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SEIKICHI AKIYAMA ET AL

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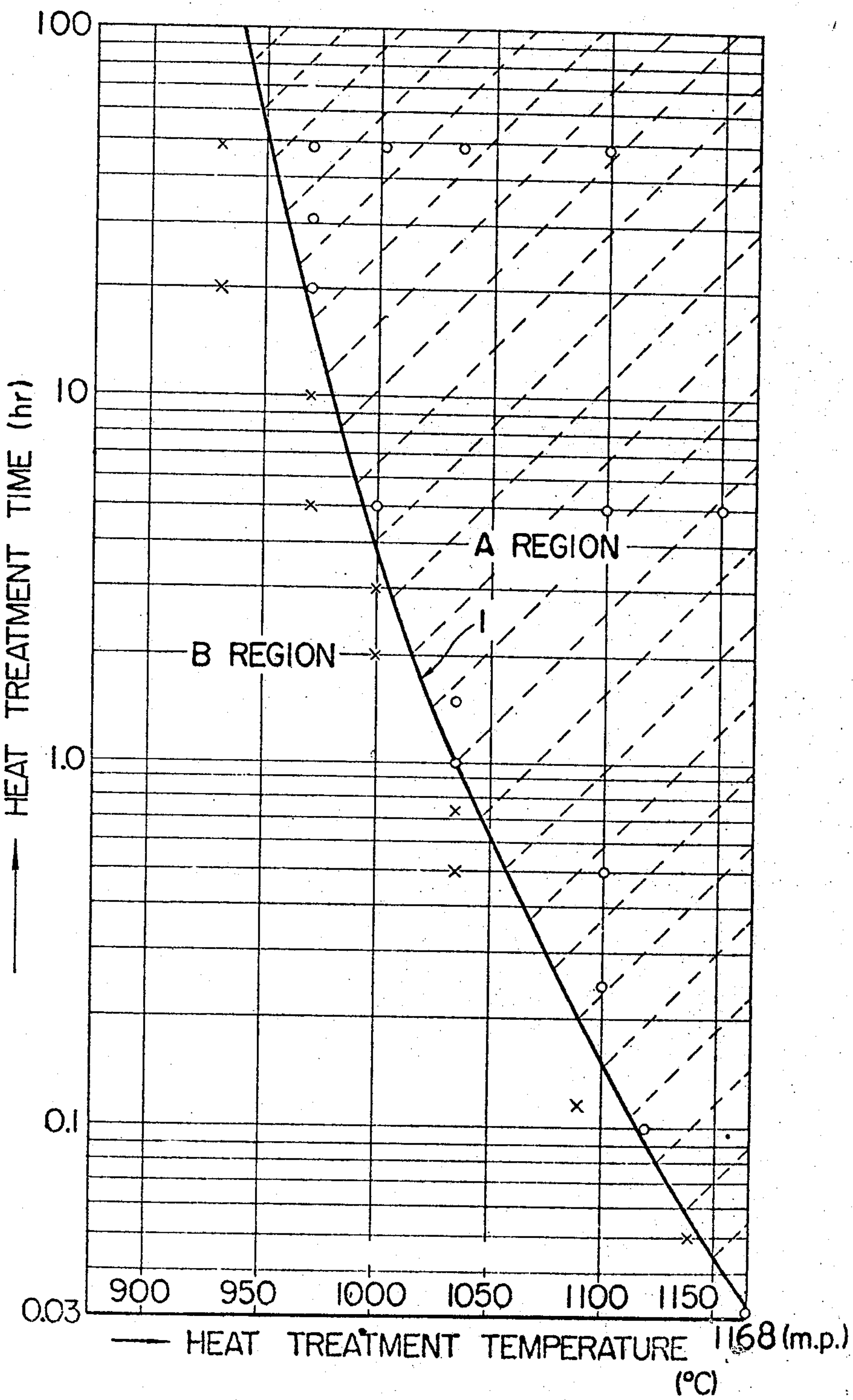

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METHOD FOR IMPROVING TRANSPARENCY OF GADOLINIUM MOLYBDATE SINGLE CRYSTAL

Seikichi Akiyama, Kokubunji, and Hirotsugu Kozuka and Koichi Megumi, Tokyo, Japan, assignors to Hitachi, Ltd., Tokyo, Japan

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U.S. Cl. 423—263 **19 Claims**

ABSTRACT OF THE DISCLOSURE

In cases where a gadolinium molybdate single crystal of low transparency is produced this crystal is subsequently subjected to heat treatment under specified conditions of temperature and time, thereby to improve its transparency. In accordance with the present method, when a crystal having, for example, a light permeability of 20% at a wavelength of 6,328 A. was heat-treated at 1,100° C. for 5 hours, the light permeability became 73% and was improved by 265%.

BACKGROUND OF THE INVENTION

The present invention relates to a method of subjecting a gadolinium molybdate ($Gd_2(MoO_4)_3$) single crystal, particularly a crystal of low transparency, to heat treatment to thereby enhance the transparency.

Since the gadolinium molybdate single crystal is a ferroelectric and ferroelastic material and is light-permeable, it has excellent features as an optical material. The single crystal is usually produced by the following procedure: Gadolinium oxide and molybdenum oxide are mixed in a mol ratio of 1:3. The mixture is fired at a temperature of 1,000° C. or so. Thereafter, the fired product is melted. With a seed crystal dipped in the melt, and then, with the seed kept rotating, the single crystal is grown by the pull method (generally called the Czochralski method). If the raw material is prepared so that the mol ratio between gadolinium oxide and molybdenum oxide may become exactly 1:3 as mentioned above, the crystal can be produced. The mol ratio, however, fluctuates due to such causes as the precision of weighing at compounding of the raw material, and a slight evaporation of molybdenum oxide in the process of producing the single crystal. Accordingly, it often occurs that the composition ratio between the gadolinium oxide and molybdenum oxide constituting the single crystal deviates from the mol ratio of 1:3. As the result, the transparency of the crystal is degraded. In addition, the crystal at low transparency includes local internal distortions. In case where such crystal is used for, e.g., an optical shutter, a voltage (usually termed the threshold voltage) required for inverting the polarization of the crystal is 2–5 times as high as one in case of employing a crystal at high transparency. Moreover, absorption of light is greater. The crystal at low transparency is therefore unsuitable for practical uses.

As is well known, an optical crystal is required to be transparent. In many cases, however, neither natural crystals or artificial crystals have sufficient transparencies. The opacity is generally considered to be attributable to deposition of heterogeneous crystals, deficiency of oxygen ions within the crystal, and the like. Also, in a gadolinium molybdate single crystal to be treated by the method of the present invention, the deposition of such heterogeneous crystals as $Gd_2O_3MoO_3$ and $Gd_2O_32MoO_3$ is known to cause low transparency.

The inventors have subjected such poorly transparent single crytal to heat treatment under various temperature conditions, and found that, when specific temperatures and periods of time are selected, the transparency can be remarkably improved.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a heat treatment method by which a gadolinium molybdate single crystal of light permeability less than 60% can be modified to a crystal having a light permeability at or above 60%.

The present invention has been accomplished on the basis of the heretofore described experiment, and is characterized in that a gadolinium molybdate single crystal of low transparency is heat-treated under the conditions of temperature and time within the region A defined by a curve **1** in the accompanying figure as will be stated below. This figure shows the conditions under which a light permeability of a crystal having permeability below 60% can be improved to at least 60%. The axis of ordinates in the figure represents the heat treatment time, and the axis of abscissas represents the heat treatment temperature. The curve **1** indicates the conditions under which the light transmission factor of 60% is attained, the region A on the right side of the curve **1** (which also includes the curve **1**) indicates the heat treatment conditions of the present invention under which a transmission permeability of at least 60% is attained, and a region B on the left side of the curve **1** is a part outside the scope of the present invention.

As is well known, a light permeability of at best approximately 60% has been attained with the prior-art technique even in the crystal of the most excellent transparency. Moreover, the percentage of yield at which such crystals having the light permeability of 60% were produced was generally low, and most crystals did not reach 60% in the light permeability. It is accordingly very significant in the crystal industry that a crystal below 60% in the light permeability is improved to one of at least 60% in accordance with the method of the present invention. How effective the present invention is, will also be apparent from the fact that the light permeability required for optical materials is generally accepted as being 60 to 70% or higher.

BRIEF DESCRIPTION OF THE DRAWING

The figure in the accompanying drawing is a characteristic curve diagram showing the relations of temperature and time which are the heat treatment conditions on gadolinium molybdate single crystals. In the figure, the region A divided by the curve **1** (which includes the curve **1**) gives the heat treatment conditions of the present invention, while the region B shows the condition of examples used for comparison purposes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be described more concretely hereunder in connection with the preferred embodiments.

Examples

The specimens of gadolinium molybdate single crystals shown in Table 1, which had been previously produced by the well-known pull method heretofore described and which exhibited various different transparencies, were heat-treated in accordance with the method of the invention within air at temperatures and for the periods of time shown. Then, as set forth in the table, the resultant crystals were evaluated. The light permeabilities for all the specimens were at least 60%. The light permeabilities were measured using as a light source a He-Ne laser which had an output of 15 mw. and a wavelength of 6,328 A. In the table, results from heat treatment conditions outside the scope of the present invention are also shown as comparative examples. As apparent from the comparative examples, outside the range of the present invention, the light permeability could not be improved up to 60% for any specimen.

Cooling after the heat treatment in each case involved quick cooling at a cooling rate of 400° C./hr.

Effects of time and temperature on the light permeability of ($Gd_2(MoO_4)_3$) single crystals

TABLE 1

	Light permeability before heat treatment, percent	Heat treatment conditions		Light permeability after heat treatment, percent
		temp., ° C.	Time, hr.	
Example No.:				
1	20	970	48	67
2	20	1,000	48	70
3	20	1,035	48	75
4	20	1,100	48	77
5	20	970	30	63
6	20	970	20	61
7	20	1,000	5	64
8	20	1,100	5	73
9	20	1,150	5	74
10	20	1,035	1.5	66
11	20	1,035	1	63
12	20	1,100	0.5	72
13	20	1,100	0.25	65
14	20	1,120	0.1	60
15	20	1,168	0.03	68
16	30	1,100	0.5	72
17	40	1,100	5	73
18	50	1,120	0.1	61
19	30	940	100	61
Comparative example:				
a	20	1,140	0.05	59
b	20	1,090	0.12	56
c	20	1,035	0.5	55
d	20	1,035	0.75	57
e	20	1,000	2	57
f	20	1,000	3	59
g	20	970	5	55
h	20	970	10	57
i	20	930	20	51
j	20	930	50	52

It will be appreciated that the cooling rate is not restricted to 400° C./hr. and that if a cooling rate of at least 200° C./hr. is employed, the crystals can be taken out of the heat treatment atmosphere without any deterioration of the transparencies improved by the heat treatment. In general the cooling rate is from 200° C. to 3000° C./hr. and preferably 200° C. to 1000° C./hr.

Furthermore, the heat treatment atmosphere is not restricted to air, but it may also be oxygen. In any case, an oxidizing atmosphere containing oxygen may be employed.

While the novel principles of the invention have been described, it will be understood that various omissions, modifications and changes in these principles may be made by one skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A method for improving the transparency of a gadolinium molybdate single crystal, wherein a gadolinium molybdate single crystal of low transparency whose light permeability at a wavelength of 6,328 A. is below 60% is heat-treated under conditions of temperature and time within the region A that is enclosed by curve **1** shown in the figure and thereafter cooling at a rate of at least 200° C./hr., whereby the light permeability is enhanced to at least 60%.

2. The method according to claim **1**, wherein the heat treatment is conducted within an oxidizing atmosphere containing oxygen gas.

3. The method according to claim **1**, wherein the gadolinium molybdate single crystal is heated for 48 hours at a temperature between 970 to 1100° C.

4. The method according to claim **1**, wherein the gadolinium molybdate single crystal is heated at a temperature of about 970° C. for 20 to 30 hours.

5. The method according to claim **1**, wherein the gadolinium molybdate single crystal is heated for about 5 hours at about 1000 to 1150° C.

6. The method according to claim **1**, wherein said gadolinium molybdate single crystal is heated at a temperature of about 1035° C. for 1 to 1.5 hours.

7. The method according to claim **1** in which said gadolinium molybdate single crystal is heated to a temperature of about 1100° C. for about 0.25 to 0.5 hours.

8. The method according to claim **1**, wherein said gadolinium molybdate single crystal is heated to a temperature of about 1120° C. for about 0.1 hours.

9. The method according to claim **1**, wherein said gadolinium molybdate single crystal is heated to a temperature of about 1168° C. for about 0.03 hours.

10. The method according to claim **1**, wherein said gadolinium molybdate crystal is heated to about 940° C. for about 100 hours.

11. A method for improving the transparency of a gadolinium molybdate single crystal produced by the pull method, said gadolinium molybdate single crystal having a light permeability at a wavelength of 6,328 A. below 60% comprising heat treating said gadolinium molybdate single crystal under conditions of temperature and time within the region A that is enclosed by curve **1** shown in the figure and thereafter cooling at a rate of at least 200° C./hr., whereby the light permeability is enhanced to at least 60%.

12. A method according to claim **11**, wherein heating of said gadolinium molybdate single crystal is accomplished at a temperature high enough and for a time long enough so that the light permeability at a wavelength of 6,328 A. is increased to 65% or higher.

13. A method according to claim **12**, wherein heating is accomplished at temperatures high enough and for a period of time long enough so that the light permeability of said crystal is increased to at least about 70%.

14. A method according to claim **11**, wherein said crystal is cooled at a rate of from about 200° C. to 3000° C. per hour after it is heat treated.

15. A method according to claim **14**, wherein said crystal is cooled at a rate of from about 200° C. to 1000° C. per hour.

16. A method according to claim **15**, wherein said crystal is cooled at a rate of about 400° C. per hour.

17. A method according to claim **14**, wherein cooling is accomplished in an oxidizing atmosphere.

18. A method according to claim **11** wherein said heat treatment is accomplished at a substantially constant temperature.

19. In a process for producing a plurality of gadolinium molybdate single crystals each having a transparency to light whose wavelength is 6,328 A. on the order of 60% in which seed crystals of gadolinium molybdate are immersed in a melt of gadolinium oxide and molybdate oxide in a molar ratio of 1:3 and thereafter each of said crystals is slowly withdrawn from the melt by the pull method to produce a gadolinium molybdate single crystal, the improvement for increasing the number of crystals having a transparency of at least 60% comprising heat treating each of said gadolinium molybdate single crystals under conditions of temperature and time within the region A that is enclosed by curve **1** shown in the figure and thereafter cooling at a rate of at least 200° C./hr.

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HERBERT T. CARTER, Primary Examiner

U.S. Cl. X.R.

423—593; 23—293, 301 SP, 305

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,836,632 Dated September 17, 1974

Inventor(s) Seikichi Akiyama, Hirotsugu Kozuka and Koichi Megumi

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Title page, insert the following:

[30] Foreign Application Priority Data

July 28, 1971 Japan...56538/71

Signed and sealed this 31st day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents