. (d) Light blue. (e) Hexagonal-rodlike crystal. (f) Trigonal crystal system with a rhombohedral lattice.
9	Ho_2O_3—28.2 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,100° C. for 5 hrs.	5.0° C./hr.	900	Holmium aluminum boborate ($HoAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Colorless. (c) Hexagonal-rodlike crystal. (d) Trigonal crystal system with a rhombohedral lattice.
10	Eu_2O_3—28.0 Al_2O_3—16.3 B_2O_3—22.4	77.0	34.8	1,050° C. for 6 hrs.	4° C./hr.	900	Europium aluminum borate ($EuAl_3B_4O_{12}$).	(a) Piezoelectric. (b) Luminescent pink. (c) Sharp lines, approximately 0.7 A. (d) Hexagonal-rodlike crystal. (e) Trigonal crystal system with a rhombohedral lattice.
11	Gd_2O_3—28.9 Cr_2O_3—24.3 B_2O_3—22.4	77.0	34.8	1,120° C. for 6 hrs.	3.2° C./hr.	850	Gadolinium chromium borate ($GdCr_3B_4O_{12}$).	(a) Piezoelectric. (b) Deep green. (c) Hexagonal-rodlike crystal. (d) Trigonal crystal system with a rhombohedral lattice.
12	Sm_2O_3—31.9 Cr_2O_3—24.3 B_2O_3—22.4	77.0	34.8	1,050° C. for 6 hrs.	4.0° C./hr.	900	Samarium chromium borate ($SmCr_3B_4O_{12}$).	(a) Piezoelectric. (b) Dark green. (c) Hexagonal-rodlike crystal. (d) Trigonal crystal system with a rhombohedral lattice.

The refractive indices, both ordinary and extraordinary, of the compounds prepared in the foregoing examples, are set forth in Table IV below.

Table IV

Compound	Refractive index	
	$n\epsilon$	$n\omega$
$GdAl_3B_4O_{12}$	1.720±0.05	1.790±0.05
$ErAl_3B_4O_{12}$	1.720±0.05	1.801±0.05
$SmAl_3B_4P_{12}$	1.720±0.05	1.780±0.05
$NdAl_3B_4O_{12}$	1.720±0.05	1.810±0.05
$DyAl_3B_4O_{12}$	1.720±0.05	1.800±0.05
$TbAl_3B_4O_{12}$	1.718±0.05	1.790±0.05
$HoAl_3B_4O_{12}$	1.720±0.05	1.800±0.05
$EuAl_3B_4O_{12}$	1.720±0.05	1.800±0.05
$GdCr_3B_4O_{12}$	Greater than 2	
$SmCr_3B_4O_{12}$	Greater than 2	

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 invention.

What is claimed is:

1. A composition of matter having the general formula $RX_3B_4O_{12}$ where R is selected from the group consisting of yttrium and rare earth elements of atomic number 62–68 and where X is selected from the group consisting of chromium and aluminum but where X is chromium R must be a rare earth element.

2. Yttrium aluminum borate having the formula $YAl_3B_4O_{12}$.

3. Gadolinium aluminum borate having the formula $GdAl_3B_4O_{12}$.

4. Erbium aluminum borate having the formula $ErAl_3B_4O_{12}$.

5. Samarium aluminum borate having the formula $SmAl_3B_4O_{12}$.

6. Neodymium aluminum borate having the formula $NdAl_3B_4O_{12}$.

7. Dysprosium aluminum borate having the formula $DyAl_3B_4O_{12}$.

8. Terbium aluminum borate having the formula $TbAl_3B_4O_{12}$.

9. Holmium aluminum borate having the formula $HoAl_3B_4O_{12}$.

10. Europium aluminum borate having the formula $EuAl_3B_4O_{12}$.

11. Gadolinium chromium borate having the formula $GdCr_3B_4O_{12}$.

12. Samarium chromium borate having the formula $SmCr_3B_4O_{12}$.

13. The method of growing single crystals of a composition having the general formula $RX_3B_4O_{12}$ where R is selected from the group consisting of yttrium and rare earth elements of atomic number 62–68 and X is selected from the group consisting of chromium and aluminum but when X is aluminum R must be a rare earth element which comprises heating the constituent components of said composition to a temperature of the order of 1200° C. with a mixture of a molybdic oxide and a potassium compound selected from the group consisting of potassium sulfate, potassium oxide and potassium carbonate, the mole ratio of potassium compound to molybdic oxide being in the range of 1:2 to 1:3, the nutrient to flux weight ratio being in the range of 1:1.8 to 1:3.0, and slowly cooling the resultant melt whereby said composition precipitates from the melt in crystals.

14. The method of claim 13 wherein said mixture consists essentially of K_2SO_4 and MoO_3.

15. The method of claim 14 in which said composition is $YAl_3B_4O_{12}$ and said melt comprises Y_2O_3, Al_2O_3, B_2O_3, K_2So_4 and MoO_3.

16. The method of claim 14 in which said composition is $TbAl_3B_4O_{12}$ and said melt comprises Tb_2O_3, Al_2O_3, B_2O_3, K_2So_4 and MoO_3.

17. The method of claim 14 in which said composition is $EuAl_3B_4O_{12}$ and said melt comprises Eu_2O_3, Al_2O_3, B_2O_3, K_2So_4 and MoO_3.

18. The method of claim 14 in which the mole ratio of K_2So_4 to MoO_3 in the flux is 1:2.7.

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