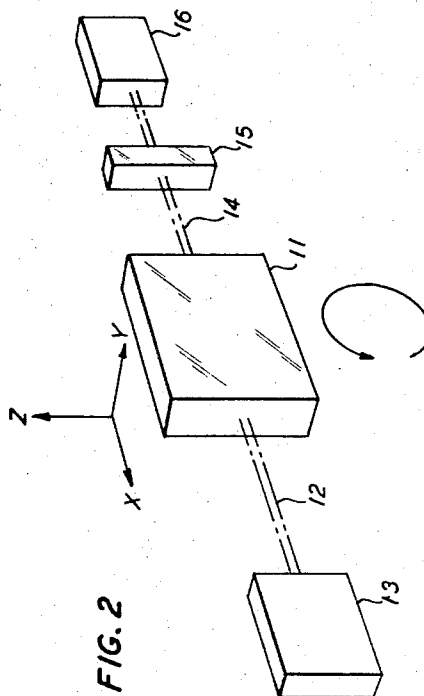
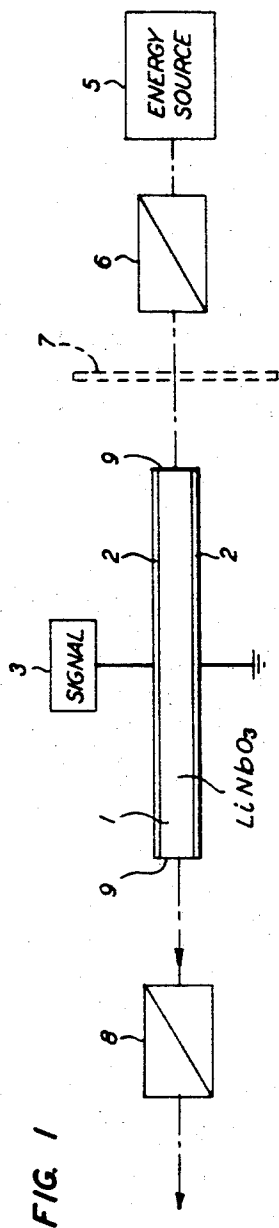


Dec. 24, 1968

G. M. LOIACONO ET AL
LITHIUM META-NIOBATE CRYSTALLINE GROWTH FROM
MELT CONTAINING MAGNESIUM OXIDE
Filed June 20, 1966

3,418,086



INVENTORS G. M. LOIACONO
K. NASSAU
BY *George S. Indig*
ATTORNEY

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**LITHIUM META-NIOBATE CRYSTALLINE
GROWTH FROM MELT CONTAINING
MAGNESIUM OXIDE**

Gabriel M. Loiacono, Lodi, and Kurt Nassau, Bernardsville, N.J., assignors to Bell Telephone Laboratories, Incorporated, Berkeley Heights, N.J., a corporation of New York

Filed June 20, 1966, Ser. No. 558,976

10 Claims. (Cl. 23—301)

ABSTRACT OF THE DISCLOSURE

Crystalline lithium meta-niobate is grown from a melt containing a magnesium value to yield from 0.02 weight percent magnesium oxide. A seed of niobate is inserted and pulled from the melt in growing the crystal rod. The rod is then poled by passage of current therethrough to eliminate ferroelectric domain walls.

This invention relates to improved techniques for the growth of lithium meta-niobate (LiNbO_3), to materials so grown, and to devices utilizing such end product.

Workers concerned with the rapidly growing technology dealing with light frequency transmission and modulation are aware of the potentialities of lithium meta-niobate. This material is considered to be by far the most efficient harmonic generating material, since it permits phase matching of fundamental and harmonic frequencies over a large portion of the visible spectrum. Other uses include modulation, in which use the composition is a fairly effective linear electro-optic material. There has also been some consideration given to the use of the material as an active laser host, for which use there are incorporated small amounts of active ingredients such as neodymium.

As is the case in so many developments dependent upon material characteristics, commercial use has been impeded by the difficulty of producing sufficient quantities of material of the requisite perfection and size. In particular, one problem which has plagued workers in the field is cracking of the crystalline material when produced by the usual Czochralski growth. This difficulty, which resulted in cracking of three out of four crystals at the early stages of development, with cracks sufficiently close to prevent selection of unflawed sections of dimensions greater than two millimeters was only aggravated when further developments required the use of purer starting materials, for example, to minimize discolorations. Use of these purer raw materials, that is, of the order of three mines or better purity, results in cracking of substantially all grown crystals.

In accordance with the present invention, it has been discovered that inclusion of small amounts of magnesium, generally added in the form of magnesium oxide or any other compound which will yield magnesium oxide under the growth conditions virtually eliminates the cracking problem when other good crystal growth practice is followed. From 0.02 weight percent to about five weight percent of MgO based on the entire melt achieves the desired effect. With this technique, uncracked crystalline samples of lengths of three inches are easily attained. An additional benefit also unexplained, is the increase in solubility for neodymium and other rare earths which accompanies the magnesium addition. It has been found that the usual distribution coefficient of neodymium, ordinarily about 0.07, is increased to a value of the order of 0.75 for a magnesium addition of 0.5 weight percent MgO based on the melt.

The broad magnesium addition range in terms of

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MgO has been found as lying from 0.02 weight percent to five weight percent. Lesser amounts of magnesium, while they result in some lessening of cracking, do not generally result in complete elimination. Amounts greater than five percent in general are considered undesirable in that they result in undue contamination with some accompanying flawing. A preferred range of from 0.1 to 2 weight percent, on the above basis, is indicated, with an optimum value lying at about one-half weight percent.

It has been determined that the distribution coefficient for magnesium during Czochralski crystal pulling is of the order of 1.3. Accordingly, crystalline materials produced in accordance with this invention contain from 0.016 weight percent to 4 weight percent magnesium based on the entire composition.

Since the end product of the inventive process is likely destined for use in a highly discriminating environment, it is, of course, desirable to minimize other sources of operational difficulty. It is recognized that domain walls produce a certain amount of beam broadening or light scattering and are otherwise undesired in devices of the class contemplated. Accordingly, the use of a poling field during growth or subsequent to growth is recommended. The procedure is described in Applied Physics Letters, volume 7, page 9 (1965). A somewhat more detailed description is presented in Journal of Physics and Chemistry of Solids, volume 27 (1966). All operating parameters, including preferred and optimum ranges, are set forth in copending application Ser. No. 516,357, filed Dec. 27, 1965 (Levinstein-Nassau 2-10).

While suitable crystal pulling conditions are well known to all those skilled in the art, a brief description of one set of conditions found adequate for the practice of this invention is set forth.

GENERAL

Presintered lithium niobate powder of nominal composition LiNbO_3 , to which is added the requisite weight percent of magnesium oxide, is melted, and the temperature is stabilized at a few degrees above the melting point (about 1260°C). A seed crystal of LiNbO_3 is inserted and is slowly withdrawn at such rate as to produce growth. Refinements include adjustment of temperature to produce the desired diameter. Growth may be carried out in air or any other oxygen-bearing medium. Either during growth or subsequent to growth, the material is poled by passage of a current, typically five milliamperes per square centimeter of cross section, through the crystal. If poling is carried out subsequent to growth, the crystal is maintained at a temperature slightly below its Curie point of about 1200°C .

The following examples serve to illustrate suitable parameters which have been practiced to result in crystalline lengths of three inches and greater without any perceptible cracking.

Example 1

200 grams of high purity (99.9+ percent) presintered lithium meta-niobate powder (of nominal composition LiNbO_3), together with one gram of magnesium oxide, were inserted into a platinum crucible. The crucible and contents were heated to a temperature of 1300°C ., and the nutrient material, once rendered molten, was maintained at a temperature between 1260°C . and 1300°C . for a period of ten minutes to ensure mixing and complete melting. A seed crystal of dimensions approximately one centimeter in length and three millimeters in diameter cut perpendicular to the hexagonal C-axis was partially immersed into the melt, was held in this position for a period of about two minutes, and was then slowly withdrawn at an initial rate of three-quarters of an inch per hour. During withdrawal, the temperature was first ad-

justed so as to produce a diameter of one-half inch in the growing crystal, after which the temperature was maintained constant. Growth was permitted to continue until a crystal length of about three inches resulted. The crystal was allowed to cool and was microscopically examined and found to be completely devoid of cracks. The end product was then poled at a temperature of about 1150° C., using a poling current of five milliamperes for one-half hour, after which crystal was cooled at a controlled rate of about 100 degrees per hour to room temperature in oxygen.

Example 2

The procedure of Example 1 was repeated, using the same amounts of starting ingredients, however with the addition of 0.75 gram of neodymium in the form of neodymium oxide (Nd_2O_3).

Final treatment was identical to that described in Example 1. The final crystal was unflawed and contained about 2.5 atom percent neodymium based on total cation content.

Example 3

The procedure of Example 1 was repeated using the same amounts of the same starting ingredients, however while passing a current of about five milliamperes through the growing crystal, with the crystal biased positive with respect to the melt. The controlled cooling (annealing) step was carried out upon removal of the crystal from the growth apparatus.

Various deviations from the practice described in the examples may be practiced. For example, growth has been carried out with a niobium excess of about one-quarter weight percent based on niobium. It is found that the stoichiometry of the growing crystal may be varied over the range including ± 3 weight percent niobium in the melt with concomitant variation in Curie point and birefringence. The examples relate to growth on a LiNbO_3 seed and this is the preferred technique. The inventive advantages, however, obtain for seeded growth on other materials as, for example, on a platinum wire, and also for spontaneous nucleation.

The attached drawing illustrates device uses in which the crystals grown in accordance with this invention are desirably incorporated. In the drawing:

FIG. 1 is a schematic representation of an electro-optic modulator utilizing lithium meta-niobate as grown herein for the active element; and

FIG. 2 is a perspective view of a nonlinear device illustratively operating as a second harmonic generator (SHG) or a parametric device, again utilizing a crystal grown in accordance with this invention.

Referring again to FIG. 1, the modulator depicted consists of active lithium meta-niobate element 1, having polished ends 9 and provided with electrodes 2, which may be constituted of a fired silver paste layer, and across which there is imposed a modulating electric field produced by modulating voltage source or signal source 3. Associated elements included in the depicted apparatus include light source 5, polarizer 6, optionally a quarter wave plate 7, and analyzer 8.

Energy source 5 for significant communication purposes generally takes the form of a coherent light source such as a laser. Polarizer 6 is oriented in such fashion as to secure maximum modulation. See, for example, Applied Physics Letters, volume 5, page 62 et seq. In other terms, the polarization direction of element 6 is at 45 degrees to an axis of the indicatrix ellipse of element 1.

The optional element 7, which may constitute a thin cleaved layer of mica or any other material of such dimension as to constitute a quarter wave plate for the frequency of electromagnetic energy to be modulated, served to "optically bias" element 1 so that the variation in transmission is approximately linearly dependent on applied field. This element is considered optional, since

its function may be performed by a D.C. bias across electrodes 2. It may be positioned before or after element 1. The use of the quarter wave plate is generally preferred for two reasons: (1) The need for separating the D.C. and A.C. fields across electrode 2 is avoided; and (2) a constant bias, possibly resulting in electrolysis problems, is avoided.

Light or other electromagnetic energy, having been produced by element 5 and having been polarized by element 6, then passes through lithium meta-niobate element 1, and upon emerging contains the information introduced by means of the signal produced by element 3 in the form of optical sidebands. The energy may at this stage be passed through an analyzer 8 and then be transmitted to a receiver, not shown, or, in the alternative, may be directly transferred to such a receiver, which is provided with an element performing the function of analyzer 8. In either event, this element is desirably oriented to produce the maximum intensity variation. This may be achieved simply by rotating the element until optimum conditions are achieved, or its position may be calculated in accordance with well-known principles. Relative to polarizer 6, analyzer 8 is preferably a crossed polarizer.

In FIG. 2 there is depicted a single crystal body 11 of LiNbO_3 . The crystallographic orientation of the body is indicated on the figure. A coherent electromagnetic beam 12 produced by source 13 is introduced into body 11, as shown. The resultant emerging beam 14 is then caused to pass through filter 15, and, upon departing, is detected by apparatus 16. For the SHG case, beam 12 is of a fundamental frequency while departing beam 14 additionally contains a wave of a frequency corresponding with the first harmonic of beam 12. Filter 15 is of such nature as to pass only the wave of concern, in the SHG instance, that of the harmonic. Apparatus 16 senses only that portion of the beam leaving filter 15. The value of θ_m may be varied in body 11 by altering the angle between beam 12 and the Z axis, as by rotating the crystal about the Y axis. As has been indicated, the maximum birefringence is obtained for an angle of 90 degrees.

The device of FIG. 2 may similarly be regarded as a three-frequency device, with beam 12 containing frequencies to be mixed or consisting of a pump frequency. Under these conditions, exiting beam 14 contains signal and idler frequencies as well as pump, representing three distinct values for nondegenerate operation. For any operation, whether two frequency or three, efficiency is increased by resonance. Such may be accomplished by coating the surfaces of crystal 11, through which the beam enters and exits. This coating may be partially reflecting only for a generated frequency, as for example for the harmonic in SHG. For the three-frequency case, it is desirable to support both generated frequencies. In most instances, this cannot be accomplished by coating the face of the crystal, and it is necessary to provide at least one spaced adjustable mirror which may be positioned at such distance from the face of the crystal 11 as to support the frequencies of concern. Simultaneous support of the pump frequency may similarly be accomplished. However, the complication so introduced is justified only when the pump level requires it.

The crystalline orientation shown as the initial position for crystal 11 in the apparatus of FIG. 2 eliminates the effect of double refraction, as has been discussed. This angle may be retained for a broad range of conditions when operating either in the degenerate or nondegenerate mode simply by controlling temperature.

It has been indicated that the device depicted in FIG. 2 is merely exemplary of a large class of nonlinear devices utilized as harmonic generators, parametric mixers, parametric amplifiers, etc. Such a class of devices is described in detail in copending United States application Ser. No. 414,366, filed Nov. 27, 1964.

Description has largely been in terms of the lithium

meta-niobium system itself, although general reference to the inclusion of an active laser material, and, specifically, neodymium, has been set forth. Other ingredients, intentional or unintentional, may be added or tolerated. Intentional ingredients, exemplified by cobalt, chromium, neodymium, other transition elements, etc., may serve to adjust color, dichroism, to introduce fluorescence, etc. Typical amounts in the final crystal may range up to several percent by weight based on the entire composition. Unintentional ingredients may include platinum, tantalum, sodium, molybdenum, and titanium. Such ingredients may be found in amounts of up to about one weight percent based on the final composition. Depending on the purpose to which the final crystal is to be put, such amounts may or may not be tolerated. From the standpoint of electro-optics and nonlinear optical devices, discolorations are to be avoided, as are unintentional ingredients which produce stress, flawing, and other mechanisms responsible for light scattering. Exemplary materials are rhodium and iridium. Such materials should be kept below a level of about .01 weight percent based on final composition for these purposes.

Starting materials have been described in terms of a presintered mass of lithium niobate and in terms of magnesium added in the form of the oxide. Alternate forms are, of course, acceptable. These include the use of lithium carbonate, together with niobium oxide and magnesium carbonate, oxalate, or any other compounds or mixtures of elements capable of producing a melt of the desired oxide composition. The invention is described largely in terms of the high resistivity material desirable for use in devices operating at visible or near visible electromagnetic frequencies. For certain other uses, it may be desirable to decrease resistivity. Such may be accomplished by the addition of certain conductivity-inducing ingredients or by the use of conditions resulting in partial reduction of the compound itself. This latter may be achieved simply by eliminating the oxygen annealing step described in each of the examples or by introducing a deliberate reduction which may involve use of heating in an inert or hydrogen-bearing atmosphere.

The invention has been described in terms of a limited number of embodiments. Various modifications are ap-

parent to those skilled in the art. The attached claims are to be construed as reading on any such variations.

What is claimed is:

1. Method for synthesizing crystalline material comprising the nominal composition LiNbO_3 comprising melting a nutrient mass comprising the said nominal composition together with magnesium values in such amount as to yield from 0.02 weight percent to 5 weight percent magnesium oxide based on the total nutrient mass, and crystallizing material from the molten mass so produced.
2. Method of claim 1 in which crystallizing is brought about by inserting a seed crystal of such material into the molten mass so produced and withdrawing said seed at such rate as to produce growth thereon.
3. Method of claim 1 in which the magnesium inclusion is within the range of from 0.1 weight percent to 2 weight percent MgO based on the entire nutrient mass.
4. Method of claim 1 in which the resulting crystalline material is poled so as to eliminate ferroelectric domain walls.
5. Method of claim 4 in which such poling is accomplished by passage of a current through the liquid-solid interface during growth.
6. Method of claim 4 in which such poling is accomplished subsequent to growth.
7. Method of claim 1 in which the crystalline material is finally annealed in oxygen.
8. Method of claim 1 in which an addition is made to the melt to produce fluorescence in the crystalline material.
9. Method of claim 8 in which such addition comprises a rare earth.
10. Method of claim 9 in which such rare earth is neodymium.

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U.S. Cl. X.R.

23—300, 302; 29—25.35, 599; 252—62.1