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(54) Title: COMPOSITION FOR OPTICAL MEMBERS AND OPTICAL MEMBER

(57) Abstract: There are provided a colorless composition for optical members that contains La and O and a transparent optical member. A composition for optical members that contains La and O and further contains at least one element selected from the group A consisting of Gd, Y, Al, Ga, and In and at least one element selected from the group B consisting of Ta and Nb, wherein the sum total of La, O, at least one element selected from the group A, and at least one element selected from the group B is 99% by mole or more while the sum total of the elements of the composition is 100% by mole.



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## DESCRIPTION

### COMPOSITION FOR OPTICAL MEMBERS AND OPTICAL MEMBER

#### Technical Field

[0001] The present invention relates to a composition for optical members and an optical member.

#### Background Art

[0002] It is known that some optical members made of inorganic materials other than glass have a pyrochlore structure. PCT Japanese Translation Patent Publication No. 2004-501856 (hereinafter referred to as PTL 1) discloses a microwave dielectric compound that is made of  $\text{Bi}_2\text{O}_3$ ,  $\text{ZnO}$ , or  $\text{Ta}_2\text{O}_5$  and has the pyrochlore structure.

[0003] However, since  $\text{Bi}_2\text{O}_3$  is yellow, the microwave dielectric compound disclosed in PTL 1 is also considered to be yellow and probably has low transmittance as an optical member for use in lenses at the wavelength bands used.

#### Citation List

##### Patent Literature

[0004] PTL 1 PCT Japanese Translation Patent Publication No. 2004-501856

#### Summary of Invention

##### Technical Problem

[0005] The present invention provides a colorless

composition for optical members that contains La and O and a transparent optical member.

### **Solution to Problem**

**[0006]** A composition for optical members according to one aspect of the present invention contains La and O and further contains at least one element selected from the group A consisting of Gd, Y, Al, Ga, and In, and at least one element selected from the group B consisting of Ta and Nb, wherein the sum total of La, O, at least one element selected from the group A, and at least one element selected from the group B is 99% by mole or more while the sum total of the elements of the composition is 100% by mole.

**[0007]** A composition for optical members according to one aspect of the present invention contains La and O and is colorless. Thus, optical members made of this composition will be transparent. Lenses made of an optical member according to one aspect of the present invention will have high transmittance at the wavelength band used.

**[0008]** Further features of the present invention will become apparent from the following description of exemplary embodiments with reference to the attached drawings.

### **Brief Description of Drawings**

**[0009]** Figure 1 is a table of the results of examples and comparative examples according to the present invention.

### **Description of Embodiments**

[0010] Although the embodiments of the present invention are described below, the present invention is not limited to these embodiments.

### **First Embodiment**

[0011] A first embodiment describes a composition for optical members.

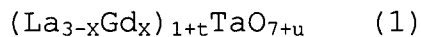
[0012] A composition for optical members according to the present embodiment contains La and O and further contains at least one element selected from the group A consisting of Gd, Y, Al, Ga, and In and at least one element selected from the group B consisting of Ta and Nb, wherein the sum total of La, O, at least one element selected from the group A, and at least one element selected from the group B is 99% by mole or more while the sum total of the elements of the composition is 100% by mole.

[0013] A composition for optical members according to the present embodiment contains the elements described above and is colorless (white). An optical member made of such a white composition will also be colorless and transparent. Thus, lenses made of an optical member that is made of a composition for optical members according to one aspect of the present invention will have high transmittance at a wavelength band used.

[0014] In one example of a composition for optical members according to the present embodiment, at least one element

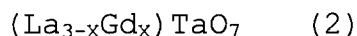
selected from the group A is Gd, at least one element selected from the group B is Ta, the sum total of La, Gd, and Ta is 100% by mole, and La is 2.4% by mole or more and 38.2% by mole or less, Gd is 37.3% by mole or more and 72.9% by mole or less, and Ta is 24.5% by mole or more and 25.3% by mole or less. In another example of a composition for optical members according to the present embodiment, at least one element selected from the group A is Gd, at least one element selected from the group B is Ta, the sum total of La, Gd, and Ta is 100% by mole, and La is 2.5% by mole or more and 37.5% by mole or less, Gd is 37.5% by mole or more and 72.5% by mole or less, and Ta is 25.0% by mole.

**[0015]** A composition for optical members according to the present embodiment may have the following formula (1):



wherein X is  $1.5 \leq X \leq 2.9$ , t is  $-0.01 \leq t \leq 0.02$ , and u is  $-0.06 \leq u \leq 0.12$ .

**[0016]** A composition for optical members according to the present embodiment may have the following formula (2):



wherein X is  $1.5 \leq X \leq 2.9$ .

**[0017]** The formula (2) corresponds to the formula (1) in which t and u are 0.

**[0018]** As described below in examples, a composition for optical members according to the present embodiment having

the formula (2) has a cubic pyrochlore structure and yields a transparent optical member.

#### Impurities in Composition for Optical Members

**[0019]** When the sum total of the elements of a composition for optical members according to the present embodiment is 100% by mole, the sum total of La, O, at least one element selected from the group A, and at least one element selected from the group B is 99% by mole or more. The composition may contain 1% by mole or less of impurities. The impurity content may be 0.1% by mole or less. Examples of the impurities include metal oxides, such as Si oxide, Fe oxide, B oxide, W oxide, Bi oxide, Co oxide, and Cu oxide.

#### Method for Determining Component Ratio of Composition for Optical Members

**[0020]** In the present embodiment, the component ratio of a composition for optical members may be determined with an inductively coupled plasma (hereinafter referred to as ICP) spectrometer. The ICP spectrometer may be CIROS CCD (manufactured by Rigaku Corp.).

#### Method for Determining Crystal Structure

**[0021]** In the present embodiment, whether the crystal structure of a composition for optical members is a cubic pyrochlore structure or not is determined as described below. The crystal structure is determined with an X-ray diffractometer RINT 2100 (manufactured by Rigaku Corp.) at

an X-ray tube voltage of 40 kV and an X-ray tube current of 40 mA.

**[0022]** First, an X-ray diffraction pattern is obtained by measuring the diffraction intensity (counts) at  $2\theta$  in the range of  $10^\circ$  to  $80^\circ$  with the X-ray diffractometer.

**[0023]** Next, an X-ray diffraction pattern having a cubic pyrochlore structure (space group Fd-3m, #227,  $Z = 8$ ) that is close to the X-ray diffraction pattern measured is chosen from the PDF database. Several refinement cycles of the lattice constant are performed by the least squares method with X-ray powder diffraction analysis software JADE (available from Rigaku Corp.) using the lattice constant of the chosen data as the initial value.

**[0024]** Next, the X-ray diffraction pattern is calculated with Mercury (manufactured by Cambridge Crystallographic Data Centre, the United Kingdom) from the space group (Fd-3m, #227,  $Z = 8$ ), the refined lattice constant, the site occupancies, and Wyckoff positions.

**[0025]** Next, the calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group Fd-3m, #227,  $Z = 8$ ) is compared with the X-ray diffraction pattern obtained by actual measurement. Agreement between the peak positions indicates that the metal oxide has the cubic pyrochlore structure. Disagreement between the peak positions or the presence of a peak not included in the calculated X-ray

diffraction pattern of the cubic pyrochlore structure indicates that the crystal structure of the metal oxide is not the cubic pyrochlore structure.

Dispersion Liquid that Contains Composition for Optical Members and Organic Monomer

**[0026]** A dispersion liquid that contains a composition for optical members according to the present embodiment and an organic monomer will be described below. Such a dispersion liquid can be prepared by the addition of the organic monomer and the composition for optical members according to the present embodiment to a polar solvent or a nonpolar solvent. A bead mill method, which is a wet dispersion method, may be used for dispersion.

**[0027]** The organic monomer may be a thermoplastic resin, such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl acetate), Teflon (registered trademark), ABS resin, AS resin, acrylic resin (PMMA), polyamide, polyacetal, polycarbonate (PC), poly(ethylene terephthalate) (PET), cyclic polyolefin (COP), or polyimide (PI), or a thermosetting resin, such as phenolic resin, epoxy resin, or polyimide (PI). In general, a hydrocarbon monomer or an alicyclic monomer is advantageously less hygroscopic and advantageously has a smaller coefficient of linear expansion than other monomers.

Composite Material that Contains Composition for Optical

## Members and Organic Polymer

**[0028]** The dispersion liquid may be irradiated with light or heated to polymerize the organic monomer, preparing a composite material that contains the composition for optical members according to the present embodiment in a polymer of the organic monomer. In general, the coefficient of linear expansion of the composition for optical members according to the present embodiment is smaller than the coefficient of linear expansion of the polymer of the organic monomer alone. Thus, the coefficient of linear expansion of the composite material is smaller than the coefficient of linear expansion of the polymer of the organic monomer. Thus, the composition for optical members according to the present embodiment may be used as an additive for decreasing the coefficient of linear expansion.

## Second Embodiment

**[0029]** A second embodiment describes an optical member.

**[0030]** An optical member according to the present embodiment has an Abbe number of 25 or more, a refractive index of 1.75 or more, and a transmittance of 20% or more and is made of the composition for optical members according to the first embodiment.

**[0031]** The optical member according to the present embodiment is made of the elements that constitute a composition for optical members and is transparent. Thus,

optical elements, such as lenses, made of the optical member according to the present embodiment will have high transmittance at the wavelength band used.

**[0032]** In one example of the optical member according to the present embodiment, the sum total of La, Gd, and Ta is 100% by mole, and La is 2.4% by mole or more and 38.2% by mole or less, Gd is 37.3% by mole or more and 72.9% by mole or less, and Ta is 24.5% by mole or more and 25.3% by mole or less. In another example of the optical member according to the present embodiment, at least one element selected from the group A is Gd, at least one element selected from the group B is Ta, the sum total of La, Gd, and Ta is 100% by mole, and La is 2.5% by mole or more and 37.5% by mole or less, Gd is 37.5% by mole or more and 72.5% by mole or less, and Ta is 25.0% by mole.

**[0033]** The optical member according to the present embodiment may have the formula (1) or (2).

**[0034]** The optical member according to the present embodiment may have an Abbe number ( $v_d$ ) and a refractive index ( $n_d$ ) that satisfy the following formulae (3) and (4).

$$2.20 \geq n_d \geq -0.01v_d + 2.25 \quad (30 \leq v_d < 55) \quad (3)$$

$$2.20 \geq n_d \geq 1.70 \quad (55 \leq v_d \leq 100) \quad (4)$$

**[0035]** Although the upper limit of the Abbe number ( $v_d$ ) is 100 and the upper limit of the refractive index ( $n_d$ ) is 2.20, future discovery of an appropriate composition or an

appropriate additive may increase the upper limits.

**[0036]** The optical member according to the present embodiment preferably has a transmittance of 60% or more, more preferably 80% or more.

#### Impurities in Optical Member

**[0037]** In the optical member according to the present embodiment, the sum total of La, O, at least one element selected from the group A, and at least one element selected from the group B is 99% by mole or more while the sum total of the elements of the optical member according to the present embodiment is 100% by mole. Thus, the optical member according to the present embodiment may contain 1% by mole or less, preferably 0.1% by mole or less, of impurities. Examples of the impurities include metal oxides, such as Si oxide, Fe oxide, B oxide, W oxide, Bi oxide, Co oxide, and Cu oxide. Examples of the impurities also include a binder and a sintering aid.

#### Binder

**[0038]** As described below, a binder in the present embodiment facilitates the binding of the components of the composition for optical members according to the present embodiment when the composition for optical members is baked. Examples of the binder in the present embodiment include poly(vinyl alcohol), poly(vinyl acetal), ethylcellulose, methylcellulose, hydroxyethylcellulose, poly(vinyl butyral),

polyacrylate, polymethacrylate, paraffin wax, liquid paraffin, microcrystalline wax, oxidized wax, maleated wax, stearic acid, oleic acid, butyl stearate, ethyl stearate, methyl stearate, microcrystalline wax, poly(vinyl butyral), polypropylene, polystyrene, polyethylene, diethyl phthalate, and polyacetal.

#### Sintering Aid

**[0039]** A sintering aid in the present embodiment is added to decrease the baking time or the baking temperature in the production of the composition for optical members according to the present embodiment or the optical member according to the present embodiment. The addition of an appropriate sintering aid to the optical member according to the present embodiment increases the hardness and transmittance of the optical member. Examples of the sintering aid in the present embodiment include MgO, Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>.

#### Method for Measuring Refractive Index and Abbe Number

**[0040]** The refractive index of the optical member according to the present embodiment can be measured by a V-block method. The refractive index in the present embodiment is the refractive index (nd) of d-line (587.6 nm) measured with a Kalnew precision refractometer KPR-2000 (manufactured by Shimadzu Device Corp.).

**[0041]** The Abbe number (vd) can be calculated by the equation of  $vd = (nd - 1) / (nF - nC)$  wherein the refractive

index (nd) of d-line (587.6 nm), the refractive index (nF) of F-line (486.1 nm), and the refractive index (nC) of C-line (656.3 nm) are measured with the apparatus for measuring the refractive index described above.

#### Method for Measuring Transmittance

**[0042]** The transmittance of the optical member according to the present embodiment is a linear transmittance measured with an ultraviolet-visible near-infrared spectrophotometer (UV-3600, Shimadzu Corp., wavelength range: 185 to 3300 nm). More specifically, the transmittance of the optical member according to the present embodiment is measured by irradiating the optical member having a thickness of 1 mm with light having a wavelength of 400 nm.

#### Method for Determining Component Ratio of Optical Member

**[0043]** In the present embodiment, the component ratio of the optical member may be determined with an ICP spectrometer in the same manner as in the method for determining the component ratio of a composition for optical members. The ICP spectrometer may be CIROS CCD (manufactured by Rigaku Corp.).

#### Method for Determining Crystal Structure of Optical Member

**[0044]** In the present embodiment, the crystal structure of the optical member may be determined with an X-ray diffractometer RINT 2100 (manufactured by Rigaku Corp.) at an X-ray tube voltage of 40 kV and an X-ray tube current of

40 mA in the same manner as in the method for determining the component ratio of a composition for optical members. An X-ray diffraction pattern is obtained by measuring the diffraction intensity (counts) at  $2\theta$  in the range of  $10^\circ$  to  $80^\circ$  with the X-ray diffractometer.

#### Applications

[0045] The applications of the optical member according to the present embodiment include, but are not limited to, optical elements, such as lenses. The optical member according to the present embodiment may also be used in scintillators and cover glasses of clock faces.

#### Third Embodiment

[0046] A third embodiment describes a lens.

#### Lens

[0047] A lens according to the present embodiment has an anti-reflection film on a polished surface of the optical member according to the second embodiment. The term "lens", as used herein, refers to an optical element for refracting incident light to diverge or converge the light in an intended direction. Examples of the lens include concave lenses, convex lenses, spherical lenses, aspheric lenses, diffractive optical elements (DOE), and gradient index (GRIN) lenses. These lenses can be used in film cameras, digital cameras (DSC), video cameras (VD), mobile phone cameras, surveillance cameras, TV cameras, movie cameras,

and projectors.

**[0048]** In the present embodiment, the anti-reflection film is not particularly limited. An intermediate layer may be disposed between the anti-reflection film and the lens. The intermediate layer is not particularly limited and may have a refractive index between the refractive index of the lens and the refractive index of the anti-reflection film.

**[0049]** The optical properties, such as refractive index, Abbe number, and transmittance, of the lens are measured, for example, at a depth of 2  $\mu\text{m}$  or more from a surface of the lens.

#### **Fourth Embodiment**

**[0050]** A fourth embodiment describes a method for manufacturing an optical member.

**[0051]** A method for manufacturing an optical member according to the present embodiment includes a process of applying a pressure to the composition for optical members according to the first embodiment to produce a formed product (process 1) and a process of baking the formed product to produce an optical member (process 2).

Method for Manufacturing Composition for Optical Members

**[0052]** An example of a method for manufacturing a composition for optical members according to the present embodiment will be described below.

**[0053]** A raw powder having an average particle size of 50

$\mu\text{m}$  or less and a purity of 99% by weight or more is ground and mixed in a mortar for 30 minutes. The phrase " $\text{La}_2\text{O}_3$  raw powder having a purity of 99% by weight or more" means that the amount of  $\text{La}_2\text{O}_3$  is 99 weight or more per 100 weight of the raw powder. The same applies hereinafter.

**[0054]** The mixed powder is charged in an alumina crucible, which is then placed in an electric furnace. The electric furnace is placed in the atmosphere. The internal temperature of the electric furnace is increased from room temperature to  $1600^\circ\text{C}$  over two hours and is maintained at  $1600^\circ\text{C}$  for three hours to bake the mixed powder. The temperature at which the mixed powder is baked is hereinafter referred to as the baking temperature ( $1600^\circ\text{C}$  in the above case). The time during which the mixed powder is baked is hereinafter referred to as the baking time (three hours in the above case). The internal temperature of the furnace is then naturally-cooled to room temperature to yield a calcined product, which is a composition for optical members.

**[0055]** The composition for optical members according to the present embodiment can be prepared by the solid phase reaction described above. The composition for optical members according to the present embodiment can also be prepared by a flame method, a gas phase reaction by a RF plasma method or an arc discharge plasma method, a normal-

pressure liquid phase reaction in an aqueous solution or an organic solvent, a high-pressure liquid phase reaction by hydrothermal synthesis or a solvothermal method, a supercritical reaction, a liquid-phase plasma reaction, an ultrasonic wave reaction, or a microwave reaction, or using a microreactor.

#### Raw Powder

**[0056]** The raw powder may be made of a metal oxide, such as La oxide, Gd oxide, or Ta oxide, a metal carbonate, or a metal hydroxide. The average particle size of the raw powder may be 50  $\mu\text{m}$  or less. A raw powder having an average particle size of more than 50  $\mu\text{m}$  probably has low reactivity in the solid phase reaction.

**[0057]** The purity of the raw powder may be 99% by weight or more. The raw powder having a purity of 99% by weight or more is resistant to coloring by impurities.

#### Grinding and Mixing Method

**[0058]** A grinding and mixing method in the present embodiment may be a dry dispersion method without using a solvent or a wet dispersion method using a solvent. The wet dispersion method may be a ball mill method, which uses a solvent and a ball mill. The solvent used in the wet dispersion method may be water or an organic solvent. The beads used in the ball mill may be made of yttria-stabilized zirconia (YSZ). The beads preferably has a diameter of 30

$\mu\text{m}$  or more and 25 mm or less, more preferably 300  $\mu\text{m}$  or more and 15 mm or less.

#### Baking Temperature

**[0059]** The baking temperature is preferably 1000°C or more and 1800°C or less, more preferably 1200°C or more and 1700°C or less. The crystals of the raw powder can grow well at a baking temperature of 1000°C or more. The refractory material of an electric furnace is durable at a baking temperature of 1800°C or less.

#### Baking Time

**[0060]** The baking time is preferably 0.5 hours or more and 24 hours or less, more preferably 1 hour or more and 10 hours or less. A baking time of 0.5 hours or more can result in high crystal growth. A baking time of 24 hours or less can result in low manufacturing costs.

#### Process 1

**[0061]** The process 1 involves applying a pressure to the composition for optical members to produce a formed product. The pressure may be applied by uniaxial pressure forming, cold isostatic pressing (CIP), injection molding, sheet forming, extrusion molding, or casting. In the process 1, the pressure may be 1000 kg/cm<sup>2</sup> or more and 3000 kg/cm<sup>2</sup> or less.

#### Process 2

**[0062]** The process 2 involves baking the formed product of

the process 1 to produce an optical member. The baking temperature and the baking time are described above in Baking Temperature and Baking Time. The baking may be performed by hot isostatic pressing (HIP), spark plasma sintering (SPS), vacuum sintering, hot pressing, or sintering in a high-oxygen atmosphere.

#### Other Processes

**[0063]** The method for manufacturing an optical member according to the present embodiment may include a process other than the processes 1 and 2. For example, the method for manufacturing an optical member according to the present embodiment may include a mixing process of mixing a composition for optical members and a binder before the process 1. The binder can prevent the aggregation of the composition for optical members. The binder may be the binder described in the first embodiment. The mixing method may be the method described above in Grinding and Mixing Method. The addition of the binder may be followed by a process of evaporating the solvent by heat treatment or spray-drying.

**[0064]** The process 1 may be preceded by a process of passing the composition for optical members through a sieve of 1 mesh or more and 750 mesh or less to make the particle size uniform. The average size of particles that pass through the sieve may be 1  $\mu\text{m}$  or more and 500  $\mu\text{m}$  or less.

**EXAMPLES**

**[0065]** Although the examples of the present invention are described below, the present invention is not limited to these examples.

**Method for Determining Crystal Structure**

**[0066]** In the example described below, the crystal structure of a composition for optical members was determined with an X-ray diffractometer RINT 2100 (manufactured by Rigaku Corp., an X-ray tube voltage of 40 kV, an X-ray tube current of 40 mA). The diffraction intensity (counts) was measured at  $2\theta$  in the range of  $10^\circ$  to  $80^\circ$ .

**Refinement of Lattice Constant**

**[0067]** The lattice constant was refined with X-ray powder diffraction analysis software JADE (available from Rigaku Corp.). An X-ray diffraction pattern having a cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ) that was close to the X-ray diffraction pattern measured was chosen from the PDF database. The lattice constant of the chosen data was used as the initial value. Several refinement cycles of the lattice constant were performed by the least squares method to determine the lattice constant that corresponds to the X-ray diffraction pattern measured. A diffraction peak at  $2\theta$  in the range of  $28.6^\circ$  to  $29.0^\circ$  was identified as a peak assigned to a (222) plane.

**[0068]** The X-ray diffraction pattern was calculated with Mercury (manufactured by Cambridge Crystallographic Data Centre, the United Kingdom) from the space group (Fd-3m, #227,  $Z = 8$ ), the refined lattice constant, the site occupancies, and Wyckoff positions.

**[0069]** The calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group Fd-3m, #227,  $Z = 8$ ) was compared with the X-ray diffraction pattern obtained by actual measurement. Agreement between the peak positions indicates that the composition for optical members had the cubic pyrochlore structure. Disagreement between the peak positions or the presence of a peak not included in the calculated X-ray diffraction pattern of the cubic pyrochlore structure indicated that the crystal structure of the metal oxide was not the cubic pyrochlore structure.

#### Determination of Calculated Density

**[0070]** The calculated density was determined with X-ray powder diffraction analysis software JADE (available from Rigaku Corp.). The volume of a composition for optical members was calculated from the space group and the refined lattice constant. The calculated density was determined from the molecular weight of the composition for optical members and the calculated volume.

#### Calculation of Crystallite Diameter

**[0071]** The crystallite diameter ( $D$ ) was calculated with X-

ray powder diffraction analysis software JADE (available from Rigaku Corp.). A diffraction peak at  $2\theta$  in the range of  $28.6^\circ$  to  $29.0^\circ$  was assigned to a (222) plane. The half-width  $\beta(222)$  was calculated from the diffraction peak ( $2\theta = 28.6^\circ$  to  $29.0^\circ$ ) measured. The crystallite diameter  $D_{(222)}$  of the (222) plane was calculated from the half-width  $\beta(222)$  by the following Scherrer equation (formula (5)). A larger diffraction intensity of the diffraction peak at  $2\theta$  in the range of  $28.6^\circ$  to  $29.0^\circ$  and a larger crystallite diameter  $D_{(222)}$  of the (222) plane indicated that the cubic pyrochlore had higher crystallinity.

$$D_{(222)} = K \times \lambda_{\text{Cu-K}\alpha 1} / \beta_{(222)} \cos \theta \quad (5)$$

$K = 0.9$ ,  $\lambda_{\text{Cu-K}\alpha 1} = 0.154056$  nm, and  $\beta(222)$  is the half-width of a diffraction peak ( $2\theta = 28.6^\circ$  to  $29.0^\circ$ ).

### Example 1

[0072] 6 mmol of lanthanum oxide ( $\text{La}_2\text{O}_3$ ), 6 mmol of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), and 4 mmol of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of the mixed powder was charged in an alumina crucible, which was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room temperature to  $1600^\circ\text{C}$  over two hours and was maintained at  $1600^\circ\text{C}$  for three hours to bake the mixed powder. After heating, the mixed powder was naturally cooled to room

temperature. The composition for optical members thus prepared was colorless (white). The X-ray diffraction pattern of the white powder was determined. The X-ray diffraction pattern was identified as a cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ). The maximum diffraction intensity of a diffraction peak at  $2\theta$  of  $28.64^\circ$  assigned to a (222) plane was 9222 counts. The crystallite diameter of the (222) plane was estimated to be 25.5 nm by the formula (5). The refinement of lattice constant with X-ray powder diffraction analysis software JADE yielded a lattice constant  $a$  of 10.786 angstroms and a calculated density of  $7.803 \text{ g/cm}^3$ . The calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ) was compared with the X-ray diffraction pattern obtained by actual measurement. Their peak positions agreed with each other, indicating that the composition for optical members had the cubic pyrochlore structure.

## **Example 2**

**[0073]** 5 mmol of lanthanum oxide ( $\text{La}_2\text{O}_3$ ), 10 mmol of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), and 5 mmol of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of the mixed powder was charged in an alumina crucible, which was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room

temperature to 1600°C over two hours and was maintained at 1600°C for three hours to bake the mixed powder. After heating, the mixed powder was naturally cooled to room temperature. The composition for optical members thus prepared was colorless (white). The X-ray diffraction pattern of the white powder was determined. The X-ray diffraction pattern was identified as a cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ). The maximum diffraction intensity of a diffraction peak at  $2\theta$  of 28.76° assigned to a (222) plane was 9525 counts. The crystallite diameter of the (222) plane was estimated to be 28.7 nm by the formula (5). The refinement of lattice constant with X-ray powder diffraction analysis software JADE yielded a lattice constant  $a$  of 10.726 angstroms and a calculated density of 8.034 g/cm<sup>3</sup>. The calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ) was compared with the X-ray diffraction pattern obtained by actual measurement. Their peak positions agreed with each other, indicating that the composition for optical members had the cubic pyrochlore structure.

### **Example 3**

**[0074]** 2 mmol of lanthanum oxide ( $La_2O_3$ ), 10 mmol of gadolinium oxide ( $Gd_2O_3$ ), and 4 mmol of tantalum oxide ( $Ta_2O_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of the mixed powder was charged in an alumina crucible, which

was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room temperature to 1600°C over two hours and was maintained at 1600°C for three hours to bake the mixed powder. After heating, the mixed powder was naturally cooled to room temperature. The composition for optical members thus prepared was colorless (white). The X-ray diffraction pattern of the white powder was determined. The X-ray diffraction pattern was identified as a cubic pyrochlore structure (space group Fd-3m, #227, Z = 8). The maximum diffraction intensity of a diffraction peak at  $2\theta$  of 28.90° assigned to a (222) plane was 12169 counts. The crystallite diameter of the (222) plane was estimated to be 37.4 nm by the formula (5). The refinement of lattice constant with X-ray powder diffraction analysis software JADE yielded a lattice constant  $a$  of 10.682 angstroms and a calculated density of 8.233 g/cm<sup>3</sup>. The calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group Fd-3m, #227, Z = 8) was compared with the X-ray diffraction pattern obtained by actual measurement. Their peak positions agreed with each other, indicating that the composition for optical members had the cubic pyrochlore structure.

**Example 4**

**[0075]** 0.4 mmol of lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), 11.6 mmol of

gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), and 4 mmol of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of the mixed powder was charged in an alumina crucible, which was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room temperature to  $1600^\circ\text{C}$  over two hours and was maintained at  $1600^\circ\text{C}$  for three hours to bake the mixed powder. After heating, the mixed powder was naturally cooled to room temperature. The composition for optical members thus prepared was colorless (white). The X-ray diffraction pattern of the white powder was determined. The X-ray diffraction pattern was identified as a cubic pyrochlore structure (space group  $\text{Fd-}3\text{m}$ , #227,  $Z = 8$ ). The maximum diffraction intensity of a diffraction peak at  $2\theta$  of  $28.98^\circ$  assigned to a (222) plane was 15648 counts. The crystallite diameter of the (222) plane was estimated to be 59.1 nm by the formula (5). The refinement of lattice constant with X-ray powder diffraction analysis software JADE yielded a lattice constant  $a$  of 10.652 angstroms and a calculated density of  $8.384 \text{ g/cm}^3$ . The calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group  $\text{Fd-}3\text{m}$ , #227,  $Z = 8$ ) was compared with the X-ray diffraction pattern obtained by actual measurement. Their peak positions agreed with each other, indicating that the composition for optical

members had the cubic pyrochlore structure.

### **Comparative Example 1**

[0076] 10 mmol of lanthanum oxide ( $\text{La}_2\text{O}_3$ ), 5 mmol of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), and 5 mmol of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of the mixed powder was charged in an alumina crucible, which was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room temperature to  $1600^\circ\text{C}$  over two hours and was maintained at  $1600^\circ\text{C}$  for three hours to bake the mixed powder. After heating, the mixed powder was naturally cooled to room temperature. The composition for optical members thus prepared was colorless (white). The X-ray diffraction pattern of the white powder was determined. The X-ray diffraction pattern obtained by actual measurement included a peak that was not present in the calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group  $\text{Fd-}3\text{m}$ , #227,  $Z = 8$ ), indicating that the composition for optical members did not have the cubic pyrochlore structure.

### **Comparative Example 2**

[0077] 6.8 mmol of lanthanum oxide ( $\text{La}_2\text{O}_3$ ), 5.2 mmol of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), and 4 mmol of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of

the mixed powder was charged in an alumina crucible, which was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room temperature to 1600°C over two hours and was maintained at 1600°C for three hours to bake the mixed powder. After heating, the mixed powder was naturally cooled to room temperature. The composition for optical members thus prepared was colorless (white). The white powder was subjected to XRD measurement. The X-ray diffraction pattern obtained by actual measurement included a peak that was not present in the calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ), indicating that the composition for optical members did not have the cubic pyrochlore structure.

### **Comparative Example 3**

**[0078]** 6.4 mmol of lanthanum oxide ( $\text{La}_2\text{O}_3$ ), 5.6 mmol of gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), and 4 mmol of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) were mixed in an agate mortar for 30 minutes. 1 g of the mixed powder was charged in an alumina crucible, which was then placed in an electric furnace. The electric furnace was placed in the atmosphere. The internal temperature of the electric furnace was increased from room temperature to 1600°C over two hours and was maintained at 1600°C for three hours to bake the mixed powder. After

heating, the mixed powder was naturally cooled to room temperature. The composition for optical members thus prepared was colorless (white). The white powder was subjected to XRD measurement. The X-ray diffraction pattern obtained by actual measurement included a peak that was not present in the calculated X-ray diffraction pattern of the cubic pyrochlore structure (space group  $Fd-3m$ , #227,  $Z = 8$ ), indicating that the composition for optical members did not have the cubic pyrochlore structure.

#### Conclusions

**[0079]** Figure 1 summarizes the results of Examples 1 to 4 and Comparative Examples 1 to 3. In Figure 1, a circle denotes that the composition for optical members had the cubic pyrochlore structure, and a cross denotes that the composition for optical members did not have the cubic pyrochlore structure. X in Figure 1 denotes X of the formula (2).

**[0080]** In Figure 1, the maximum diffraction intensity 1) is a measured X-ray diffraction peak intensity at  $2\theta$  in the range of  $28.6^\circ$  to  $29.0^\circ$  assigned to the (222) plane of the cubic pyrochlore structure. The crystallite diameter 2) is the crystallite diameter  $D_{(222)}$  of the cubic pyrochlore (222) plane calculated by the Scherrer equation (the formula (5)) from the half-width of the X-ray diffraction peak ( $2\theta = 28.6^\circ$  to  $29.0^\circ$ ). The crystallite diameter was calculated

with X-ray powder diffraction analysis software JADE (available from Rigaku Corp.).

**[0081]** The refinement of lattice constant 3) and the determination of calculated density 4) were performed with X-ray powder diffraction analysis software JADE (available from Rigaku Corp.).

**[0082]** Figure 1 shows that the compositions for optical members according to the examples had the cubic pyrochlore structure. In addition to the component ratios according to the examples that provided the cubic pyrochlore structure, the component ratios between the highest component ratio and the lowest component ratio will also provide the cubic pyrochlore structure. For example, Examples 1 and 2 show that when La is 37.5% by mole, Gd is 37.5% by mole, and Ta is 25.0% by mole, or when La is 2.5% by mole, Gd is 72.5% by mole, and Ta is 25.0% by mole, the composition for optical members had the cubic pyrochlore structure. Thus, when the component ratio is between these values, for example, when La is 20.0% by mole, Gd is 55.0% by mole, and Ta is 25.0% by mole, the composition for optical members will also have the cubic pyrochlore structure.

**[0083]** While the present invention has been described with reference to exemplary embodiments, it is to be understood that the invention is not limited to the disclosed exemplary embodiments. The scope of the following claims is to be

accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

**[0084]** This application claims the benefit of Japanese Patent Application No. 2011-018270, filed January 31, 2011, which is hereby incorporated by reference herein in its entirety.

**CLAIMS**

[1] A composition for optical members that contains La and O, the composition further comprising:

at least one element selected from the group A consisting of Gd, Y, Al, Ga, and In; and

at least one element selected from the group B consisting of Ta and Nb,

wherein the sum total of La, O, at least one element selected from the group A, and at least one element selected from the group B is 99% by mole or more while the sum total of the elements of the composition is 100% by mole.

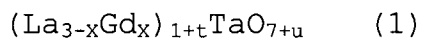
[2] The composition for optical members according to Claim 1, wherein the sum total of La, Gd, and Ta is 100% by mole, and La is 2.4% by mole or more and 38.2% by mole or less, Gd is 37.3% by mole or more and 72.9% by mole or less, and Ta is 24.5% by mole or more and 25.3% by mole or less.

[3] The composition for optical members according to Claim 2, wherein at least one element selected from the group A is Gd, at least one element selected from the group B is Ta, the sum total of La, Gd, and Ta is 100% by mole, and La is 2.5% by mole or more and 37.5% by mole or less, Gd is 37.5% by mole or more and 72.5% by mole or less, and Ta is 25.0%

by mole.

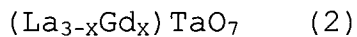
[4] The composition for optical members according to any one of Claims 1 to 3, wherein the composition has a cubic pyrochlore structure.

[5] The composition for optical members according to any one of Claims 1 to 4, wherein the composition has the following formula (1):



wherein X is  $1.5 \leq X \leq 2.9$ , t is  $-0.01 \leq t \leq 0.02$ , and u is  $-0.06 \leq u \leq 0.12$ .

[6] The composition for optical members according to Claim 5, wherein the composition has the following formula (2):



wherein X is  $1.5 \leq X \leq 2.9$ .

[7] An optical member, comprising the composition for optical members according to any one of Claims 1 to 6, wherein the optical member has an Abbe number of 25 or more, a refractive index of 1.75 or more, and a transmittance of 20% or more.

[8] A lens, comprising an anti-reflection film on a

polished surface of an optical member according to Claim 7.

[9] A method for manufacturing an optical member,  
comprising:

applying a pressure to the composition for optical  
members according to any one of Claims 1 to 6 to produce a  
formed product; and

baking the formed product to produce an optical member.

FIGURE 1

|                          | COMPONENT RATIO<br>(mol%) |      |      | X   | BAKING<br>TEMPERATURE (°C) | BAKING<br>TIME (h) | COLORING OF<br>COMPOSITION FOR<br>OPTICAL MEMBERS | WHETHER CUBIC<br>PYROCHLORE<br>STRUCTURE OR NOT | MAXIMUM<br>DIFFRACTION<br>INTENSITY <sup>(1)</sup> (counts) | CRYSTALLITE<br>DIAMETER <sup>(2)</sup> (nm) | LATTICE<br>CONSTANT <sup>(3)</sup> (Å) | CALCULATED<br>DENSITY <sup>(4)</sup> (g/cm <sup>3</sup> ) |
|--------------------------|---------------------------|------|------|-----|----------------------------|--------------------|---------------------------------------------------|-------------------------------------------------|-------------------------------------------------------------|---------------------------------------------|----------------------------------------|-----------------------------------------------------------|
|                          | La                        | Gd   | Ta   |     |                            |                    |                                                   |                                                 |                                                             |                                             |                                        |                                                           |
| EXAMPLE 1                | 37.5                      | 37.5 | 25.0 | 1.5 | 1600                       | 3                  | NONE                                              | O                                               | 9222                                                        | 25.5                                        | 10.786                                 | 7.803                                                     |
| EXAMPLE 2                | 25.0                      | 50.0 | 25.0 | 2.0 | 1600                       | 3                  | NONE                                              | O                                               | 9525                                                        | 28.7                                        | 10.726                                 | 8.034                                                     |
| EXAMPLE 3                | 12.5                      | 62.5 | 25.0 | 2.5 | 1600                       | 3                  | NONE                                              | O                                               | 12169                                                       | 37.4                                        | 10.682                                 | 8.233                                                     |
| EXAMPLE 4                | 2.5                       | 72.5 | 25.0 | 2.9 | 1600                       | 3                  | NONE                                              | O                                               | 15648                                                       | 59.1                                        | 10.652                                 | 8.384                                                     |
| COMPARATIVE<br>EXAMPLE 1 | 50.0                      | 25.0 | 25.0 | 1.0 | 1600                       | 3                  | NONE                                              | x                                               | -                                                           | -                                           | -                                      | -                                                         |
| COMPARATIVE<br>EXAMPLE 2 | 42.5                      | 32.5 | 25.0 | 1.3 | 1600                       | 3                  | NONE                                              | x                                               | -                                                           | -                                           | -                                      | -                                                         |
| COMPARATIVE<br>EXAMPLE 3 | 40.0                      | 35.0 | 25.0 | 1.4 | 1600                       | 3                  | NONE                                              | x                                               | -                                                           | -                                           | -                                      | -                                                         |

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/052198

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C01G35/00 (2006.01) i, C01G33/00 (2006.01) i, C04B35/50 (2006.01) i,  
G02B1/00 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C01G35/00, C01G33/00, C04B35/50, G02B1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996  
Published unexamined utility model applications of Japan 1971-2012  
Registered utility model specifications of Japan 1996-2012  
Published registered utility model applications of Japan 1994-2012

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus/JMEDPlus/JST/580 (JDreamII), CPlus (STN), REGISTRY (STN)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                         | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X<br>A    | JP 2000-247793 A (Victor Company of Japan, Limited) 2000.09.12, 【0001】 , 【0003】 , 【0008】 - 【0016】 (No Family)                                                                              | 1<br>2-9              |
| X<br>A    | JP 11-199392 A (Victor Company of Japan, Limited) 1999.07.27, 【0001】 , 【0023】 - 【0048】 (No Family)                                                                                         | 1<br>2-9              |
| X<br>A    | JP 2007-047712 A (Canon Inc.) 2007.02.22, 【0001】 , 【0024】 (No Family)                                                                                                                      | 1<br>2-9              |
| A         | L.H.BRIXNER et al., X-RAY EXCITED EMISSION SPECTROSCOPY OF Gd <sup>3+</sup> IN SOME ATaO <sub>4</sub> COMPOUNDS, Journal of Physics and Chemistry of Solids, 1991, Vol.52, No.4, p.623-627 | 1-9                   |

☐ Further documents are listed in the continuation of Box C.
☐ See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&amp;” document member of the same patent family

Date of the actual completion of the international search

24.04.2012

Date of mailing of the international search report

15.05.2012

Name and mailing address of the ISA/JP

**Japan Patent Office**

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2012/052198

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

D1-D3 discloses the subject matter of claim 1. Therefore, claim 1 lacks novelty over D1-D3, and involves no special technical features. Thus, there are plural inventions in the claims of this application.

Note that claim 1, which involves no special technical features, and Claims 3-8 dependent on claim 2 are grouped into Invention 1.

D1:JP 2000-247793 A (Victor Company of Japan, Limited) 2000.09.12 (No Family)

D2:JP 11-199392 A (Victor Company of Japan, Limited) 1999.07.27 (No Family)

D3:JP 2007-047712 A (Canon Inc.) 2007.02.22 (No Family)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.