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(54) **CRYSTAL GROWTH ATMOSPHERE FOR OXYORTHOSILICATE MATERIALS PRODUCTION**

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(52) **U.S. Cl. 252/301.4 F; 117/20**

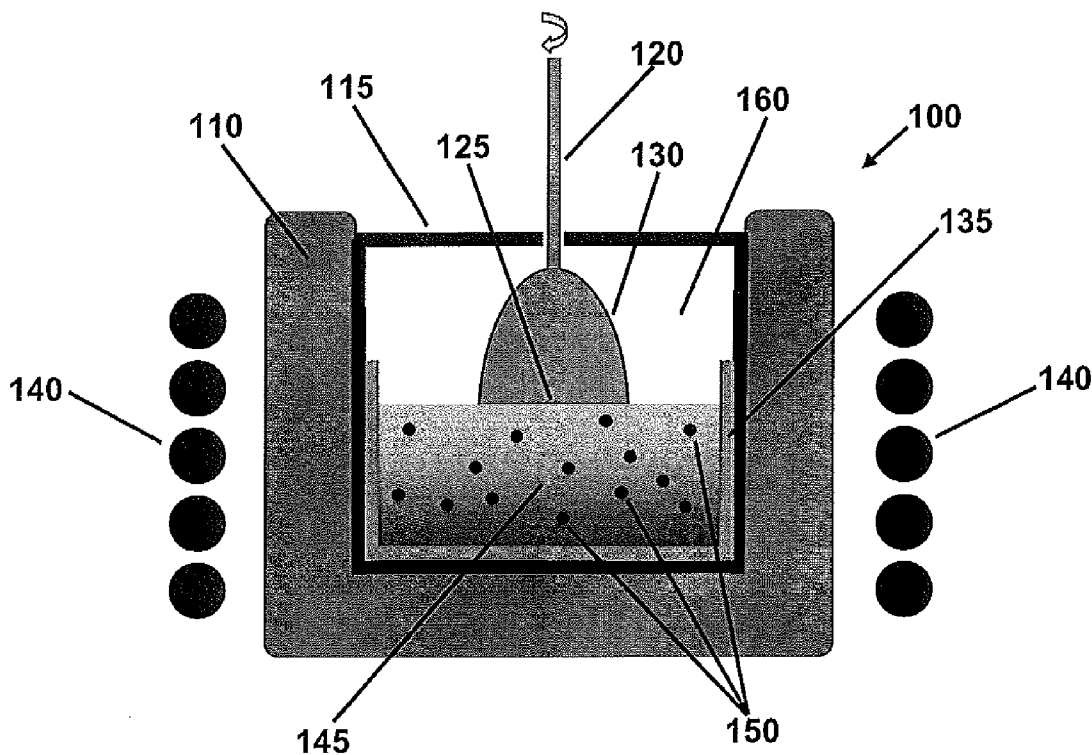
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(57) **ABSTRACT**

A method of growing a rare-earth oxyorthosilicate crystal, and crystals grown using the method are disclosed. The method includes preparing a melt by melting a first substance including at least one first rare-earth element and providing an atmosphere that includes an inert gas and a gas including oxygen.

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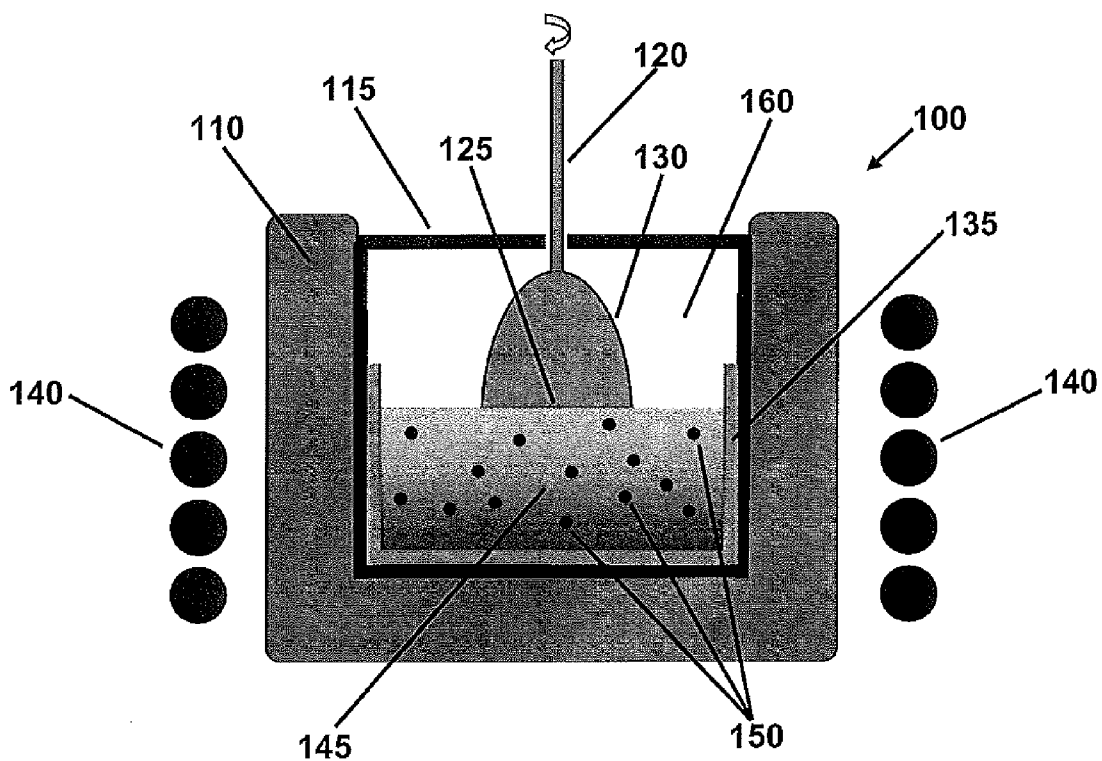


Fig. 1

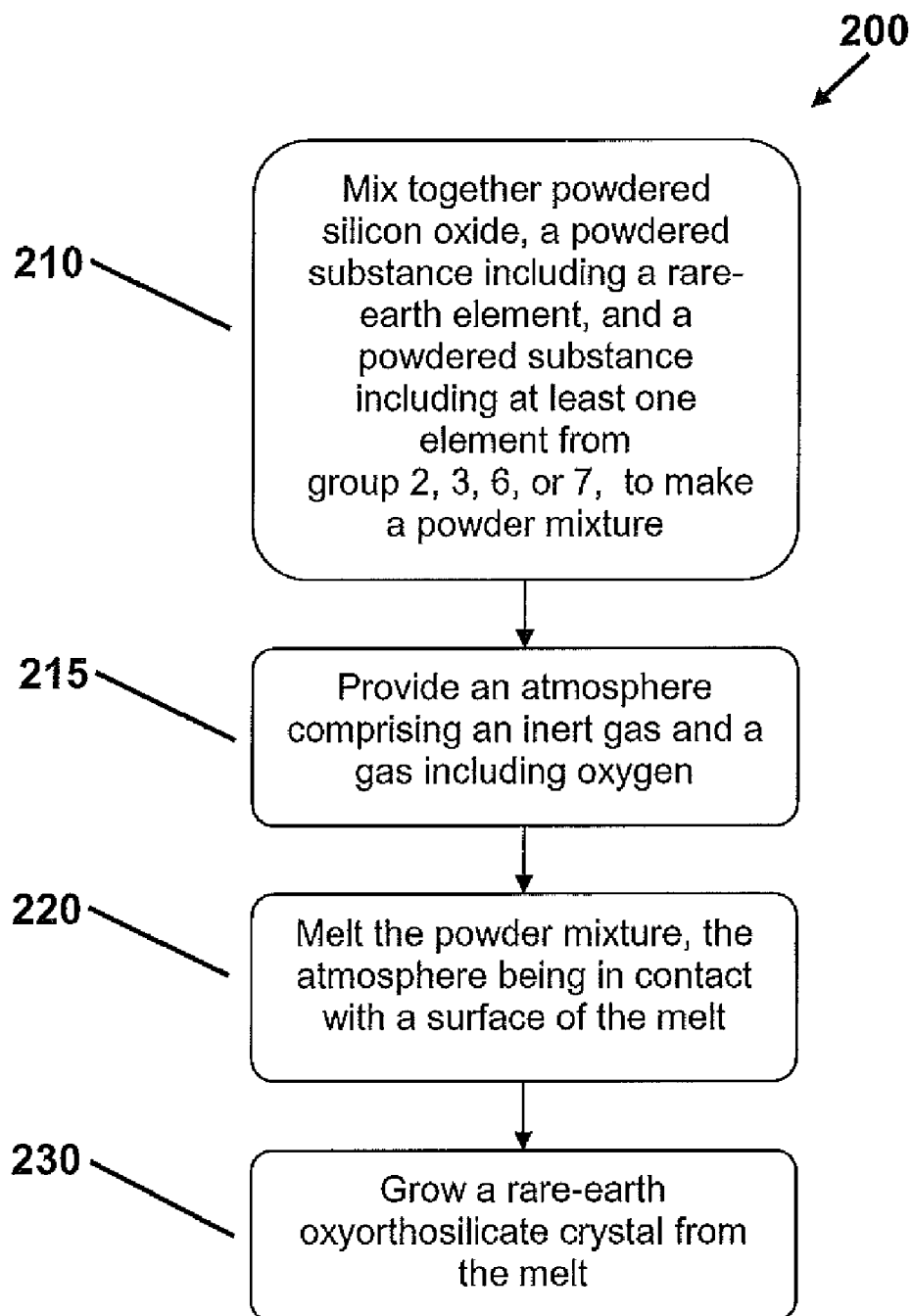


Fig. 2

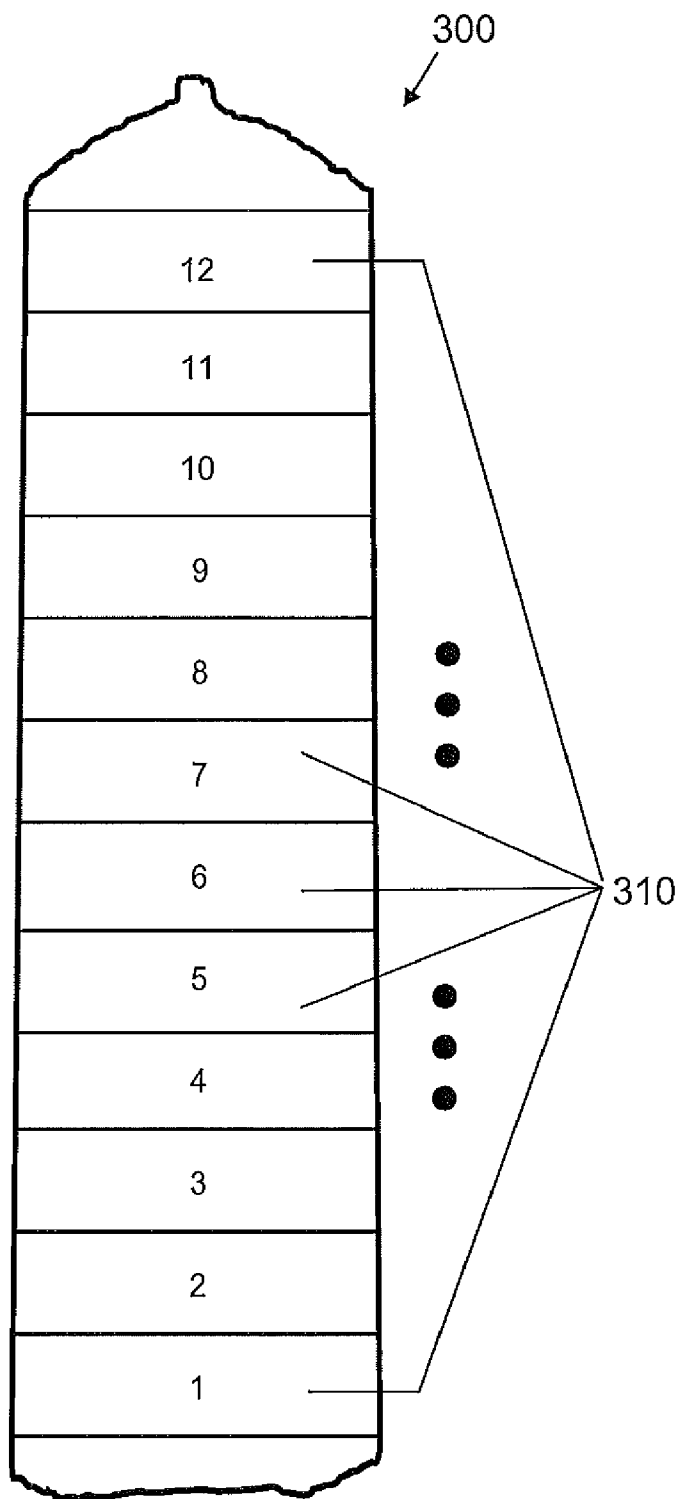


Fig. 3

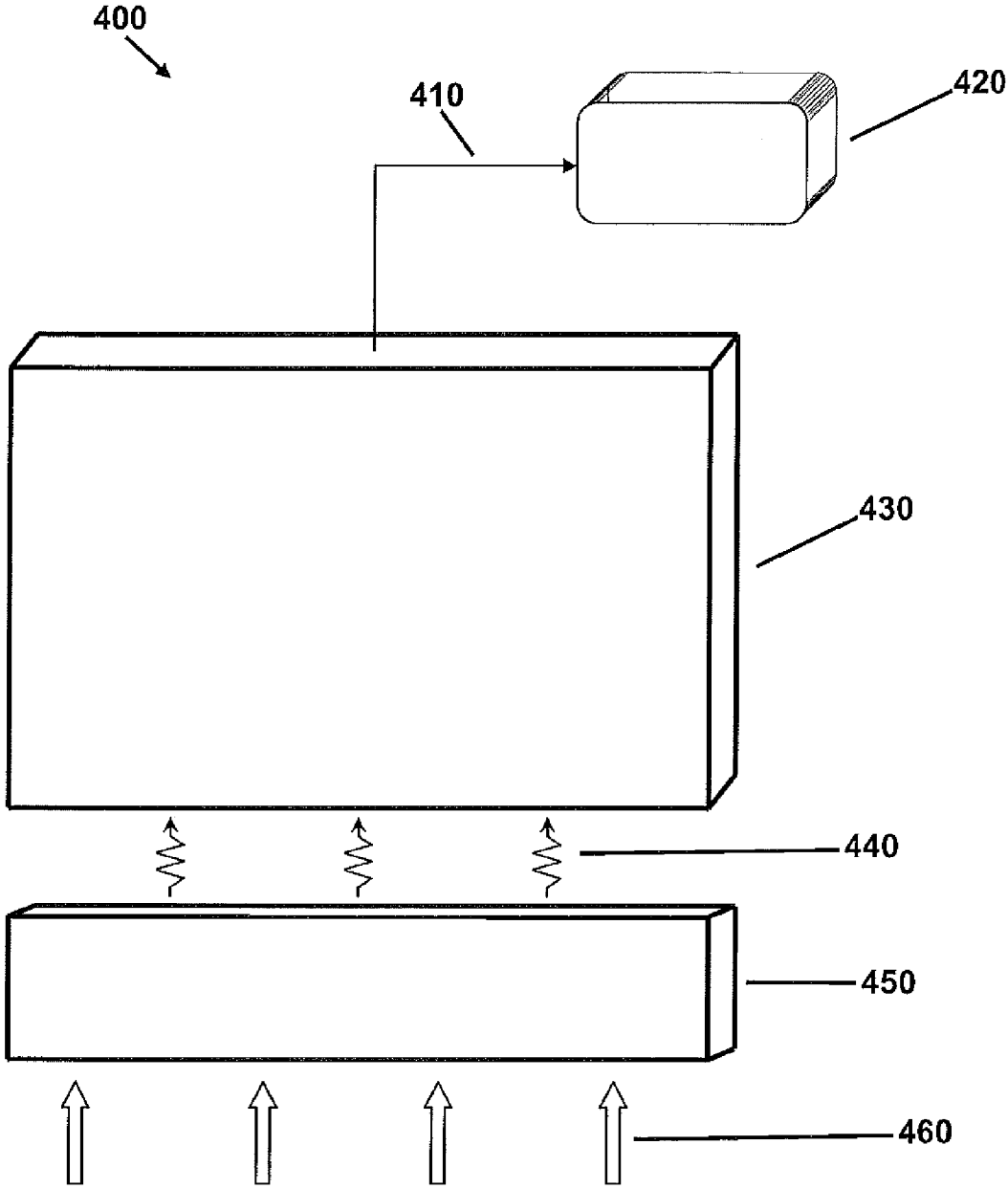


Fig. 4

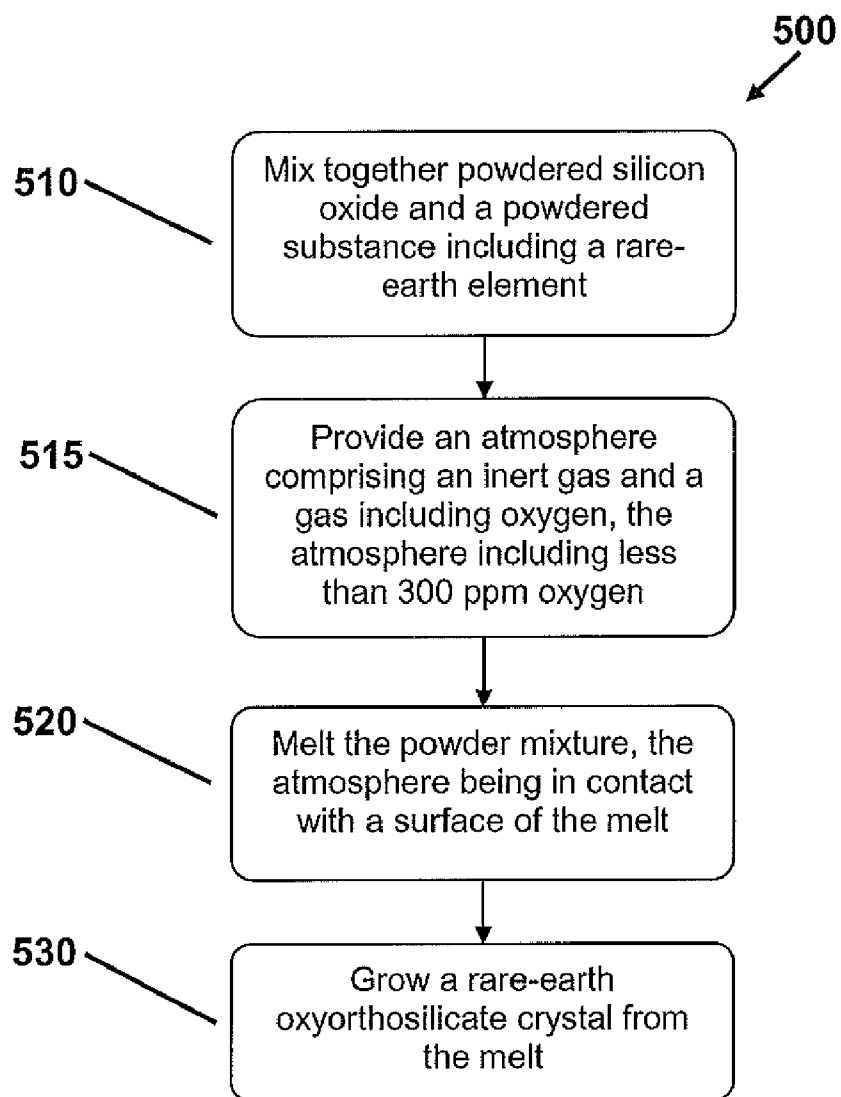


Fig. 5

CRYSTAL GROWTH ATMOSPHERE FOR OXYORTHOSILICATE MATERIALS PRODUCTION

FIELD OF INVENTION

[0001] This application relates to the growth of crystals.

BACKGROUND

[0002] In some methods for growing crystals, such as the Czochralski method, a seed crystal is brought into contact with the surface of a melt and then withdrawn from the melt. A crystal grows on the seed as it is withdrawn. The seed and growing crystal are sometimes also rotated about a vertical axis as they are withdrawn. Growth instabilities often occur in large crystals grown using this technique. As an example, the crystal may begin to grow in a spiral shape instead of a desired cylindrical shape. Growth instabilities may result in stresses due to variations in thermal expansion coefficients within the crystal, which may cause the crystal to shatter. This shattering is more likely when significant temperature gradients are present in the melt and in the atmosphere above the melt in which the crystal grows.

[0003] Growth instabilities may be caused by sufficiently large temperature gradients, accumulation of impurities in the melt, changes in the charge states of some of the melt constituents leading to creation of different molecular complexes, as well as by excesses of melt constituents accumulating at the interface between the surface of the melt and the growing crystal.

[0004] In the growth of rare-earth oxyorthosilicate scintillator crystals, oxygen vacancies in the crystal lattice may act as charge traps that lower the amount of charge carriers (electrons and holes) generated when the crystal absorbs ionizing radiation. The results are a lowering of scintillation efficiency and an undesirable persistent emission of light from the crystal known as afterglow. Reducing concentration of such oxygen vacancies is therefore desirable. This has been partially achieved by annealing the grown crystal in an oxygen-containing atmosphere. This is an extra step in the preparation of such crystals.

SUMMARY

[0005] A method of growing rare-earth oxyorthosilicate crystals and the crystals grown with the method are disclosed. The method includes providing an atmosphere for crystal growth including an inert gas and a gas including oxygen.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 shows an example apparatus for growing a crystal.

[0007] FIG. 2 is an example flow chart showing a method for growing a crystal.

[0008] FIG. 3 shows an example crystal boule.

[0009] FIG. 4 shows an example of a scintillation counter.

[0010] FIG. 5 is an example flow chart showing another method for growing a crystal.

DETAILED DESCRIPTION

[0011] Control of the atmosphere above a melt during crystal growth using a method such as the Czochralski method may be crucial for controlling growth stability and controlling properties of the grown crystal. In particular, in the growth of

rare-earth oxyorthosilicate scintillator crystals, careful control of the atmosphere and the melt composition may simultaneously minimize at least three problems in the growth of these crystals.

[0012] A first problem is the inclusion of oxygen vacancies in the grown crystal, which reduce the scintillation efficiency of the crystal and give rise to an undesirable persistent emission of light from the crystal known as afterglow. These oxygen vacancies may arise from a deficiency of oxygen during crystal growth. Rare-earth oxyorthosilicate scintillator crystals may be grown from a melt prepared by melting a rare-earth compound, such as an oxide, with a silicon oxide, such as SiO_2 . Temperatures of 2000°C . or higher may be needed to melt these substances. At these temperatures it may be desirable to use a nearly inert atmosphere to prevent introducing impurities into the melt. If a pure inert atmosphere is used, however, the SiO_2 may decompose into SiO (silicon monoxide) and oxygen. The result is a change in the stoichiometry of the grown crystal and the introduction of the undesirable oxygen vacancies. It has been found that introducing an oxygen containing species, such as carbon dioxide (CO_2), carbon monoxide (CO), or oxygen (O_2) into the atmosphere may reduce the concentration of the oxygen vacancies in the crystal and thereby achieve desired scintillation performance without a need for the above described post-growth anneal. Other gases that may decompose and liberate elemental oxygen include, as examples, sulfur trioxide (SO_3), several different oxides of nitrogen NO_2 , N_2O , NO , N_2O_3 , N_2O_5 and phosphorous pentoxide P_2O_5 . However, except for nitrous oxide N_2O , these gasses are more reactive than CO_2 with materials making up the interior of the furnace.

[0013] At the same time, the amount of oxygen introduced into the atmosphere must be kept low enough to avoid appreciable oxidation of materials used in the growth apparatus, such as the iridium and iridium alloys of the crucible, often used to contain the melt for the growth of these crystals. Oxidation of an iridium crucible may introduce contaminants into the melt and shorten the usable lifetime of the expensive iridium crucible. Thus, the amount of oxygen introduced must be carefully chosen.

[0014] A second problem with these crystals is cracking of the crystal during growth, which may result from excessive temperature gradients in growth chamber. This problem may be addressed by reducing the thermal conductivity of the growth atmosphere. Thermal conductivity contributes to the thermal diffusivity, which determines how rapidly any temperature change diffuses through an atmosphere. Lower thermal conductivity results in greater stability of temperature gradients in the growth chamber, isolating a crystal boule from any fluctuation in temperature in the surrounding environment.

[0015] At the same time, it may be desirable to control temperature gradients in the melt that stimulate the oxygen transport in the crystal-melt interface. One way benefits may occur is through the phenomenon known as Marangoni flow, a type of fluid flow driven by gradients in surface tension. The surface tension gradients may, in turn, be produced by increasing the temperature gradients in the melt surface.

[0016] A third problem arises in the growth of these crystals, in particular with cerium-doped lutetium oxyorthosilicate scintillator crystals. If grown as described above in an oxygen-containing atmosphere, some of the cerium in the crystal may undergo a change of oxidization state, from the desired $3+$ state to a $4+$ state. The result is a yellowing of the

crystal, which adversely affects the scintillation performance of the crystal, while reducing optical clarity. It has been found that adding to the melt at least one element from group 2, group 3, group 6, or group 7 of the periodic table in any combination will effectively eliminate this yellowing. It has also been found that the adding at least one such element further stabilizes the growth of the crystal, preventing such instabilities as spiral structures and other departures from cylindrical growth. Group 2 elements include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba). Group three elements include scandium and yttrium. Group 6 elements include chromium (Cr), molybdenum (Mo), and tungsten (W). Group 7 elements include manganese (Mn) and rhenium (Re). By careful choice and control of growth atmosphere and melt composition, therefore, both physical stability and composition of the crystal may be controlled to achieve multiple desirable results.

[0017] FIG. 1 shows an embodiment of a crystal-growing apparatus **100** including a melt **145**. Melt **145** may be made by melting a first substance that includes at least one first rare-earth element, and a second substance that includes at least one element **150** from group 2, group 3, group 6, or group 7. Alternatively, at least one rare-earth element and at least one element from group 2, group 3, group 6, or group 7, may both be included in one substance. The first substance may be an oxide of the first rare-earth element. Melt **145** may also include melted stoichiometric SiO_2 (silica). Melt **145** may also include a melted third substance that includes a second rare-earth element distinct from the first rare-earth element.

[0018] Melt **145** may be contained in a crucible **135**, which may be made of iridium. Crucible **135** is contained in an enclosure **115**. Enclosure **115** may be utilized to control an ambient atmosphere **160** above the melt surface in which a rare-earth oxyorthosilicate crystal is growing as a crystal boule **130**. Surrounding enclosure **115** is a thermally insulating material **110**. Melt **145** is maintained in a molten state by inductive heating of crucible **135**, the heating produced by RF induction coil **140**. Crystal boule **130** grows at or near an interface **125** between a portion of the boule that is already grown and a surface of melt **145**. Growth of crystal boule **130** is initiated by attaching a seed crystal (not shown) to a rod **120**. Rod **120** is slowly lifted upward as crystal growth proceeds. Rod **120** may also be rotated, as indicated by an arrow. Although the arrow indicates rotation of rod **120** in a clockwise direction as seen from above, rod **120** may also be rotated counterclockwise as seen from above.

[0019] Melt **145** may include a melted third substance that includes a second rare-earth element. The second rare-earth element may be, but is not limited to, cerium (Ce). The second rare-earth element may be incorporated into crystal boule **130**. The second rare-earth element may be incorporated into crystal boule **130** as a dopant. It may be incorporated as a substitutional dopant in the lattice of crystal boule **130**. For example, a dopant atom of Ce may occupy a lattice position normally occupied by an Lu atom in a crystalline lattice of lutetium oxyorthosilicate.

[0020] Atmosphere **160** comprises at least one inert gas and at least one gaseous substance that includes oxygen. Atmosphere **160** is in contact with a surface of melt **145**. As explained above, it may be desirable to use an inert gas with a lower thermal conductivity. The inert gas may comprise at least one of helium (He), argon (Ar), krypton (Kr), xenon (Xe), or nitrogen. If maintaining thermal gradients is less crucial, nitrogen, having a higher thermal conductivity, may

be used. Thermal conductivity of the inert gas may be less than or equal to $150 \text{ mW/m-}^\circ\text{K}$ (milliwatts per meter- $^\circ\text{K}$) at the temperature of the atmosphere during crystal growth. For example, the thermal conductivity of nitrogen at 2000°C . has been measured to be between about 70 and about $125 \text{ mW/m-}^\circ\text{K}$, and the thermal conductivity of argon at 2000°C . has been measured to be between about 80 and about $100 \text{ mW/m-}^\circ\text{K}$.

[0021] The gaseous substance including oxygen may include carbon dioxide, which may disassociate to carbon monoxide and additional oxygen. The gaseous substance including oxygen may include other oxygen-containing compounds that disassociate to oxygen, such as carbon monoxide, oxygen, sulfur trioxide (SO_3), phosphorous pentoxide (P_2O_5) or an oxide of nitrogen, all of these in any combination. The oxide of nitrogen may include NO_2 , N_2O , NO , N_2O_3 , or N_2O_5 in any combination. Atmosphere **160** may comprise from 100 parts per million (ppm) to 100000 ppm (0.01 to 10 percent) of oxygen by volume, inclusive. Alternatively, atmosphere **160** may comprise oxygen by volume in a range between and including any two integer values of ppm between 100 and 100000. In particular, atmosphere **160** may contain less than 300 ppm oxygen by volume. In particular, atmosphere **160** may contain less than 200 ppm oxygen by volume.

[0022] FIG. 2 shows a first embodiment of a method of growing a rare-earth oxyorthosilicate crystal in a controlled atmosphere. As illustrated in FIG. 2, a powdered substance comprising at least one first rare-earth element may be mixed with a powdered silicon oxide such as silica (SiO_2) **210**. A powdered substance that includes at least one element from group 2, 3, 6, or 7 is added to make a powder mixture **210**. The powdered substance comprising at least one first rare-earth element may be a rare-earth oxide or a mixture of such oxides, such as Lu_2O_3 , Gd_2O_3 , or La_2O_3 , or a mixture thereof. An oxide of an additional element, such as Y_2O_3 , may also be added **210**. The group 7 element may be, but is not limited to, manganese or rhenium. In addition, one or more substances including at least one element from group 2 of the periodic table may be introduced into the mixture at step **210**. The addition of group 2 elements may contribute stabilizing growth of the crystal. A second powdered substance comprising a second rare-earth element may be mixed with the powder mixture at step **210**. The second powdered substance may be a rare-earth oxide or any rare-earth compound including an oxygen moiety. As an example, a powdered substance including cerium, such as a cerium oxide CeO_2 may be introduced into the powder mixture for the purpose of growing an oxyorthosilicate crystal doped with cerium as a scintillator crystal.

[0023] In step **215** an atmosphere, **160** in FIG. 1, is provided comprising an inert gas and a gas including oxygen, as described above.

[0024] In step **220** the powder mixture is melted in crucible **135** to produce melt **145**, atmosphere **160** being in contact with a surface of the melt. In step **230** a rare-earth oxyorthosilicate crystal is grown from melt **145** in the presence of atmosphere **160**.

[0025] FIG. 5 shows a second embodiment of a method of growing a rare-earth oxyorthosilicate crystal in a controlled atmosphere. A powdered substance comprising a first rare-earth element may be mixed with a powdered silicon oxide such as silica (SiO_2) **510**. A second powdered substance comprising a second rare-earth element may be mixed with the powder mixture at step **510**. The second powdered substance

may be a rare-earth oxide or any rare-earth compound including an oxygen moiety. As an example, a powdered substance including cerium, such as a cerium oxide CeO_2 , or any other material that can be calcined to cerium oxide, may be introduced into the powder mixture for the purpose of growing an oxyorthosilicate crystal doped with cerium as a scintillator crystal.

[0026] In step 515 an atmosphere, 160 in FIG. 1, is provided comprising an inert gas and a gas including oxygen, or a compound that disassociates to oxygen, such that the atmosphere includes less than 300 ppm oxygen.

[0027] In step 520 the powder mixture is melted in crucible 135 to produce melt 145, atmosphere 160 being in contact with a surface of the melt. In step 230 a rare-earth oxyorthosilicate crystal is grown from melt 145 in the presence of atmosphere 160.

[0028] The embodiments illustrated in FIGS. 2 and 5 include the use of powders for the silicon oxide, for a substance comprising at least one first rare-earth element, for a substance comprising at least one element from group 2, 3, 6, or 7, and, optionally, a substance comprising at least one second rare-earth element. Another embodiment includes use of different forms of matter for some or all of these example substances, including, but not limited to, liquids, sintered substances, granulated substances, pressed tablets, or solids that are not powdered.

[0029] FIG. 3 shows an example of a crystal boule 300 grown according to a method described above. To evaluate the scintillation properties of crystals made by the methods illustrated in FIG. 2 or 3, boules were cut into multiple samples (slabs) and each sample was evaluated separately. FIG. 3 shows a boule cut into twelve samples 310. Sample 1 is taken from the bottom of the boule, that is, the last part of the boule to be grown. Sample 12 is taken from the top of the boule, that is, the first section to be grown.

[0030] Oxyorthosilicate crystals may be grown over the following ranges of conditions: temperature from 1900° C. to 2200° C. inclusive, withdrawal rates from 0.001 mm/hr to 10 mm/hr inclusive, and rotation rates from 0 to 100 rotations per minute (RPM), inclusive. These ranges are exemplary and under the methods described herein any one or more of these conditions may be varied within or outside these ranges as known in the art. Oxyorthosilicate crystals may be grown over ranges of temperature, withdrawal rate, and rotation rate that are restricted to being between any two integer values, and including those integer values, within the above ranges. Exemplary cerium-doped lutetium oxyorthosilicate scintillator crystal boules were grown according to an embodiment of the method described above. The crystals were grown in an atmosphere including argon and CO_2 . The crystals were grown to about 80 mm in diameter and about 240 mm in length. Slabs 20 mm in thickness were cut from the crystals and numbered, starting from the bottom section of the crystal boule as shown in FIG. 3. Light output measurements were done under excitation with Cs^{137} gamma source (662 keV). The scintillation light was collected using a Hamamatsu R877 photomultiplier.

[0031] Table 1 shows light output, energy resolution, and decay time of a scintillator crystal grown in an atmosphere as described above. Results are presented in Table 1 using arbitrary scales defined by numbers of channels of a Multichannel Analyzer (MCA) unit used in the measurements. A bismuth germanate crystal ($\text{Bi}_4\text{Ge}_2\text{O}_{12}$; BGO) was used as a reference. (BGO photopeak was set to the channel 100 position).

TABLE 1

Slab #	Thickness [mm]	Light Output [Ch MCA]*	ER [%]	Decay Time [ns]
1	20	594	13	45.2
2	20	590	12	45.3
3	20	605	12	45.8
4	20	642	13	45.9
5	20	640	11	46.7
6	20	634	11	46.5
7	20	634	12	47.3
8	20	642	10	47.0
9	20	646	11	47.2
10	20	640	11	47.0
11	20	645	11	46.9
12	20	626	11	46.4
13	20	612	12	45.5

[0032] Results shown in Table 1 are characteristic of rare-earth oxyorthosilicate scintillator crystals of the highest optical quality and efficiency. As pointed out above, this has been achieved without any post growth anneal.

[0033] FIG. 4 shows a scintillation counter 400 using as a detector a rare-earth oxyorthosilicate crystal 450 grown according to the method described above. Radiation 460, such as gamma photons, are absorbed by oxyorthosilicate crystal 450, resulting in emission of scintillation light 440 from oxyorthosilicate crystal 450. Scintillation light 440 is detected by light detector 430, such as a photomultiplier tube, avalanche photodiode, or any other light sensor. An electrical signal produced by light detector 430 is conveyed by electrical connection 410 to analyzing electronics 420. Information such as energy spectra and timing of radiation 460 may be extracted using analyzing electronics 420.

[0034] While the preceding description refers to certain embodiments, it should be recognized that the description is not limited to those embodiments. Rather, many modifications and variations may occur to a person of ordinary skill in the art which would not depart from the scope and spirit defined in the appended claims.

What is claimed is:

1. A method of growing a rare-earth oxyorthosilicate crystal, comprising: preparing a melt by:
 - melting a first substance comprising at least one first rare-earth element;
 - melting at least one of: a substance comprising a group 2 element, a substance comprising a group 3 element, a substance comprising a group 6 element, or a substance comprising a group 7 element;
 - providing an atmosphere comprising an inert gas and a gas including oxygen, the atmosphere being in contact with a surface of the melt;
 - providing a seed crystal;
 - contacting the surface of the melt with the seed crystal; and
 - withdrawing the seed crystal from the melt.
2. The method of claim 1, wherein the gas including oxygen comprises an oxygen-containing compound that disassociates to oxygen.
3. The method of claim 1, wherein the inert gas has a thermal conductivity less than or equal to 150 mW/m-° K at the temperature used during crystal growth.
4. The method of claim 1, wherein the gas including oxygen comprises carbon dioxide.

5. The method of claim 1, wherein the gas including oxygen comprises at least one of carbon monoxide, oxygen, sulfur trioxide, phosphorous pentoxide or an oxide of nitrogen.

6. The method of claim 1, wherein the oxide of nitrogen comprises at least one of NO_2 , N_2O , NO , N_2O_3 , or N_2O_5 .

7. The method of claim 1, wherein the atmosphere comprises 0.01-10 percent oxygen by volume, inclusive.

8. The method of claim 1, wherein the atmosphere comprises less than 300 parts per million of oxygen.

9. The method of claim 1, wherein the atmosphere comprises less than 200 parts per million of oxygen.

10. The method of claim 9, wherein the inert gas comprises at least one of helium, argon, krypton, or xenon.

11. The method of claim 9, wherein the inert gas comprises nitrogen.

12. The method of claim 1, further comprising melting a second substance comprising a second rare-earth element, the second rare-earth element being incorporated into the rare-earth oxyorthosilicate crystal as a dopant.

13. The method of claim 12, wherein the second rare-earth element is cerium.

14. The method of claim 1, wherein the growing of the oxyorthosilicate crystal comprises growing a lutetium oxyorthosilicate crystal.

15. A method of decreasing oxygen vacancies incorporated in a rare-earth oxyorthosilicate crystal, the method comprising:

preparing a melt by melting a first substance comprising at least one first rare-earth element;

providing an atmosphere comprising an inert gas and a gas including oxygen, the atmosphere including less than 300 ppm oxygen, the atmosphere being in contact with a surface of the melt;

providing a seed crystal;

contacting the surface of the melt with the seed crystal; and withdrawing the seed crystal from the melt.

16. The method of claim 15, wherein the gas including oxygen comprises an oxygen-containing compound that dissociates to oxygen.

17. The method of claim 15, wherein the inert gas has a thermal conductivity less than or equal to $150 \text{ mW/m}^\circ\text{K}$ at the temperature used during crystal growth.

18. The method of claim 15, wherein the gaseous substance comprising oxygen comprises carbon dioxide.

19. The method of claim 15, wherein the gaseous substance comprising oxygen comprises at least one of carbon monoxide, oxygen, sulfur trioxide, phosphorous pentoxide or an oxide of nitrogen.

20. The method of claim 15, wherein the oxide of nitrogen comprises at least one of NO_2 , N_2O , NO , N_2O_3 , or N_2O_5 .

21. An oxyorthosilicate scintillator crystal, the crystal comprising an oxyorthosilicate of at least one first rare-earth element and further comprising at least one of: a group 2 element, a group 3 element, a group 6 element, or a group 7 element;

the crystal grown from a melt in an atmosphere comprising an inert gas and a gas including oxygen.

22. The scintillator crystal of claim 21, wherein the inert gas has a thermal conductivity less than or equal to $150 \text{ mW/m}^\circ\text{K}$ at the temperature used during crystal growth.

23. The scintillator crystal of claim 21 wherein the gas including oxygen comprises at least one of carbon dioxide, carbon monoxide, or oxygen.

24. The scintillator crystal of claim 21 wherein the atmosphere comprises 0.01-10 percent oxygen by volume, inclusive.

25. The scintillator crystal of claim 21 wherein the atmosphere comprises less than 300 parts per million of oxygen.

26. The scintillator crystal of claim 21 wherein the atmosphere comprises less than 200 parts per million of oxygen.

27. The scintillator crystal of claim 21, wherein the inert gas comprises at least one of helium, argon, krypton, or xenon.

28. The scintillator crystal of claim 21, wherein the inert gas comprises nitrogen.

29. The scintillator crystal of claim 21 further comprising a second rare earth element incorporated as a dopant.

30. The scintillator crystal of claim 29, wherein the second rare-earth element is cerium.

31. The oxyorthosilicate scintillator crystal of claim 21 wherein the first rare-earth element is lutetium.

32. A scintillator crystal, the crystal comprising an oxyorthosilicate of at least one first rare-earth element;

the crystal grown from a melt in an atmosphere, the atmosphere comprising an inert gas and less than less than 300 ppm oxygen.

33. The scintillator crystal of claim 32, wherein the inert gas has a thermal conductivity less than or equal to $150 \text{ mW/m}^\circ\text{K}$ at the temperature used during crystal growth.

34. The scintillator crystal of claim 32 further comprising a second rare earth element incorporated as a dopant.

35. The scintillator crystal of claim 34, wherein the second rare-earth element is cerium.

36. The oxyorthosilicate scintillator crystal of claim 32 wherein the first rare-earth element is lutetium.

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