

April 8, 1969

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3,437,432

SINGLE CRYSTALS

Filed July 21, 1966

Sheet 1 of 2

FIG. 1

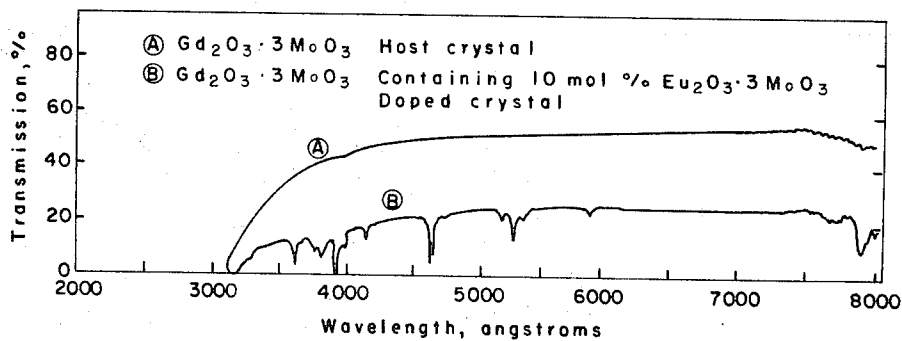
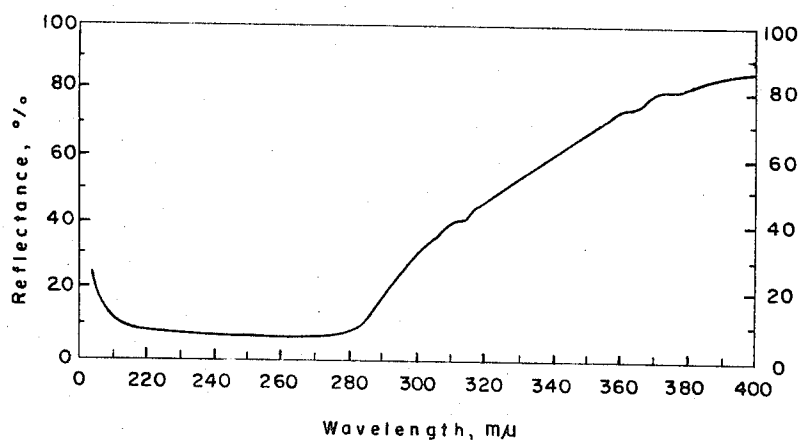


FIG. 2



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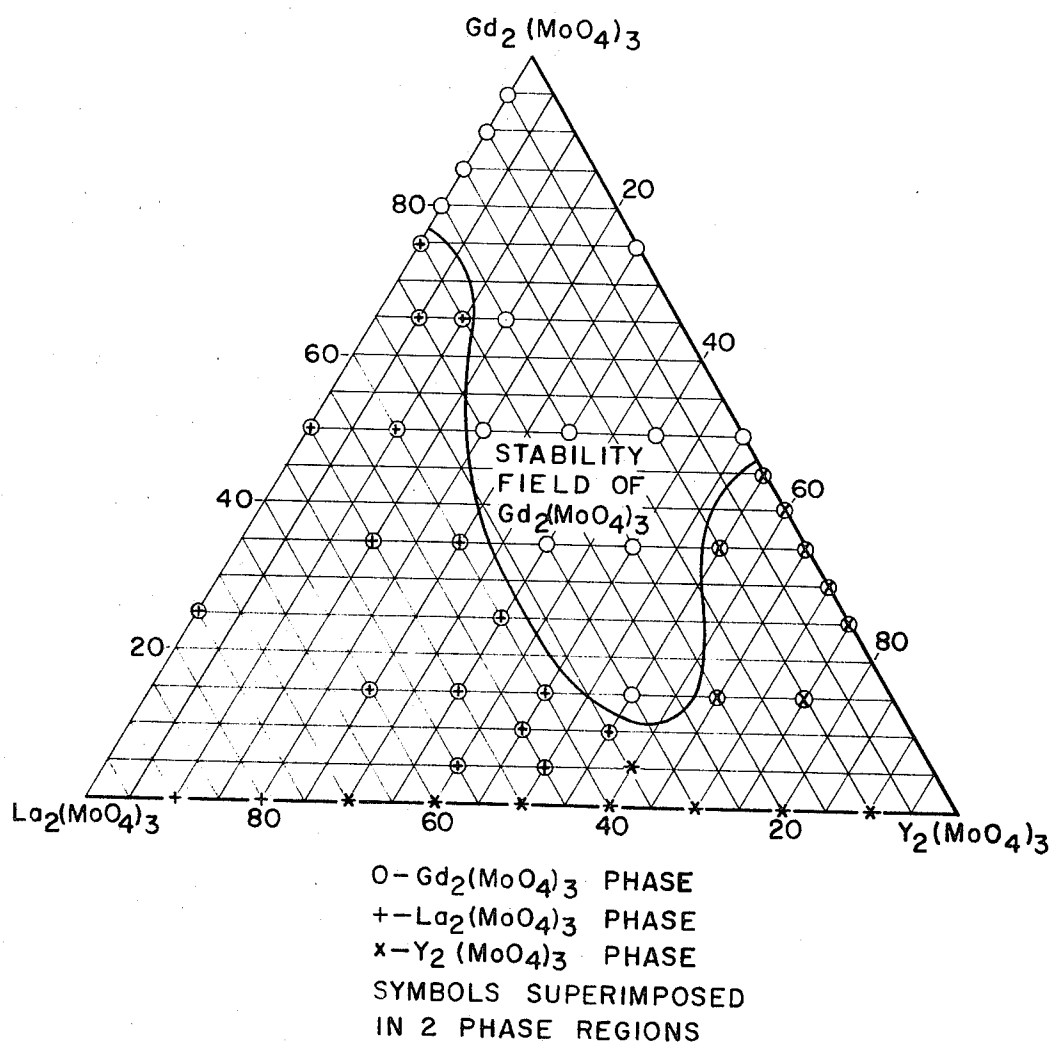
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SINGLE CRYSTALS

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Sheet 2 of 2

FIG. 3



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1

3,437,432

SINGLE CRYSTALS

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Continuation-in-part of application Ser. No. 418,206, Dec. 14, 1964. This application July 21, 1966, Ser. No. 570,121

The portion of the term of the patent subsequent to June 1, 1982, has been disclaimed

Int. Cl. C01g 39/00

U.S. Cl. 23—51

16 Claims

ABSTRACT OF THE DISCLOSURE

Stable single crystals having the gadolinium molybdate structure and unit cell dimensions wherein a and b are equal to 10.39 ± 0.07 Å. and c is 10.69 ± 0.09 Å. said crystals having one dimension at least 0.01 mm. and represented by the formula $(R_x R'_{1-x})_2 O_3 \cdot 3 Mo_{1-e} W_e O_3$ wherein R and R' represent at least one rare earth element having atomic number of from 57–71, scandium and yttrium, x is from 0 to 1.0 and e is from 0 to 0.2. The crystals are made by conventional single crystal techniques and have fluorescent and ferroelectric properties. The crystals are useful as ceramic insulators, as filters for screening out ultraviolet radiation, as laser materials, as transducers, and as ultrasonic generators.

This application is a continuation-in-part of application Ser. No. 150,477, filed Nov. 6, 1961, now abandoned, application Ser. No. 186,602, filed Apr. 6, 1962, now Patent 3,250,722, application Ser. No. 264,065, filed Mar. 11, 1963, now abandoned, and application Ser. No. 418,206, filed Dec. 14, 1964, now abandoned.

The present invention relates to single crystals of $Gd_2 O_3 \cdot 3 MoO_3$ and single crystals having the same crystal structure as single crystals of $Gd_2 O_3 \cdot 3 MoO_3$ wherein other atoms have been substituted for at least a portion of the gadolinium or molybdenum or both.

Known monocrystalline bodies of rare earth compounds are very few in number. Those rare earth compounds which do grow in single crystals generally possess disadvantages which make them unsuitable for electrical or optical uses. For example, yttrium tungstate and yttrium molybdate, do grow as single crystals but these crystals are not stable and hydrate when exposed to moist air, thus severely limiting their usefulness. Efforts to grow lanthanum tungstate, lanthanum molybdate and gadolinium tungstate have failed.

Another group of rare earth containing crystals is the substituted scheelites. These are materials such as $CaWO_4$ and $CaMoO_4$, where a portion of the calcium is replaced by a rare earth. Such materials are relatively easy to grow in single crystal form, partly because of their symmetrical tetragonal structure. However, they are limited in three ways by having a divalent cation sublattice which normally accommodates Ca^{+2} :

(1) Only partial substitution of trivalent rare earth element for divalent calcium is possible and this only by inclusion of a charge compensator such as an alkali metal

2

(monovalent) which dilutes the rare earth concentration.

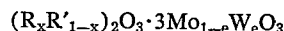
(2) The charge compensator and rare earth ion tend to pair causing the rare earth ion to be in a nonsymmetrical environment. This affects the optical properties of the rare earth ion.

(3) During crystal growth, segregation tends to occur in such multicomponent systems and often results in a nonuniform distribution of rare earth ion within the crystal.

A need exists for single crystals of rare earth compositions because of the usefulness of such crystals as contrasted to powdered materials.

It has been discovered that gadolinium molybdate, i.e., $Gd_2 O_3 \cdot 3 MoO_3$, or alternatively expressed $Gd_2 (MoO_4)_3$, or compositions having the gadolinium molybdate structure do grow in the form of stable, e.g., nonhygroscopic, single crystals. It has further been found that all or a part of the gadolinium can be replaced by rare earth ions which form isostructural molybdates and part of the gadolinium or other ion which forms isostructural molybdates can be replaced by other rare earth ions having ionic radii close to that of gadolinium without substantially changing the crystal structure.

The single crystals of the present invention have the gadolinium molybdate structure and unit cell dimensions wherein a and b are equal to 10.39 ± 0.07 Å and c is 10.69 ± 0.09 Å., said crystals having one dimension at least about 0.1 mm. and represented by the formula:

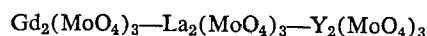


wherein R and R' are at least one rare earth element, e is from about 0 to 0.20 and x is from 0 to 1. The term "rare earth element" as used herein includes scandium and yttrium and elements having an atomic number of 57 through 71.

More particularly, the preferred stable single crystals of the present invention have the gadolinium molybdate structure with an orthorhombic unit cell wherein the dimensions of a and b are equal to 10.39 ± 0.07 Å. and c is 10.69 ± 0.09 Å., said crystals having one dimension at least about 0.1 mm. and having a composition represented by the formula:



wherein A is europium, samarium, gadolinium, terbium or dysprosium, B , C , D and E are the same as A or scandium, yttrium, lanthanum, cerium, raseodymium, neodymium, holmium, erbium, thulium, ytterbium or lutetium; when B , C , D and E are selected from the group represented by A , x , y , z and d can range from 0 to 1, the sum of $x+y+z+d$ being not greater than 1; when B , C , D or E is other than A the values of x , y , z and d are, of course, limited to those values giving a gadolinium molybdate structure, i.e., unit cell dimensions for the gadolinium molybdate structure are 10.39 ± 0.07 Å. in the a and b direction and 10.69 ± 0.09 Å. in the c direction, the sum of x , y , z and d being not greater than 1; and e is from 0 to 0.20. For example, FIGURE 3 illustrates a ternary composition diagram of the system



It can be seen from the diagram that where either or both

yttrium and lanthanum are substituted for gadolinium, the $Gd_2(MoO_4)_3$ structure is stable over a wide range of compositions. Compositions that are especially preferred are those wherein A is europium, gadolinium, terbium or dysprosium or mixtures thereof.

The term single crystal as employed in the present invention refers to orthorhombic crystalline material in which the single crystals have gross physical dimensions such that at least one dimension of the crystal is at least 0.1 millimeter. A single crystal for the purposes of this invention is one which satisfies the well known, external morphological, optical and X-ray criteria for singularity. The criterion of singularity with respect to domain structure is not a mandatory specification. The single crystals are all substantially homogeneous although small imperfections may exist without impairing their utility. This means that x is such a value that no second phase separates. The single crystals of the present invention are nonhygroscopic and can be grown to a length of 4 cm. or more with a diameter of 1 cm. or more. Weissenberg and precession X-ray photographs of single crystals of $Gd_2O_3 \cdot 3MoO_3$ can be indexed on the basis of a tetragonal unit cell having cell constants as follows: a and $b=10.39 \pm 0.07$ A. and $c=10.69 \pm 0.09$ A. A strong piezo-electric signal is observed from these crystals, e.g., a crystal about 1 x 2 x 3 mm. in size, showing that the structure is not centro symmetric and that the true symmetry is not tetragonal but orthorhombic and the space group is $Pba2$. This X-ray data and that presented subsequently were all determined at room temperature. The gadolinium molybdate single crystals have a melting point of $1180^\circ C. \pm 10^\circ$. The experimentally determined density is 4.52 g./cm.³ (theory for the observed unit cell=4.59 g./cm.³).

$Sm_2O_3 \cdot 3MoO_3$, $Eu_2O_3 \cdot 3MoO_3$, $Tb_2O_3 \cdot 3MoO_3$ and $Dy_2O_3 \cdot 3MoO_3$

are isostructural with $Gd_2O_3 \cdot 3MoO_3$ and the lattice constants as calculated from powder patterns, given below, have the same unit cell dimensions as the single crystal compounds. These compounds all have the $Gd_2O_3 \cdot 3MoO_3$ structure and come within the critical unit cell dimensions of said structure as defined in the application.

TABLE I

Sample	a (A.)	b (A.)	c (A.)
$Sm_2O_3 \cdot 3MoO_3$	10.45 $\pm$ 0.01	10.45 $\pm$ 0.01	10.77 $\pm$ 0.01
$Eu_2O_3 \cdot 3MoO_3$	10.42 $\pm$ 0.01	10.42 $\pm$ 0.01	10.72 $\pm$ 0.01
$Gd_2O_3 \cdot 3MoO_3$	10.38 $\pm$ 0.01	10.38 $\pm$ 0.01	10.69 $\pm$ 0.01
$Tb_2O_3 \cdot 3MoO_3$	10.35 $\pm$ 0.01	10.35 $\pm$ 0.01	10.63 $\pm$ 0.01
$Dy_2O_3 \cdot 3MoO_3$	10.33 $\pm$ 0.01	10.33 $\pm$ 0.01	10.61 $\pm$ 0.01

The rare earth compounds and solid solution of this invention can be characterized by conventional X-ray diffraction techniques and composition. X-ray spectra can be conveniently determined on a Norelco X-ray diffractometer, CuK_α radiation, 1° slits, a nickel filter and a scan rate of 1° of 2θ /min. If greater resolution is desired, a Guinier camera can be employed. The X-ray patterns of the compositions of this invention are characteristic thereof and are different from the patterns of the reactants leading to their formation. For instance, it is significant to note that the X-ray diffraction pattern for $Gd_2O_3 \cdot 3MoO_3$ is different from, and not the summation of, the patterns for Gd_2O_3 and MoO_3 .

The novel compositions of the present invention are single crystals of chemical compounds and solid solutions of chemical compounds as shown by X-ray diffraction spectra and not mixtures of the rare earth oxides with molybdic oxide. The complete X-ray powder diffraction patterns for several of the compositions of this invention having the $Gd_2O_3 \cdot 3MoO_3$ structure as defined in the application are given in Tables II through VI. These diffraction patterns are considerably different from patterns of MoO_3 , Gd_2O_3 , or mixtures thereof. When an excess of any one of the constituents used in making the compound is mixed with the compound, the X-ray diffrac-

tion pattern of the mixture contains lines characteristic of the compound and of the constituent added.

TABLE II
[$Sm_2O_3 \cdot 3MoO_3$]

d (A.)	I/I ₀	d (A.)	I/I ₀	d (A.)	I/I ₀
10.72	13	2.398	26	1.765	19
6.08	19	2.393	18	1.738	11
5.37	55	2.337	17	1.697	30
4.691	59	2.275	22	1.653	16
4.343	8	2.149	6	1.631	13
3.743	69	2.144	5	1.620	15
3.689	79	2.113	12	1.616	14
3.583	70	2.107	20	1.601	8
3.489	100	2.101	9	1.580	9
3.298	73	2.090	5	1.498	10
3.222	12	2.084	7	1.482	15
3.156	12	2.081	7	1.421	8
3.147	12	2.065	10	1.398	7
3.125	21	2.029	44	1.366	12
3.041	90	2.024	27	1.265	8
2.953	75	1.989	49	1.230	8
2.814	23	1.984	32	1.228	5
2.810	40	1.957	24	1.218	7
2.686	11	1.954	24	1.215	10
2.616	17	1.913	13	1.198	5
2.605	20	1.846	11	1.193	8
2.538	4	1.791	25	1.125	8
2.529	4	1.782	20		
2.430	9	1.776	23		

Lattice constants: $a=10.45 \pm 0.01$ A.; $b=10.45 \pm 0.01$ A.; $c=10.77 \pm 0.01$ A.

TABLE III
[$Eu_2O_3 \cdot 3MoO_3$]

d (A.)	I/I ₀	d (A.)	I/I ₀	d (A.)	I/I ₀
10.57	13	2.057	2	1.258	3
6.04	7	2.040	2	1.246	2
5.89	2	2.038	3	1.242	3
5.33	93	2.021	13	1.225	2
5.19	3	1.980	12	1.201	3
5.05	2	1.949	5	1.198	3
4.751	3	1.929	10	1.192	3
4.657	17	1.881	3	1.176	1
4.320	2	1.867	3	1.162	1
4.084	2	1.861	2	1.153	2
3.948	1	1.840	3	1.138	1
3.726	16	1.827	2	1.112	1
3.671	16	1.810	2	1.097	1
3.564	100	1.785	6	1.073	1
3.474	26	1.770	5	1.042	1
3.416	2	1.756	4	1.030	1
3.371	6	1.737	1	1.007	1
3.283	17	1.728	1	2.717	2
3.204	3	1.712	2	2.674	13
3.136	22	1.702	5	2.606	11
3.087	12	1.659	7	2.560	2
3.076	12	1.653	4	2.417	2
3.058	16	1.625	2	2.389	4
3.027	22	1.614	4	2.322	4
2.972	2	1.599	4	1.575	5
2.940	17	1.414	2	1.519	1
2.861	9	1.362	2	1.495	2
2.806	10	1.340	4	1.477	4
2.746	1	1.325	1	1.444	2
2.139	3	1.307	2	1.433	2
2.104	4	1.298	2	1.417	2
2.099	4	1.279	2		
2.078	2	1.276	2		

Lattice constants: $a=10.42 \pm 0.01$ A.; $b=10.42 \pm 0.01$ A.; $c=10.72 \pm 0.01$ A.

TABLE IV
[$Tb_2O_3 \cdot 3MoO_3$]

d (A.)	I/I ₀	d (A.)	I/I ₀	d (A.)	I/I ₀
10.59	16	1.837	4	1.255	6
6.04	33	1.831	6	1.233	6
5.32	92	1.785	8	1.221	3
5.17	8	1.775	22	1.218	4
4.652	61	1.761	15	1.215	3
4.300	9	1.749	14	1.208	7
4.239	3	1.724	7	1.205	6
3.711	71	1.703	4	1.184	5
3.657	81	1.690	19	1.175	3
3.548	83	1.679	21	1.169	4
3.458	98	1.645	14	1.155	5
3.273	77	1.641	16	1.147	4
3.191	11	1.628	5	1.131	3
3.125	14	1.617	7	1.114	4
3.011	100	1.605	15	1.108	4
2.925	59	1.597	5	1.106	3
2.788	43	1.588	7	2.035	8
2.660	10	1.568	11	2.027	10
2.586	19	1.509	2	2.011	48

TABLE IV—Continued

d (A.)	I/I ₀	d (A.)	I/I ₀	d (A.)	I/I ₀
2.547	4	1.489	6	2.003	7
2.508	3	1.486	6	1.970	47
2.405	9	1.470	12	1.939	22
2.379	19	1.461	6	1.895	5
2.314	18	1.436	4	1.387	4
2.153	2	1.423	4	1.354	7
2.123	5	1.412	4	1.337	3
2.090	12	1.409	6	1.332	4
2.060	6	1.394	3	1.316	3
2.044	8	1.271	3	1.298	5
1.853	3	1.258	5	1.289	4

Lattice constants: $a=10.35\pm 0.01$ A.; $b=10.35\pm 0.01$ A.; $c=10.63\pm 0.01$ A.TABLE V
[Dy₂O₃·3MoO₃]

d (A.)	I/I ₀	d (A.)	I/I ₀	d (A.)	I/I ₀
10.56	15	1.828	6	1.201	7
6.01	6	1.772	26	1.181	6
5.32	81	1.758	16	1.172	4
5.17	6	1.749	14	1.165	2
4.65	64	1.743	15	1.162	2
4.295	9	1.721	7	1.151	4
3.702	81	1.699	5	1.143	4
3.651	90	1.681	18	1.123	2
3.534	85	1.673	18	1.111	3
3.453	100	1.641	13	1.078	2
3.266	85	1.636	12	1.062	2
3.179	10	1.624	5	1.042	2
3.122	12	1.614	7	1.020	2
3.009	91	1.600	20	1.016	5
2.917	65	1.585	8	1.013	4
2.781	41	1.563	12	0.9924	2
2.651	10	1.483	7	2.006	39
2.580	17	1.465	11	1.989	6
2.538	4	1.454	5	1.962	40
2.503	2	1.431	4	1.933	21
2.399	9	1.421	3	1.893	5
2.374	20	1.405	5	1.850	3
2.309	20	1.351	6	1.294	5
2.259	2	1.337	3	1.285	6
2.119	6	1.333	4	1.267	4
2.085	15	1.327	4	1.256	4
2.059	5	1.316	3	1.252	7
2.036	8	1.296	5	1.229	3
2.023	11	1.215	4		
1.835	4	1.204	7		

Lattice constants: $a=10.33\pm 0.01$ A.; $b=10.33\pm 0.01$ A.; $c=10.61\pm 0.01$ A.TABLE VI
[Gd₂O₃·3MoO₃]

d (A.)	I/I ₀	d (A.)	I/I ₀	d (A.)	I/I ₀
10.57	14	1.779	12	1.208	4
6.03	14	1.765	8	1.189	3
5.32	100	1.752	8	1.178	2
5.17	4	1.735	2	1.159	3
4.652	32	1.728	4	1.156	2
4.304	5	1.707	3	1.150	2
4.062	1	1.689	10	1.134	3
3.934	2	1.685	11	1.118	3
3.714	36	1.649	6	1.109	2
3.666	41	1.645	6	1.070	2
3.553	97	1.621	4	1.049	2
3.469	46	1.610	9	1.047	2
3.278	38	1.592	4	1.035	2
3.197	7	1.573	5	1.015	2
3.134	8	1.492	3	2.071	3
3.095	3	1.474	7	2.050	4
3.019	51	1.465	3	2.033	5
2.932	34	1.441	4	2.016	22
2.793	21	1.428	2	1.975	22
2.668	10	1.414	3	1.945	11
2.592	9	1.410	3	1.900	3
2.550	3	1.402	2	1.860	2
2.517	2	1.398	2	1.337	5
2.412	5	1.391	3	1.321	2
2.384	8	1.359	3	1.304	2
2.319	11	1.341	3	1.302	3
2.131	4	1.238	2	1.295	3
2.094	10	1.225	2	1.277	2
1.842	3	1.219	2	1.273	2
1.836	3	1.211	3	1.260	4

Lattice constants: $a=10.38\pm 0.01$ A.; $b=10.38\pm 0.01$ A.; $c=10.69\pm 0.01$ A.

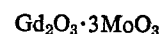
The space group and unit cell dimensions characterize the structure of the crystals which are the subjects of this invention. The unit cell dimensions have a range of values dependent in part upon the size of the cation(s) employed. If the cation is too large or too small a different structure will result. The Ahrens ionic radii of the rare earth ions of atomic numbers 60 to 67 are as follows: Nd³⁺ 1.04 A. (Pm does not occur naturally), Sm³⁺ 1.00 A., Eu³⁺ 0.98 A., Gd³⁺ 0.97 A., Tb 0.93 A., Dy 0.92 A., and Ho 0.91 A. It is found that the compounds R₂O₃·3MoO₃ where R is samarium, europium, gadolinium, terbium and dysprosium are isostructural, all having the Gd₂O₃·3MoO₃ structure, whereas the cognate compounds of neodymium and holmium have different structures. Thus, the range of unit cell dimensions of the single crystals having the Gd₂O₃·3MoO₃ structure which are the subject of this invention are defined as those having unit cell dimensions where a and b are equal to 10.39 ± 0.07 A. and c is 10.69 ± 0.09 A.

In the substitution of ions other than those represented by A for gadolinium, a combination of ions, one smaller and one larger than gadolinium can be used to insert a larger quantity of substituent ions into the Gd₂O₃·3MoO₃ structure. In addition to the ions mentioned hereinbefore small quantities of other trivalent ions (up to about 1%) such as gallium and aluminum can be substituted for the gadolinium without substantially distorting the lattice. Also oxygen can partially replace another ion. Substitution of such ions is contemplated by this invention. Also ions of valence other than three can be substituted provided that the electrical neutrality of the system is maintained by incorporation of other ions to make the average valence three.

The compounds of this invention are prepared by mixing materials comprising a rare earth component and a component which contributes MoO₃ and, when desired, WO₃, and thereafter heating the resulting mixture at elevated temperatures; alternately, the preformed rare earth molybdates can be mixed and heated at elevated temperature. A reaction temperature of at least about 700° C., and usually at least about 900° C., is employed. However, since the reaction time decreases as the reaction temperature increases, to insure complete reactions in practical periods of time, high reaction temperatures approaching, e.g., within 100° C. of, but in any case below, the temperature at which localized fusion of the reaction mass begins are preferred. If relatively low-melting eutectics are formed locally during the reaction, it may be desirable to heat the reaction mixture for a period at, e.g., 500–600° C., then regrind the resulting product and finish the reaction at higher temperature.

The rare earth components preferably are introduced into the reaction mixture as oxides. However, rare earth components which decompose to the oxide on heating, for example, rare earth hydroxides, oxalates, carbonates, citrates, acetates and tartrates can be employed. The WO₃ or MoO₃-contributing component also is preferably introduced into the mixture in the form of an oxide, such as tungsten oxide or molybdenum oxide. However, this reactant need not necessarily be an oxide. It can be, for example, a compound such as tungstic acid, or molybdic acid, or ammonium tungstate, which on ignition is converted to the oxide. Reactants are preferably introduced in the form of finely ground particulate material, preferably having a particle size of less than 10 microns.

The quantities of reactants employed in preparing the compositions of this invention are preferably approximately stoichiometric based on the desired composition of the final product. Thus, for example, in preparing



three moles of MoO₃ would be heated with one mole of Gd₂O₃.

After the powdered materials are prepared they are heated to form a melt and the single crystals having the

gadolinium molybdate structure are pulled from the melt by conventional methods. The techniques used for pulling the novel single crystals from the melt are described in Preparation of Single Crystals, Lawson and Nielson, Butterworth, 1958, particularly pp. 10-31 and 176-210. Because the crystals are grown from a homogeneous melt they have substantially the same composition as the melt.

The single crystals of the present invention are useful as ceramic insulators and as filters for screening out ultraviolet radiation. The near ultraviolet and visible spectra of two single crystals are shown in FIGURE 1. This figure shows that absorption of ultraviolet light is substantially complete in the region from 2000 to about 3200 Å.

As exemplified hereinafter, some of the single crystals of the present invention are also useful as laser materials. As is well known, the acronym, laser, means light amplification through stimulated emission of radiation and numerous references are available which describe the principles and operation of lasers.

The single crystals of the present invention have been demonstrated to possess ferroelectric properties. Ferroelectric properties of several crystals are given in Table VII below. The procedures for measuring the ferroelectric properties are described and referenced in Applied Physics Letters, vol. 8, No. 2, pp. 50-52, Jan. 15, 1966. The discovery of materials which exhibit both laser and ferroelectric properties is very surprising. This combination of properties in a single material is novel.

The single crystals of the present invention are also useful because of their piezo- and ferroelectric properties, as transducers and ultrasonic generators.

All the single crystals of the present invention are useful as ceramic insulators. The electrical properties of the single crystal of $Gd_2O_3 \cdot 3MoO_3$ are shown below:

TABLE VIII.—PROPERTIES OF $Gd_2O_3 \cdot 3MoO_3$

5	Compound ($Gd_2O_3 \cdot 3MoO_3$):	
	Resistivity (ohm/cm.)	5×10^{14}
	Dielectric constant	8.8
	Dissipation factor	0.80

10 Electric properties of the other single crystals are similar. By machining or sawing the crystals into the proper shape they are suitable as, for example, insulating materials in electronic components.

15 The following specific examples illustrating the invention are given below.

EXAMPLE 1

Gd_2O_3 (361.8 parts) is intimately mixed with MoO_3 (431.7 parts). About 1% paraffin is added as a binder and the mixture pressed into pellets. These pellets are heated in air in a platinum vessel for 4 hours at 900° C. During the heating the paraffin is burned away. The mixture is converted into the compound $Gd_2O_3 \cdot 3MoO_3$ for which the X-ray diffraction pattern is given in Table VI.

25 A platinum-rhodium crucible (60-40) measuring $1\frac{1}{2} \times 1\frac{1}{2}$ inches (0.060 inch-thick wall) located in an electrical induction coil which will carry 10 kilowatts at 450 kilocycles is half filled with $Gd_2O_3 \cdot 3MoO_3$ prepared as above which is melted at approximately 1185° C. A platinum-rhodium wire (80-20) 0.045 inch diameter is 30 dipped into the melt and rotated at approximately 120

TABLE VII.—FERROELECTRIC PROPERTIES OF SINGLE CRYSTALS OF RARE EARTH MOLYBDATES

No.:	Crystal Composition	T_c , ° C.	T_r , ° C.	P_s , Micro-coulombs/cm. ²	E_c , Kilo-volts/cm.
1.....	$Gd_2O_3 \cdot 3MoO_3$	159	25	.17	5.0
2.....	$Tb_2O_3 \cdot 3MoO_3$	157	25 100 140	.18 .13 .08	6.3 5.2 2.9
3.....	$Eu_2O_3 \cdot 3MoO_3$	161	25 100 150	.12 .10 .08	9.4 10.7 6.7
4.....	$Sm_2O_3 \cdot 3MoO_3$	190	25 100 180	(-) .19 .08	(-) 8.5 6.2
5.....	$(Gd_{0.25}Tb_{0.75})_2O_3 \cdot 3MoO_3$	157	25 100 150	.24 .10 .06	8.0 3.4 1.8
6.....	$(Gd_{0.5}Y_{0.5})_2O_3 \cdot 3MoO_3$	147	25 100 140	.21 .13 .05	11.5 7.6 2.4
7.....	$(Gd_{0.5}Eu_{0.5})_2O_3 \cdot 3MoO_3$	160	25 100 140	.14 .10 .07	9.5 5.8 4.5
8.....	$(Gd_{0.5}Eu_{0.5})_2O_3 \cdot 3MoO_3$	157	25 100 140	.22 .11 .07	6.9 3.8 1.7
9.....	$(Tb_{0.5}Eu_{0.5})_2O_3 \cdot 3MoO_3$	159	25 100 150	.15 .09 .05	8.8 4.4 1.8
10.....	$(Gd_{0.57}Nd_{0.43})_2O_3 \cdot 3MoO_3$	159	25 100 140	.17 .14 .09	10.5 13.3 11.6
11.....	$(Tb_{0.5}Eu_{0.5})_2O_3 \cdot 3MoO_3$	170	25 100 160	.08 .09 .06	6.6 7.3 5.3
12.....	$Gd_2O_3 \cdot 3(Mo_{0.85}W_{0.15})O_3$	148	25 100 140	.13 .13 .07	7.5 4.3 1.1

T_c = Curie temperature.

P_s = Spontaneous polarizations.

E_c = Coercive fields.

r.p.m. until solidification on the wire occurs. The wire is then withdrawn from the melt at about $\frac{1}{3}$ inch per hour. The power to the induction coil is increased until the crystal diameter is approximately 1 mm. The power is then decreased until the crystal diameter is about $\frac{3}{8}$ to $\frac{1}{2}$ inch. The power is then held such that the crystal maintains a diameter of $\frac{3}{8}$ to $\frac{1}{2}$ inch as it is being drawn at $\frac{1}{3}$ inch per hour. This drawing is continued until the crystal is about 2 inches long. To remove the crystal from the crucible, a split tube furnace 10 inches long by 1 inch in diameter is preheated to approximately 400° C. and placed immediately above the crucible and around the pulling rod to which the wire is attached. The crystal is pulled rapidly (about 6 inches/minute) into the middle of the furnace. The voltage to the furnace is programmed downward from about 60 volts to 0 linearly over approximately 5 hours. The crystal is then removed.

The fluorescence of a $Gd_2O_3 \cdot 3MoO_3$ crystal is measured with a Bausch and Lomb spectrograph producing plates with a dispersion of 8 Å./mm. and a spectral resolution of 0.1 Å. The fluorescence is measured with exciting wave lengths of 2537 Å. and 3600 Å. both at room temperature and immersed in liquid nitrogen (77° K.). The 3600 Å. exciting source is a Gates and Co. HBO 100 W/2 high pressure mercury lamp equipped with a Corning 5840 filter and a piece of heat-absorbing glass. The 2537 Å. exciting source is an Ultra-Violet Products Pen Ray lamp used with a Corning 9863 filter and a 1.8 cm. chlorine gas cell. Exposures with this latter source require several hours while the high-pressure mercury lamp requires only a few minutes. Following development the plates are analyzed with a Jarrett-Ash densitometer.

The $Gd_2O_3 \cdot 3MoO_3$ crystal gives a white broad-band

fluorescence at 77° K. centered at 5800 Å. (half-width 600 Å.) with a 2537 Å. exciting source.

A similar crystal prepared in substantially the same manner, but containing 10 mole percent europium, gives two strong doublets at about 6150 Å. and 6170 Å. At room temperature these doublets each form one band with 8-15 Å. half width. At liquid nitrogen temperatures the doublets are well defined with half-widths of about 1 Å. for each line.

The absorption of the crystals is measured with a Bausch and Lomb Spectromic 505 spectrophotometer. The $Gd_2O_3 \cdot 3MoO_3$ single crystal has strong absorption below 3200 Å. but little absorption above. The europium doped single crystal also has strong absorption below 3200 Å. as well as in several bands between 3200 and 6200 Å. as shown in FIGURE 1.

The reflectance spectrum of a $Gd_2O_3 \cdot 3MoO_3$ powder is measured with a Beckmann spectrophotometer using a Beckmann reflectance attachment on a USP magnesium carbonate black as reference material. The reflectance is low between 2000 and 2800 Å. but increases rapidly after 2800 Å., as shown in FIGURE 2.

EXAMPLES 2 THROUGH 54

The procedure described in Example 1 is used for preparing the following single crystals. The amounts of the reactants shown in the following table are heated to just below the fusion point of the compound to form a solid solution. Where terbium is one of the constituents it was added as Tb_2O_3 . Under the influence of heat this form is converted to Tb_2O_3 . The order of the amounts of the reactants is the same as the formula to the left side of the table. Then the compounds are further heated to from a melt and the single crystals are pulled from the melt as described in Example 1.

Number:	Single Crystal	MoO ₃ (parts)	Rare Earth Oxides (parts)
2	$Tb_2O_3 \cdot 3MoO_3$	863.6	748.8
3	$(Gd_{0.97}Nd_{0.03})_2O_3 \cdot 3MoO_3$	431.8	351.0
4	$(Gd_{0.99}Nd_{0.01})_2O_3 \cdot 3MoO_3$	431.8	325.6
5	$(Gd_{0.99}Eu_{0.01})_2O_3 \cdot 3MoO_3$	431.8	325.6
6	$(Gd_{0.99}Eu_{0.01})_2O_3 \cdot 3MoO_3$	431.8	289.4
7	$Sm_2O_3 \cdot 3MoO_3$	431.8	348.7
8	$Eu_2O_3 \cdot 3MoO_3$	431.8	352.0
9	$Dy_2O_3 \cdot 3MoO_3$	431.8	372.9
10	$(Gd_{0.9}Y_{0.1}La_{0.01})_2O_3 \cdot 3MoO_3$	431.8	180.9
11	$(Eu_{0.9}Tb_{0.1})_2O_3 \cdot 3MoO_3$	863.6	176
12	$(Eu_{0.9}Tb_{0.1})_2O_3 \cdot 3MoO_3$	863.6	352.0
13	$(Eu_{0.9}Tb_{0.1})_2O_3 \cdot 3MoO_3$	863.6	528.0
14	$(Dy_{0.9}Sm_{0.1})_2O_3 \cdot 3MoO_3$	431.8	298.3
15	$Gd_{0.9}Sm_{0.1}Dy_{0.1}O_3 \cdot 3MoO_3$	431.8	217.1
16	$(Eu_{0.9}Nd_{0.1})_2O_3 \cdot 3MoO_3$	431.8	316.8
17	$(Tb_{0.9}Nd_{0.1})_2O_3 \cdot 3MoO_3$	863.6	726.3
18	$(Gd_{0.9}Y_{0.1}La_{0.01}Pr_{0.01})_2O_3 \cdot 3MoO_3$	431.8	217.1
19	$(Tb_{0.9}Nd_{0.05}Pr_{0.05})_2O_3 \cdot 3MoO_3$	690.0	711.4
20	$(Gd_{0.9}Y_{0.1}La_{0.01}Er_{0.01})_2O_3 \cdot 3MoO_3$	431.8	217.1
21	$(Gd_{0.9}Tb_{0.1}Eu_{0.2}Dy_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
22	$(Gd_{0.9}Tb_{0.1}Eu_{0.2}Dy_{0.1}Pr_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
23	$(Tb_{0.9}Eu_{0.4}Ho_{0.1})_2O_3 \cdot 3MoO_3$	777.2	374.4
24	$(Tb_{0.9}Eu_{0.4}Tm_{0.1})_2O_3 \cdot 3MoO_3$	863.6	374.4
25	$(Gd_{0.9}Tb_{0.1}Tm_{0.1}Y_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
26	$(Gd_{0.9}Sm_{0.05})_2O_3 \cdot 3MoO_3$	431.8	343.7
27	$(Gd_{0.9}Tm_{0.05})_2O_3 \cdot 3MoO_3$	431.8	343.7
28	$(Tb_{0.9}Y_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
29	$(Gd_{0.9}Tb_{0.1}Eu_{0.3}Nd_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
30	$(Gd_{0.9}Tb_{0.1}Eu_{0.3}Tm_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
31	$(Tb_{0.9}Eu_{0.4}Y_{0.1})_2O_3 \cdot 3MoO_3$	863.6	374.4
32	$(Gd_{0.9}Er_{0.05})_2O_3 \cdot 3MoO_3$	431.8	343.7
33	$(Tb_{0.9}Ho_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
34	$(Tb_{0.9}Y_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
35	$(Gd_{0.9}Y_{0.1}La_{0.05}Ho_{0.05})_2O_3 \cdot 3MoO_3$	431.8	217.1
36	$(Gd_{0.9}Tb_{0.2}Dy_{0.1}Eu_{0.01}Ho_{0.01})_2O_3 \cdot 3MoO_3$	863.6	361.8
37	$(Tb_{0.9}Tm_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
38	$(Gd_{0.9}Ho_{0.05})_2O_3 \cdot 3MoO_3$	431.8	343.7
39	$(Tb_{0.9}Er_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
40	$(Gd_{0.9}Pr_{0.05})_2O_3 \cdot 3MoO_3$	431.8	343.7
41	$(Gd_{0.9}Y_{0.1}La_{0.05}Y_{0.05})_2O_3 \cdot 3MoO_3$	431.8	217.1
42	$(Tb_{0.9}Sm_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
43	$(Gd_{0.9}Y_{0.1}La_{0.05}Tm_{0.05})_2O_3 \cdot 3MoO_3$	431.8	217.1
44	$(Tb_{0.9}Pr_{0.05})_2O_3 \cdot 3MoO_3$	863.6	711.4
45	$(Tb_{0.9}Y_{0.1}La_{0.05}Dy_{0.05})_2O_3 \cdot 3MoO_3$	863.6	449.3
46	$(Gd_{0.9}Y_{0.1}La_{0.05}Eu_{0.05})_2O_3 \cdot 3MoO_3$	431.8	217.1
47	$(Gd_{0.9}Y_{0.1}La_{0.05}Sm_{0.05})_2O_3 \cdot 3MoO_3$	431.8	217.1
48	$(Gd_{0.9}Y_{0.1}La_{0.05}Nd_{0.05})_2O_3 \cdot 3MoO_3$	431.8	217.1
49	$(Gd_{0.9}Y_{0.1}La_{0.05}Tb_{0.05})_2O_3 \cdot 3MoO_3$	863.6	434.2
50	$(Gd_{0.9}Tb_{0.1}Eu_{0.3}Sm_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
51	$(Gd_{0.9}Tb_{0.1}Eu_{0.3}Ho_{0.1})_2O_3 \cdot 3MoO_3$	863.6	217.1
52	$(Sm_{0.9}Y_{0.1})_2O_3 \cdot 3MoO_3$	431.8	279.0
53	$(Sm_{0.9}Er_{0.1})_2O_3 \cdot 3MoO_3$	431.8	313.8
54	$(Sm_{0.9}Ho_{0.1})_2O_3 \cdot 3MoO_3$	431.8	479.0

a cf. Figure 3.

b Plus 46.4 parts of WO_3 .

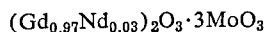
c Plus 23.2 parts of WO_3 .

EXAMPLE 55.—DEMONSTRATION OF FERROELECTRICITY

A crystal of $Gd_2O_3 \cdot 3MoO_3$, prepared as in Example 1, was cut to provide a wafer circa 1 cm. in diameter and 0.04 cm. thick and electrodes 0.4×0.5 cm. were attached to it. The sample was oriented with its *c*-axis normal to the electrodes. It was tested in a ferroelectric loop tracer built after the design of Diamant et al. (Rev. Sci. Instr. 28, 30 (1957)) where a dielectric hysteresis loop was observed at room temperature at 60 c.p.s., establishing that the material is ferroelectric. The coercive field was found to be approximately 5000 v./cm. and the spontaneous polarization approximately 0.17 microcoulomb/cm.² at room temperature. The values of these properties at two other temperatures are given in Table VII.

EXAMPLE 56.—DEMONSTRATION OF LASING ACTION

A single crystal having the composition



(prepared as in Example 3) and a diameter of $\frac{1}{4}$ inch and a length of 1 inch is polished flat at both ends. A mirror is applied at both ends of the crystal by conventional techniques which is 100% reflecting at one end and 95% reflecting at the other. The crystal is then cemented in a brass holder with $\frac{27}{32}$ inch of the crystal extending beyond the holder.

The crystal and holder is then inserted in the head of a Trion model C-102-85 laser system using an FT-100B flashlamp. Emission of radiation from the 95% reflecting mirror end of the crystal is measured by an infrared photomultiplier in conjunction with an oscilloscope which gives a trace of intensity versus time.

Successively higher energies are flashed into the crystal. Up to 925 joules ordinary fluorescence of neodymium is seen. At 945 joules the first evidence of stimulated emission is seen and at 975 joules stimulated emission is very pronounced.

In a similar experiment in which the crystal is cooled to 134° K. in a current of cold nitrogen the threshold energy is 340 joules.

I claim:

1. Stable single crystals having the gadolinium molybdate structure and unit cell dimensions wherein *a* and *b* are equal to 10.39 ± 0.07 Å. and *c* is 10.69 ± 0.09 Å. said crystals having one dimension at least about 0.1 mm. and represented by the formula $(R_xR'_{1-x})_2O_3 \cdot 3Mo_{1-e}W_eO_3$ wherein R and R' represent at least one rare earth element having an atomic number of from 57 through 71, scandium and yttrium, *x* is from 0 to 1.0 and *e* is from 0 to 0.2.

2. The single crystal of claim 1 wherein R is gadolinium and R' represents europium, dysprosium, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, holmium, erbium, thulium, ytterbium, lutetium, and terbium.

3. The single crystal of claim 1 wherein R is europium and R' represents dysprosium, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, holmium, erbium, thulium, ytterbium, lutetium, and terbium.

4. The single crystal of claim 1 wherein R is dysprosium and R' represents scandium, yttrium, lanthanum,

cerium, praseodymium, neodymium, samarium, holmium, erbium, thulium, ytterbium, lutetium, and terbium.

5. The single crystal of claim 1 wherein R is terbium and R' represents scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, holmium, erbium, thulium, ytterbium, lutetium, and terbium.

6. The single crystal of claim 1 where R is samarium and R' is scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, holmium, erbium, thulium, ytterbium and lutetium.

7. The single crystal of claim 1 wherein R is gadolinium and R' is europium.

8. The single crystal of claim 1 wherein R is gadolinium and R' is neodymium.

9. The single crystal of claim 1 wherein R is gadolinium and R' is terbium.

10. The single crystal of claim 1 wherein R is europium and R' is terbium.

11. The stable single crystal of claim 1, $Gd_2O_3 \cdot 3MoO_3$.

12. The stable single crystal of claim 1, $Sm_2O_3 \cdot 3MoO_3$.

13. The stable single crystal of claim 1, $Eu_2O_3 \cdot 3MoO_3$.

14. The stable single crystal of claim 1, $Tb_2O_3 \cdot 3MoO_3$.

15. The stable single crystal of claim 1, $Dy_2O_3 \cdot 3MoO_3$.

16. Stable single crystals having the gadolinium molybdate structure with an orthorhombic unit cell wherein the dimensions of *a* and *b* are equal to 10.39 ± 0.07 Å. and *c* is 10.69 ± 0.09 Å., said crystals having one dimension at least about 0.1 mm. and having a composition represented by the formula



wherein A is selected from the group consisting of samarium, europium, gadolinium, terbium, and dysprosium; B, C, D and E are selected from the group consisting of A, scandium, yttrium, lanthanum, cerium, praseodymium, holmium, erbium, thulium, ytterbium, and lutetium; when B, C, D and E are selected from the group represented by A, *x*, *y*, *z* and *d* are 0 through 1, the sum of *x*, *y*, *z* and *d* being not greater than 1; when B, C, D, and E is other than from the group represented by A the values of *x*, *y*, *z* and *d* are limited to those giving a gadolinium molybdate structure, the sum of *x*, *y*, *z* and *d* being not greater than 1; and *e* is from 0 to 0.2.

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U.S. Cl. X.R.

106—39; 252—301.5, 301.4, 62.9, 63.5, 300

U.S. DEPARTMENT OF COMMERCE

PATENT OFFICE

Washington, D.C. 20231

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,437,432

April 8, 196

Hans J. Borchardt

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

Column 12, line 36, "praseodymium, holmium," should read -- praseodymium, neodymium, holmium --.

Signed and sealed this 7th day of April 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents