Journal of Korean Association of Crystal Growth
Vol. 4, No. 3 (1994) 230-237

The growth and application of LBO crystal

Jinghe Liu , Jianli Li, Kuisheng Yang, Xiyan Zhang, Yagui Lei, Mu Na, Yuqi Zou and Renhua Zhang
Chang Chun Institute of Optics and Fine Mechanics, Chang Chun, 130022, China

LBO 결정성장과 응용

유경화, 이강리, 양규성, 장희연, 래야규, 나무, 주유치, 장인화
장춘광학정밀기계학원, 장춘 130022, 중국

Abstract The paper studies the growth and application of LBO Crystal and points that thermodynamics and dynamics model of crystal growth should be developed in high-η(viscosity) melt. The measurement on properties of crystal resonator and press-controlled oscillator indicates that this kind of crystal is one kind of piezo-electric crystal materials which has large-market application potentiality.

요 약 본 논문은 LBO 결정성장 및 응용과 높은 점성을 갖는 용액에서 결정성장의 열역학과 동역학의 모델에 관하여 연구하였다. 결정공명과 press-controlled oscillator의 특성에 대한 측정은 이러한 종류의 결정이 많은 응용 가능성을 갖는 압전 결정재료의 한 종류임을 나타내 준다.

1. Introduction

Lithium tetraborate crystal, also called lithium pyroaborate crystal and LBO or LTB for short, was invented with great efforts over ten years ago. It is one kind of piezo-electric crystal materials with good properties. This crystal belongs to pyramidal system, its point group is 4 mm, crystal lattice constants are 9.475 Å (a) and 10.283 Å (c), density is 2.44 g/cm^3, Moh's hardness is 6, primary time-delay temperature coefficient (TCD) and primary frequency temperature coefficient (TCF) are in the area of zero tangent. The electromechanical coupling coefficient K_S^2 of the crystal is high and about 10 times over that of quartz crystal. In this crystal sound transmission quickly and the reflectivity on surface Al electrode is high. Meanwhile it has good features of little density, cheap starting materials, low melting point, no phase change, no polarization and fine cooling treatment, so it is fit for designation and production of high-frequency, wide-band, low-insert loss and highly-stable SAW and BAW device. It is one kind of piezo-electric crystal materials which has large-market application pontentiality.

$Li_2B_4O_7$ was discovered to have property of thermoluminescence in the field of nucleus physics and it is one of important material to make thermoluminescence detector. Moreover, $Li_2B_4O_7$ is still one kind of nonlinear optical crystal and is considered to be applied to laser technique. It is also used to make static-pressure sensor which approachs to low temperature of liquid nitrogen, telecontrol sensor and temperature sensor.

Now, Japanese Toshiba Company Institute and Development Center, which is the best level in the world has produced LBO crystal of 50×100 mmϕ. Starting materials are LBO powder or pured polycrystal powder (99.99%). Rotation rate and linear growth rate are 10～40 rpm and 0.5～5 mm/h respectively. The SAW and BAW device made of LBO are mainly used for productions which requests high properties of device. In China the 1426 Institute have produced crystal of 32×5 mmϕ and core defect < 1 mmϕ by Cz method. Its piezo-electric parameters is conformed to overseas reports. The property of cutting treatment is good. This result is thought ot be advanced level in china and up to the advanced level of overseas 1980s. The scientists in Beijing polytechnic University and Beijing 707 Factory together manufactured 25×30 mmϕ transpsrent crystal with no core. They also manufactured the kind of crystal resonator and successfully applied it to band-passed filter and press-controlled oscillator. Shanghai Institute of Silicate of Chinese Academy of Science produced the crystal of large diameter (50～80 mm) by adopting original-creation crucible dropping method and obtained macroscopic and entire crystal with no core, no stripe, no cracking and no scattering. They also made high-frequency SAW resonator filter with plane photo etching technique (stripping method) [1].

In short, $Li_2B_4O_7$ is kind of piezo-electric crystal materials which has large-market application potentially. Further work need to be undertaken to develop and study the crystal.

2. Preparation of starting materials

H_3BO_3 and Li_2CO_3 were melted in a Pt crucible with dimension of 80×60 mmϕ. Both H_3BO_3 and Li_2CO_3 are anglytical pure. Excessive (0.5～1.2) B_2O_3 was added because of the great composition difference between consistent melting composition and chemical composition. It is considered that the optimization of H_3BO_3 content is 0.8 mol% excessive. Twice melting technique was used to avoid volume sharp expanding during melting. The melt of H_3BO_3 and Li_2CO_3 was kept at T_m for a specific time to reduce gas content inside melt for H_2O and

CO_2 volalilizing completely.

3. LBO crystal growth

3.1. Growth method

Crystal growth was in a single crystal stove with Pt crucible by using resistance heating Cz method. Pulling and rotation controlling device is equiped with WCK781 temperature program controller and DWK-702 temperature precise controller to dominate the problems of crystal rotation rate, pulling rate and equal diameter.

3.2. Growth technical parameters and their choices

3.2.1. growth technical parameters

The vertical temperature gradient above liquid surface in 5℃/mm, pulling rate is 0.3～1 mm/hr, rotation rate is 5～10 r/min, the rate of dropping temperature must be slow.

3.2.2. the choice of growth technical parameters

Because of high η melt and little convection and little conduction, crystal grows hardly and the melt changes into glassical state in the temperature field of no or little temperature gradient. If it is little convection and difficult impurities, the defects of components supercooling, inclusion and cloud layer will be easily occured. These macroscopic defects will be difficultly cleaned, even by changing crystal rotation rate and pulling rate.

In order to decrease η of melt and increase convection, crystal was produced large temperature field gradient which effectively restrain the macroscopic defects owing to supercooling segregation by using quicker rotation rate. It is an important character that a large temperature gradient was given during the designation of temperature field.

4. Properties and their comparations of LBO crystal

4.1. The macroscopic properties

Through installing reasonable temperature field (adjusting the corresponding positions of crucible and heater, designing fit-shape keeping-temperature device and part-cooling seed, etc) and optimizing technical parameters (little pulling rate, large gradient because of high η of the melt, the rotation rate should be increased and the cooling rate should be reduced to a permitting extent). The defects of crystal spinodal, cracking, cloud layer, circle-shape layer and scattering grains can be removed by

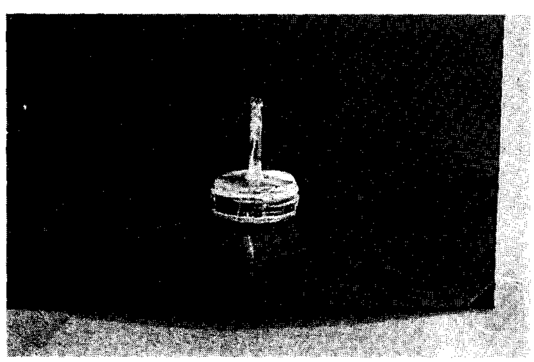

Fig. 1. $Li_2B_4O_7$ crystal.

taking the measurement mentioned above. The crystal with dimension 32 mmϕ × 30 mm^3 and core-shape defect < 1 mmϕ were produced. See Fig. 1.

4.2. The comparation of LBO crystal properties

The properties parameters of crystal are consistent to those of reported in China. See Table 1. The property of cutting treatment is good and these properties have been being up to the advanced level in China. LBO crystal are made up into resonator and press-controlled oscillator, whose properties are stable by measurement. LBO is fit to be made up into wide-band device. The comparation of device properties see Table 2 and Table 3.

4.3. Analysis of macroscopic defects of crystal

4.3.1. core

One of the most serious defects is core which is easily formed along the growth direction in the center of crystal rotation. The formation of core mainly originates from gases contained in the materials and impurities gathering caused by components deviation. The starting materials were not treated properly, the core formed in the initial period of crystal growth usually is a windpipe in shape. But in later stage, the formed core exists as deviated component melt and gathered impurities because of gathered impurities and components deviation. When there appears defect of cloud layer in crystal, the core became thicker and more and more serious in later growth period.

The gases in materials come mainly from the undecomposed H_2O and CO_2. Components deviation is caused by inequitably volatilizing of components in the melt at crystal growth stage. It was proved that the volatilization of B is more than that of Li by analysis. This caused the longer crystal growth period, the more serious melting components deviation, then the more serious, the core was formed. The parts of transparent-loss consists of $Li_2B_4O_7$ phase and $2Li_2O \cdot 5H_2O$ phase. It can be seen that the part of transparent-loss is the result of components deviation [2].

The formation of thin central core is not only caused by impurities. It is well know from fluid dynamics theory that the form of fluid movement is another important factor. Bacause of high-η $Li_2B_4O_7$ melt. The rotation rate can be increased to a permitted extent in order to recude core forming.

4.3.2. cloud layer

There is defect of cloud layer shape on crystal surface and inside crystal. These are mainly glassy body and incomplete crystallizing substance. Because melt viscosity η is high and convection is slow and solute diffuse slow, a thicker supercooling solute boundary layer was formed during the crystal growth. In this case, crystal is coexisting substance which is made up of stable crystallizing phase and metastable-state supercooling phase. The supercooling phase macrscopically appears as cloud layer.

It is found that releasing shoulder rate, temperature gradient, temperature fluctation and mechanical vibration are all related to cloud later. The quicker the shoulder is released, the

Table 1

The elastic and piezo-electric properties of LBO crystal

Parameter	Unit	Chang chun	Beijing	1426 Inst.	Japan
Elastic parameters (×10 n/m)	C^E_{11}	12.8	12.6	13.3	13.5
	C^E_{12}	0.39	0.361	0.38	0.357
	C^E_{13}	2.95	3.64	3.10	3.53
	C^E_{33}	5.40	5.30	5.46	5.68
	C^E_{44}	5.81	5.88	5.77	5.85
	C^E_{66}	4.76	4.20	4.77	4.67
P-e coeff. (c/m^2)	C^E_{15}	0.48	0.473	0.47	0.472
	C^E_{31}	0.23	0.291	0.250	0.290
	C^E_{33}	0.9	0.931	0.870	0.928
Geometric size (mm^3)		$\phi 32 \times 30$	$\phi 25 \times 30$	$\phi 32 \times 35$	$\phi 50 \times 100$

Table 2

Properties comparation of $Li_2B_4O_7$ and quartz resonators

Crystal resonator parameters		LBO	Quartz
f_s	series resonator (MHz)	22.817	25.29
f_P	parallel resonator (MHz)	23.278	25.34
R	dynamic resistance (Ω)	7.5	12.1
C_0/C	ratio of static to dynamic resistance	24.7	22.86
C_0	static capacity (pF)	2.6	4.8
Q	Q value	8860	24100
K^2_S	e-m coupling coefficient	0.0478	0.00486

Table 3

Properties of LBO crystal filter

f_0 (MHz)	3dB band-wideness (kHz)	Pass-band fluctuation (dB)	Inlay loss (dB)	Stop-band decay (dB)	Rectangle coefficient	Inport and export impedance (kΩ)
10.7	108	0	0	50	3.6	1.2

more serious the cloud layer is. The slower shoulder is released, the less the cloud layer is. Thus strictly controlling the time of releasing shoulder can effectively avoid components supercooling and get rid of cloud layer and supercooling cycle. Finally the high quality crystal will be obtained grow. Meanwhile, large temperature fluctuation and mechanical vibration can produce glassy body and incomplete crystallizing substance and form defect of cloud layer.

4.3.3. crystal cracking

In the entire crystal growth period, it is an important property of large temperature dropping. This will cause over large thermal stress and destory the perfection of crystal. The most serious situation is crystal cracking. It needs to drop temperature gradient above S-L interface by bettering temperature field. For large-size crystal, there is a relation between the maximum temperature rate and crystal radius.

$$\left(\frac{dT}{dt}\right)_{max} = 4\sqrt{2}\ \varepsilon cK/\alpha R$$

note : dropping temprature rate must be slow in order to reduce thermal stress and improve crystal perfection [3].

Moveover, structure and defect stress caused impurities gathering also have effect on crystal cracking. This requests to resolve the problems about purity of starting materials and volatilization of different components in crystal growth period.

5. Applications of $Li_2B_4O_7$ crystal

5.1. $Li_2B_4O_7$ crystal resonator

This kind of $Li_2B_4O_7$ crystal has high electro-mechanical coupling coefficient and good property of mechanical cutting. Its Moh's hardness is 6 and it is more soft than quartz crystal (Moh's hardness is 7). It can be conveniently made up into resonator. Its manufactural technique is basically similar to quartz's.

Directional cutting → grinding → cleaning → being polarized with electricity → stalling frame → adjusting frequency → sealing.

The crystal is easily dissolved in acid. The dissolvent rate in concentrated HNO_3 is 1 μm/min, so it should be avoided acid solution in treating process. The comparation about results of $Li_2B_4O_7$ crystal resonator properties and those of quartz resonator see Table 2 [4].

From Table 2, it is found that the electromechanical coupling coefficient of $Li_2B_4O_7$ crystal resonator is approximately ten times over that of quartz. Thus the crystal is fit for being made up into wide-frequency band device, for example, filter and press-controlled oscillator which has wide adjusting-frequency extent.

The frequency-temperature property of $Li_2B_4O_7$ crystal resonator is parabola in shape and the temperature of transition point is at room temperature, i.e., -10℃~55℃, the change of frequency-spectrum responding. The undesired frequency is 180 kHz higer than the frequency of main oscillation and the wane is more than 30 dB. All these can satisfy requirments.

5.2. The properties of $Li_2B_4O_7$ crystal resonator

Table 4
The adjustment of $Li_2B_4O_7$ crystal press-controlled oscillator

Parameters	Values							
Voltage(V)	0	1	2	3	4	5	6	7
f (MHz)	22.654	22.676	22.693	22.708	22.723	22.740	22.762	22.796

At present, wide-band crystal filter is usually made of quartz filter added widened coil. It is no doubt that adding widened coil will affect the entire properties of resonator. Making use of the high electric mechanical coupling coefficient of $Li_2B_4O_7$ crystal, we have produced wide-band crystal filter of stable properties and little loss insertion. Adopted electric circuit is differential bridge circuit added no widened coil. Table 3 is property norms of $Li_2B_4O_7$ crystal filter.

It is no difficuty to be seen that the corresponding wildness of 3 dB band wideness about $Li_2B_4O_7$ crystal filter is 1 %, which (The maximum value is 0.4 %) is much larger than that of quartz [5].

5.3. $Li_2B_4O_7$ crystal press-controlled oscillator

$Li_2B_4O_7$ crystal press-controlled oscillator was produced which has wide adjusted-frequency extent by taking advantage of high electromechanial coupling coefficient of $Li_2B_4O_7$ crystal. Table 4 is the result of measurement. The adjustment is 0.47 %, which is ten times over that of quartz crystal press-controlled resonator (adjustment is 0.04 %).

From the explaination above, we can see that crystal is a good material to make wide-frequency band and low-loss crystal device. Though the property of $Li_2B_4O_7$ temperature is not better than that of quartz, it can satisfy the requirments of average device. If the temperature-compensated device is used and constant-temperature device is added, the temperature property will be good. Meanwhile, the applications rely on improvement of the crystal properties.

6. Results

1. The purity of starting material in crystal growth process are very important. The problem of starting materials volume sharply expanding was solved by using special technique.
2. Adopting large temperature gradient and quick rotation rate can effectively restrain the problem of supercooling segregation.
3. The crystal is a new type of piezo-electric material.
4. From now then, we will reinforce the controlling equal diameter, produce large and good LBO crystal and develop thermodynamics and dynamics of crystal growth under high-η melt besides application and exploitation.

References

[1] Jinghe Liu, *et al.*, the Polycrystal Material Preparation and Single Crystal Growth of LBO, 1989(8).

[2] D.S. Robertson and I.M. Young, Journal of Material Science 17 (1982) 1729.

[3] Yanning Zheng and Yadong Zhou, The Rotation Choice of $Li_2B_4O_7$ Single Crystal Growth by Pulling Method, Artificial Crystal Letter, Vol. 120, No. 3-4, (1991).

[4] Fanshiji Macro Perfection Growth of Lithium Tetrabrate Crystal is Three Inch Diameter, Journal of Synthetic Crystal, Vol. 120, No. 3-4 (1991).

[5] J.D. Garrett, M.N. Iyer and J.E. Greedan, J. Crystal Growth 41 (1977) 225.