

METHOD FOR PREPARING LARGE-SIZE LITHIUM TANTALATE CRYSTALS

TECHNICAL FIELD

5 The present invention relates to the field of piezoelectric crystals, and specifically relates to a method for preparing lithium tantalate crystals.

BACKGROUND

10 In recent years, as high-frequency and multi-frequency communication has been widely used in wireless communication represented by mobile phones, the demand for a surface acoustic wave (SAW) filter is greatly increased, and the requirement for the quality of the SAW filter is also higher. With continuous development of an SAW technology, there are continuously expanded application fields and broader market prospects for SAW devices, and simply the SAW filter can be expected to have a
15 broad market prospect. Since the 1990s, the application of SAW filters in mobile phones is growing rapidly, and each smart phone requires at least 6 SAW devices.

 In 2016, the annual demand for the SAW devices in the global mobile phone market was more than 8.4 billion, and the demand is increasing rapidly. With rapid development of the Internet, there
20 are more and more Internet users all over the world, and the application of high-performance SAW filters in cable television network-based broadband multimedia data broadcasting systems (such as VOD) also develops rapidly. In addition, a large number of medium-frequency SAW filters are also required in an automotive electronics market, wireless LAN and transmission systems of digital televisions. However, due to the use of multiple frequency bands, the number of the SAW devices in
25 a single apparatus is increased, which results in increasing market demand for the SAW devices. Meanwhile, miniaturization of a communication device requires each part be manufactured more precisely, and as a result, the SAW device is also miniaturized.

 During growth of large-size lithium tantalate crystals, due to apparent density of powders,
30 lithium tantalate raw material cannot be added into a crucible at one time, and thereby heating and cooling need to be conducted twice to melt all lithium tantalate raw material, which has great influence on the purity of the raw material and the uniformity of elements. Moreover, as the large-

size lithium tantalate crystals have high internal charge activity, spontaneous discharge is likely to occur and thereby make the crystal cracked.

5 SUMMARY

An objective of the present invention is to provide a method for preparing large-size lithium tantalate crystals.

10 In order to achieve the above-mentioned objective, the present invention provides the following technical solutions.

A method for preparing large-size lithium tantalate crystals comprise the following steps:

(a) molding formulated lithium tantalate raw material into a round cake with a size of $\Phi 220 \times 50$ mm by using an isostatic press;

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(b) placing the molded lithium tantalate raw material into a crucible, and heating the crucible to 1450–1500 °C at a heating rate of 300–400 °C/h for melting the lithium tantalate raw material into a molten liquid;

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(c) lowering a seed crystal to be in contact with the molten liquid, controlling the rotating speed to be 10–12 rpm/min, subjecting the seed crystal to necking to 2–3 mm, and allowing for automatic growth;

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(d) controlling a cooling speed of the crystal to be 50–60 °C/h, and subjecting the crystal to static electricity elimination by using a static electricity eliminating device when the crystal is cooled to 100 °C.

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In step (a), the raw material is formulated by mixing Li_2CO_3 and Ta_2O_5 at a molar ratio of 48.45:52.65 and then subjected to molding by using the isostatic press. An isostatic pressure is required to be 300 MPa. A container used in the molding is made of latex.

In step (b), Lr is used as a crucible blank, and Pt is plated on the crucible blank. The Lr crucible blank is required to have a thickness of 2 mm, and a Pt cladding is required to have a thickness of 0.2 mm.

5 In step (c), the crystal grows in the atmosphere featuring the temperature of 30–35 °C and the humidity of 50–60% RH, and the crystal is cooled in an environment featuring the temperature of 35–40 °C and the humidity of 60–80% RH.

10 In step (d), during the process of static electricity elimination, an airflow generated by the static electricity eliminating device acts on the surface of the crystal through a hollow seed crystal rod at an air volume of 1.0–2.0 m³/min.

Compared with the prior art, the present invention has the following beneficial effects.

15 (1) In the process disclosed herein, as the isostatic press is used, the density of the raw material is increased, and thus the problem that heating and cooling need to be conducted twice on the raw material due to apparent density of powders is solved, and the volatilization of Li is reduced, so that the crystal has higher consistency in Curie temperature and is more similar to a near-stoichiometric crystal.

20 (2) As the Pt-plated Lr crucible is used, the strength of the crucible is improved, the influence caused by high-temperature oxidation of the Lr on the crystal is reduced, and thus the crystal is more similar to an optical crystal.

25 (3) As the temperature and humidity are controlled, and the static electricity elimination is conducted at low temperature, the problem that the piezoelectric crystal is cracked due to spontaneous discharge is effectively solved.

DETAILED DESCRIPTION

30 The technical solutions in the embodiments of the present invention will be clearly and completely described below. Apparently, the described embodiments are merely a part, rather than all of the embodiments of the present invention. Based on the embodiments in the present invention, all

other embodiments obtained by those of ordinary skill in the art without making any creative effort fall in the protection scope of the present invention.

Example 1

5 Molding of raw material: A lithium tantalate polycrystal material was formulated by mixing Li_2CO_3 and Ta_2O_5 at a molar ratio of 48.45:52.65, and then placed into a latex bag. The latex bag was placed on a vibrating machine for vibrating at a frequency of 50 HZ to reduce gaps of the raw material. The latex bag was sealed by using a stainless steel cover, and then placed into an isostatic pressing chamber for pressing, wherein a pressure for pressing is required to be 300 Mpa, and ultrapure water
10 is used as a pressing liquid. The molded raw material had a density of 0.047 g/mm^3 .

Crystal growth:

(1) The molded lithium tantalate raw material was put into a Pt-plated Lr alloy crucible, and the Pt-plated Lr alloy crucible was heated, by using a medium-frequency induction power supply, to
15 1450 °C or above within 4–6 h for melting the piezoelectric crystal raw material into a molten liquid.

(2) Crystal introduction: An induction heating output power was adjusted to form stable heat convection at a liquid level temperature of 1260–1650 °C. A constant induction heating output power was maintained for 4 h or more to keep the raw material molten liquid in a thermal stable state, and
20 the rotating speed is controlled to be 10–12 rpm/min. A seed crystal was lowered from the place right above the center of the convection to allow the seed crystal to be in contact with the liquid level. The induction heating output power was finely adjusted to 10–80 W to make the seed crystal immersed in the liquid level necked to 2–3 mm.

25 (3) Shouldering: The seed crystal was slowly pulled at a rate of 0.16 mm/h, and the induction heating output power was reduced at a rate of 10–50 W/h, so as to achieve uniform increase of the weight of the crystal.

(4) Constant-diameter growth: When an outer diameter of the crystal reached about 105 mm, the
30 growth of the crystal was automatically controlled by a program. The outer diameter of the crystal was calculated by the program by measuring the change of the weight of the crystal, and the output power was automatically adjusted to achieve constant-diameter growth of the crystal. The crystal grew in the atmosphere featuring the temperature of 30–35 °C and the humidity of 50–60% RH.

(5) Cutting: After the crystal had a set weight, the crystal was pulled at a rate of 10 m/min for 20–30 mm to be completely separated from the molten liquid. An output power of an induction coil was maintained for 0.2–0.5 h, and then the induction heating output power was reduced at a rate of 50–60 °C/h. The crystal was cooled in an environment featuring the temperature of 35–40 °C and the humidity of 60–80% RH.

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Static electricity elimination: When the crystal was cooled to 100 °C, the crystal is subjected to static electricity elimination by using a static electricity eliminating device with an air volume of 1.0–2.0 m³/min and an airflow area of 250*250 mm.

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After an appearance test, it was found that the piezoelectric crystal grew according to this example was not cracked, and it was light green and high in permeability; after a conoscopic image test, it was found that the crystal had a uniform and regular interference ring and was free of cross deformation of the central black cross, and the crystal was similar to an optical crystal. After a test with a laser pen, it was found that the crystal had no flashes or bubbles inside. The head of the crystal had a Curie temperature of 605°, the tail part of the crystal had a Curie temperature of 605.5°, and thus the crystal featured high consistency. After Raman analysis was conducted on the crystal by using a microscope, it was found that a proportion of [Li]/[Li+Ta] was 49.5%, and thus the crystal was similar to a stoichiometric crystal.

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In order to highlight the beneficial effects of the present invention, experiments for comparative examples were also carried out in the following.

25 **Comparative Example 1**

Molding of raw material: A lithium tantalate polycrystal material was formulated by mixing Li₂CO₃ and Ta₂O₅ at a molar ratio of 48.45:52.65, and then pressed by using an ordinary oil press, and the molded raw material had a density of 0.016 g/mm³.

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Crystal growth:

(1) The lithium tantalate raw material was put into a Pt-plated Lr alloy crucible, where a planned feeding amount was 20 kg while an actual feeding amount was 14.5 kg, with 5.5 kg of raw material left. The Pt-plated Lr alloy crucible was heated, by using a medium-frequency induction power supply,

to 1450 °C or above within 4–6 h for melting the raw material. After dissolution, the raw material was cooled to room temperature at a rate of 150 °C/h. The remaining 5.5 kg of the lithium tantalate raw material was then added, and the mixture was heated to 1450 °C or above within 4–6 h for melting the piezoelectric crystal raw material again into a molten liquid.

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(2) Crystal introduction: An induction heating output power was adjusted to form stable heat convection at a liquid level temperature of 1260–1650 °C. A constant induction heating output power was maintained for 4 h or more to keep the raw material molten liquid in a thermal stable state, and the rotating speed is controlled to be 10–12 rpm/min. A seed crystal was lowered from the place right
10 above the center of the convection to allow the seed crystal to be in contact with the liquid level. The induction heating output power was finely adjusted to 10–80 W to make the seed crystal immersed in the liquid level necked to 2–3 mm.

(3) Shouldering: The seed crystal was slowly pulled at a rate of 0.16 mm/h, and the induction
15 heating output power was reduced at a rate of 10–50 W/h, so as to achieve uniform increase of the weight of the crystal.

(4) Constant-diameter growth: When an outer diameter of the crystal reached about 105 mm, the growth of the crystal was automatically controlled by a program. The outer diameter of the crystal
20 was calculated by the program by measuring the change of the weight of the crystal, and the output power was automatically adjusted to achieve constant-diameter growth of the crystal. The crystal grew in the atmosphere featuring the temperature of 30–35 °C and the humidity of 50–60% RH.

(5) Cutting: After the crystal had a set weight, the crystal was pulled at a rate of 10 m/min for
25 20–30 mm to be completely separated from the molten liquid. An output power of an induction coil was maintained for 0.2–0.5 h, and then the induction heating output power was reduced at a rate of 50–60 °C/h. The crystal was cooled in an environment featuring the temperature of 35–40 °C and the humidity of 60–80% RH.

30 Static electricity elimination: When the crystal was cooled to 100 °C, the crystal is subjected to static electricity elimination by using a static electricity eliminating device with an air volume of 1.0–2.0 m³/min and an airflow area of 250*250 mm.

After a test with a laser pen, it was found that the piezoelectric crystal grew according to this comparative example had no defects. After a Curie temperature test with a differential thermal analyzer, it was found that the head of the crystal had a Curie temperature of 600°, the tail part of the crystal had a Curie temperature of 610°, and the head and the tail part had a difference of 10°. After Raman analysis was conducted on the crystal by using a microscope, it was found that a proportion of [Li]/[Li+Ta] was 48.5%, and the crystal was not a stoichiometric crystal. The reason was that after the crystal was heated and cooled twice, Li ions were volatilized, resulting in high deviation of components.

Comparative Example 2

Molding of raw material: A lithium tantalate polycrystal material was formulated by mixing Li_2CO_3 and Ta_2O_5 at a molar ratio of 48.45:52.65, and then placed into a latex bag. The latex bag was placed on a vibrating machine for vibrating at a frequency of 50 HZ to reduce gaps of the raw material. The latex bag was sealed by using a stainless steel cover, and then placed into an isostatic pressing chamber for pressing, wherein a pressure for pressing is required to be 300 Mpa, and ultrapure water is used as a pressing liquid. The molded raw material had a density of 0.047 g/mm³.

Crystal growth:

(1) The molded lithium tantalate raw material was put into an iridium crucible, and the iridium crucible was heated, by using a medium-frequency induction power supply, to 1450 °C or above within 4–6 h for melting the piezoelectric crystal raw material into a molten liquid.

(2) Crystal introduction: An induction heating output power was adjusted to form stable heat convection at a liquid level temperature of 1260–1650 °C. A constant induction heating output power was maintained for 4 h or more to keep the raw material molten liquid in a thermal stable state, and the rotating speed is controlled to be 10–12 rpm/min. A seed crystal was lowered from the place right above the center of the convection to allow the seed crystal to be in contact with the liquid level. The induction heating output power was finely adjusted to 10–80 W to make the seed crystal immersed in the liquid level necked to 2–3 mm.

(3) Shouldering: The seed crystal was slowly pulled at a rate of 0.16 mm/h, and the induction heating output power was reduced at a rate of 10–50 W/h, so as to achieve uniform increase of the weight of the crystal.

5 (4) Constant-diameter growth: When an outer diameter of the crystal reached about 105 mm, the growth of the crystal was automatically controlled by a program. The outer diameter of the crystal was calculated by the program by measuring the change of the weight of the crystal, and the output power was automatically adjusted to achieve constant-diameter growth of the crystal. It was required that the crystal grow in a closed furnace chamber, and a mixed gas of nitrogen and oxygen at a ratio
10 of 500:20 was introduced.

(5) Cutting: After the crystal had a set weight, the crystal was pulled at a rate of 10 m/min for 20–30 mm to be completely separated from the molten liquid. An output power of an induction coil was maintained for 0.2–0.5 h, and then the induction heating output power was reduced at a rate of
15 50–60 °C/h.

Static electricity elimination: When the crystal was cooled to 100 °C, the crystal is subjected to static electricity elimination by using a static electricity eliminating device with an air volume of 1.0–2.0 m³/min and an airflow area of 250*250 mm.

20 After an appearance test, it was found that the piezoelectric crystal grew according to this comparative example was dark yellow and low in permeability. After a conoscopic image test, it was found that the crystal had a nonuniform and irregular interference ring, and cross deformation of the central black cross was present. After a test with a laser pen, it was found that due to oxygen vacancy
25 of the crystal and iridium oxidation, the crystal had flashes inside.

Comparative Example 3

Molding of raw material: A lithium tantalate polycrystal material was formulated by mixing
30 Li₂CO₃ and Ta₂O₅ at a molar ratio of 48.45:52.65, and then placed into a latex bag. The latex bag was placed on a vibrating machine for vibrating at a frequency of 50 HZ to reduce gaps of the raw material. The latex bag was sealed by using a stainless steel cover, and then placed into an isostatic pressing

chamber for pressing, wherein a pressure for pressing is required to be 300 Mpa, and ultrapure water is used as a pressing liquid. The molded raw material had a density of 0.047 g/mm³.

Crystal growth:

5 (1) The molded lithium tantalate raw material was put into a Pt-plated Lr alloy crucible, and the Pt-plated Lr alloy crucible was heated, by using a medium-frequency induction power supply, to 1450 °C or above within 4–6 h for melting the piezoelectric crystal raw material into a molten liquid.

10 (2) Crystal introduction: An induction heating output power was adjusted to form stable heat convection at a liquid level temperature of 1260–1650 °C. A constant induction heating output power was maintained for 4 h or more to keep the raw material molten liquid in a thermal stable state, and the rotating speed is controlled to be 10–12 rpm/min. A seed crystal was lowered from the place right above the center of the convection to allow the seed crystal to be in contact with the liquid level. The induction heating output power was finely adjusted to 10–80 W to make the seed crystal immersed in
15 the liquid level necked to 2–3 mm.

(3) Shouldering: The seed crystal was slowly pulled at a rate of 0.16 mm/h, and the induction heating output power was reduced at a rate of 10–50 W/h, so as to achieve uniform increase of the weight of the crystal.

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(4) Constant-diameter growth: When an outer diameter of the crystal reached about 105 mm, the growth of the crystal was automatically controlled by a program. The outer diameter of the crystal was calculated by the program by measuring the change of the weight of the crystal, and the output power was automatically adjusted to achieve constant-diameter growth of the crystal. The crystal
25 grew in the atmosphere.

(5) Cutting: After the crystal had a set weight, the crystal was pulled at a rate of 10 m/min for 20–30 mm to be completely separated from the molten liquid. An output power of an induction coil was maintained for 0.2–0.5 h, and then the induction heating output power was reduced at a rate of
30 50–60 °C/h.

(6) Cooling: The crystal was cooled until the output power was zero, and then was naturally cooled for 24 h. Then, a thermal field was removed, and the crystal was taken out.

After a test, it was found that the piezoelectric crystal grew according to this comparative example was internally cracked due to discharge of the crystal.

5 Although the embodiments of the present invention have been shown and described, it will be understood by those of ordinary skill in the art that various changes, modifications, substitutions and alterations may be made to these embodiments without departing from the principle and spirit of the present invention, and the scope of the present invention is defined in the appended claims and equivalents thereof.

CLAIMS

What is claimed is:

1. A method for preparing a large-size lithium tantalate crystal, comprising the following steps:

5 (a) molding formulated lithium tantalate raw material into a round cake with a size of $\Phi 220 \times 50$ mm by using an isostatic press;

(b) placing the molded lithium tantalate raw material into a crucible, and heating the crucible to 1450–1500 °C at a heating rate of 300–400 °C/h for melting the lithium tantalate raw material into a molten liquid;

10 (c) lowering a seed crystal to be in contact with the molten liquid, controlling the rotating speed to be 10–12 rpm/min, subjecting the seed crystal to necking to 2–3 mm, and allowing for automatic growth; and

(d) controlling a cooling speed of the crystal to be 50–60 °C/h, and subjecting the crystal to static electricity elimination by using a static electricity eliminating device when the crystal is cooled to 15 100 °C.

2. The method for preparing a large-size lithium tantalate crystal according to claim 1, wherein in step (a), the raw material is formulated by mixing Li_2CO_3 and Ta_2O_5 at a molar ratio of 48.45:52.65 and then subjected to molding by using the isostatic press.

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3. The method for preparing a large-size lithium tantalate crystal according to claim 2, wherein an isostatic pressure is required to be 300 MPa.

4. The method for preparing a large-size lithium tantalate crystal according to claim 3, wherein 25 a container used for the molding is made of latex.

5. The method for preparing a large-size lithium tantalate crystal according to claim 1, wherein in step (b), Lr is used as a crucible blank, and Pt is plated on the crucible blank.

30 6. The method for preparing a large-size lithium tantalate crystal according to claim 5, wherein

the Lr crucible blank is required to have a thickness of 2 mm, and a Pt cladding is required to have a thickness of 0.2 mm.

5 7. The method for preparing a large-size lithium tantalate crystal according to claim 1, wherein in step (c), the crystal grows in the atmosphere featuring the temperature of 30–35 °C and the humidity of 50–60% RH, and the crystal is cooled in an environment featuring the temperature of 35–40°C and the humidity of 60–80% RH.

10 8. The method for preparing a large-size lithium tantalate crystal according to claim 1, wherein in step (d), during the process of static electricity elimination, an airflow generated by the static electricity eliminating device acts on the surface of the crystal through a hollow seed crystal rod at an air volume of 1.0–2.0 m³/min.