RYD 7152-EE-01

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LANGASITE CRYSTALS GROWTH WITH QUALITY FACTOR Q, THAT EXCEEDS THE Q OF QUARTZ, AND WHICH ARE SUITABLE FOR HIGH-PRECISION RESONATORS

Final Technical Report

by

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March 1995

United States Army
EUROPEAN RESEARCH OFFICE OF THE U.S.ARMY
London England
CONTRACT NUMBER N 68171-94-C-9004
NAVAL REGIONAL CONTRACTING CENTER
DEPARTMENT LONDON BLOCK2, WING II
DoE COMPLEX, EASTCOTE ROAD
RUISLIP, MIDDX, HA4 8BS

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31st March 95	Final 16 Dec.94- 31Mar.95

4. TITLE AND SUBTITLE Langasite crystals growth with quality factor Q, that exceeds the Q of quartz, and which are suitable for high-precision resonators

5. FUNDING NUMBERS
C
N 6817194C9004

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

LANTAN
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8. PERFORMING ORGANIZATION REPORT NUMBER
Final report

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
NAVAL REGIONAL CONTRACTING CENTER
DETACHMENT LONDON, BLOCK 2, WING 11
DoE COMPLEX, EASTCOTE ROAD
RUISLIP, MIDDX, HA4 8BS

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Processes of langasite crystal growth are considered. Distribution of temperature fields, heat assembley design, pulling and rotation rates are optimized. Composition of charge, impurity content and technology of its manufacture have been studied. Influence of annealing regimes and gaseous medium on crystal quality are discussed. The main defect types encountering in crystals are identified. Langasite resonator at 5 MHz, 3rd overtone has been developed.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Langasite, crystal, charge, defect, resonator, quality factor	24
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

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INTRODUCTION

Gallosilicate of lanthanum ($La_3Ga_5SiO_{14}$) is a promising material for piezoelectric engineering, because it possesses unique piezoelectric parameters: wide resonance spacing, small dielectric permeability, temperature-compensated cuts, good resonance frequency vs temperature stability, phase transitions are absent in it up to the melting temperature.

The purpose of this contract was to work out in detail technological regimes of growing up high-quality langasite crystals aimed at manufacturing langasite resonators having a Q-factor comparable with that of quartz crystal units.

For this aim the influence of the following technological processes on crystal quality was investigated: temperature field distribution for heat assembly optimization, technological parameters of growth process (pulling and rotation rates), gaseous medium, annealing regimes, initial charge components and improvement of synthesis technology.

Chemical etch method was used for detection and identification of main defect types occurring in LGS-crystal structure.

The influence of elementary cell parameter deviations on Q-factor was studied. For resonator manufacturing from "as grown" langasite crystals a suitable resonator design was selected, technological processes of cutting, lapping and polishing crystal elements, their metallization and mounting.

INVESTIGATION OF TECHNOLOGICAL REGIMES INFLUENCE ON CRYSTAL QUALITY

Optimization of heat assembly design

For optimization of the heat assembly design we investigated the influence of temperature field distributions on the crystal quality. Five crystals have been grown up at different values of axial temperature gradient above the melt ranging from 8 to 40 ^{o}C/cm, with constant values of rotation and pulling rates.

Axial gradient variation was attained by design variations of upper heat assembly part, consisting of platinum and ceramic screens (Fig. 1). Crystals grown with axial temperature gradients over the melt above 40 ^{o}C/cm contained macroblocs, within 20-40 ^{o}C/cm they cracked during cutting. On the contrary with low gradient values, < 8 ^{o}C/cm, the crystal quality drastically deteriorated, supposedly due to a bad convection. Axial temperature gradient of 15-20 ^{o}C/cm turned out to be optimum for this design, but we did not manage to make significant improvement to the crystal quality.

Radial gradient was varied by changing low part of the heat assembly, consisting of ceramic segments, cylinders and rings. We could not increase radial gradients considerably, because under such high temperatures a danger exists of local platinum crucible overheating, which could cause its destruction. Due to technical complexity we could not determine quantitatively radial temperature gradientes, therefore their evaluation was made by quality of grown crystals.

Two crystal growth runs have been made aimed at investigation of radial gradient influence on the crystal quality, one of them has been carried out using Ir-crucible. The quality of the last crystal was slightly better, but many Ir-inclusions were present in the crystal.

However, a non-homogeneous stressed region was present, which was narrower than in the preceding experiments. We could not remove this defect completely and think that the number of experiments was insufficient for complete investigation of the problem.

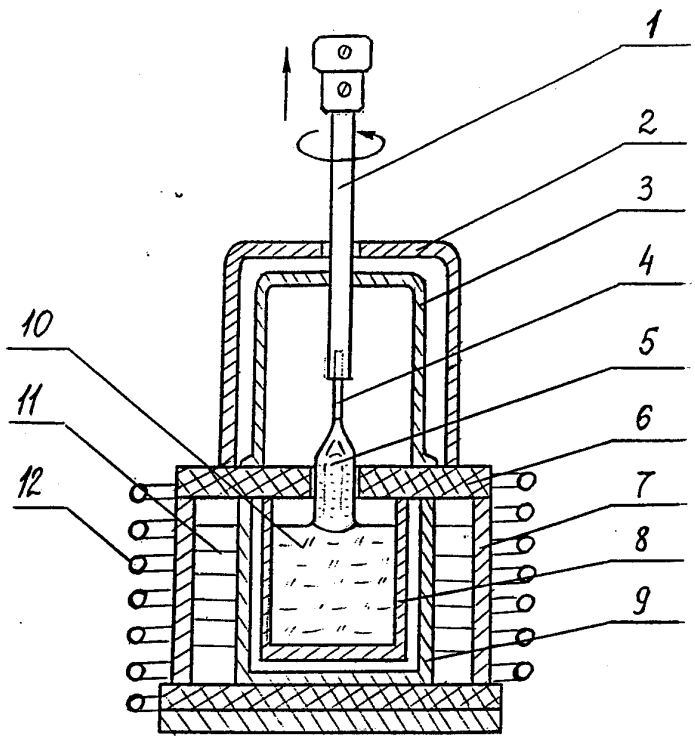

Fig. 1 Heat assembly design

1 - platinum holdes;
2 - ceramic screan;
3 - platinum screen;
4 - seed;
5 - crystal;
6 - ceramic Al_2O_3 ring;
7 - reramic Al_2O_3 screen;
8 - platinum crucible;
9 - ceramic shell;
10 - melt;
11 - heat isolating;
12 - inductor

Optimization of pulling and rotation rates

Initially, we have grown langasite crystals with the pulling rate of V=3-3.5 mm/h, the rotation rate being ω =21 rev/min. However, under these conditions "as grown" crystal were stressed, had a considerable impurity content and a pronounced microblock structure. Therefore, we have lowered the pulling rate up to 1.5-2 mm/h. With lower rates the crystal quality did not change, and the process became less productive.

Pulling rate change in crystals caused the necessity of rotation rate change for keeping crystallization front shape. Therefore for pulling rate V=1.5-2 mm/h new values of rotation rate have been selected. With these pulling rates, the permissible rotation rate range turned out to be narrower than with V=3 mm/h. For example, with the rotation rate ω =17 rev/min the crystallization front is flat, but the grown up crystals had non-homogeneous stressed region. Besides of this with ω =16 rev/min a growth column appeared. With ω=18 rev/min the crystallization front became already strongly concave which contributed to impurity trapping increase in crystals and a strongly stressed centre was observed in them. Hence, pulling rate and, subsequently, rotation rate reducing allowed us to limit impurity content in crystals by 1.5 times (see table 5) and to reduce both microblock structure and elementary cell parameter spread. However, this did not help to remove the central non-homogeneous stressed region.

For improving conical crystal part we have also selected rotation rates at the cone. With ω =16-18 rev/min the cone grows in the preinversion regime and has a large number of bubble inclusions in it, which can be inherited by the growing cylindrical part of crystal. For suppression of natural convection the growth of crystal began with higher rotation rate (21 rev/min) , which then gradually lowered along the cone length. This enabled us to remove bubble inclusions (knags) from the cone, while the growth column remained within the area of the conical part (Fig. 2). All this had no influence on non-homogeneously stressed region. Therefore the influence of additional crystal annealing was investigated.

Annealing process influence

At the initial stage of investigations "as grown" crystals were annealed in a crystallization chamber with the exposure at t=1200 °C, the time of exposure being 10-12 h, and the cooling rate 50 °C/h.

This was, however, insufficient because an inductor with a special turn for annealing was absent and crystals could crack during cutting. We performed additional annealing in a muffle furnace in the air atmosphere at different temperatures of exposure within the range from 1100 °C to 1350 °C, the time of exposure being 12 h. Annealed crystals were then cooled with the rate of 25-40 °C/h. The best results have been obtained at the temperatures of 1300-1350 °C. Crystals, annealed under these conditions, have shown a more pronounced pattern in crossed polaroids and even crystals with strong stresses did not crack during cutting.

Crystals annealed at t>1100 °C changed their colour (rose shade disappeared) and became yellower. This fact has been fixed during absorption spectrum measurement by using spectrophotometer over the wavelength range of 350-2400 nm (Fig. 3,4)

As one can see from the figure, absorption over the range of 800-2400 nm is absent. The crystal color is caused by absorption in the visible region of the spectrum (400-700 nm before annealing and 400-600 nm after annealing). However, the high-temperature annealing did not allow us to reduce significantly non-homogeneous stressed region available in crystals.

Effects of gaseous medium

At the synthesis and charge melting stages the dissociation - evaporation process of Ga_2O_3 and platinum oxidation proceeds in accordance with reaction equations:

$$Ga_2O_3 = Ga_2O + 2O$$

$$Pt + O_2 = Pt\,O_2$$

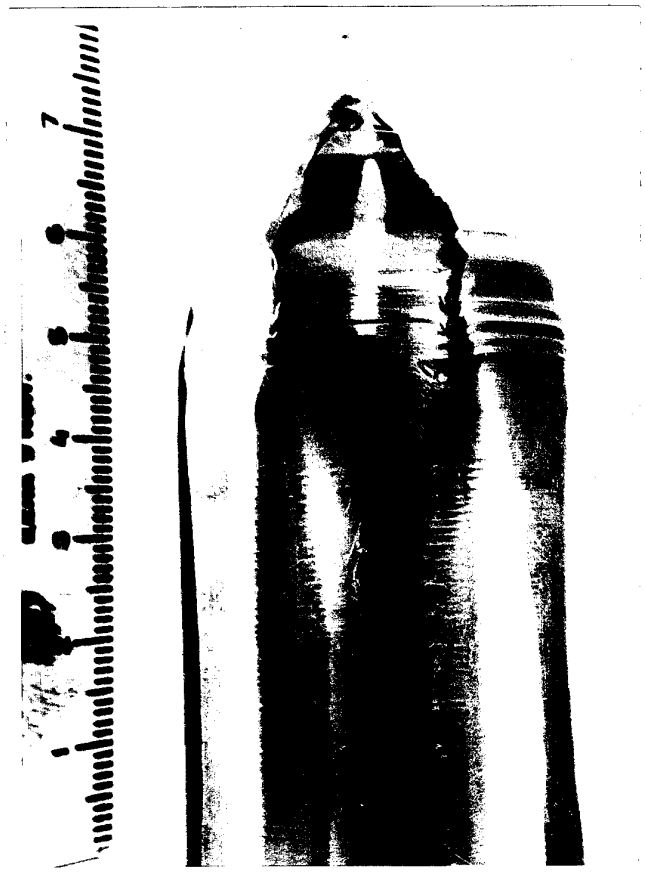

Fig. 2. Growth column within the area of the conical part of crystal

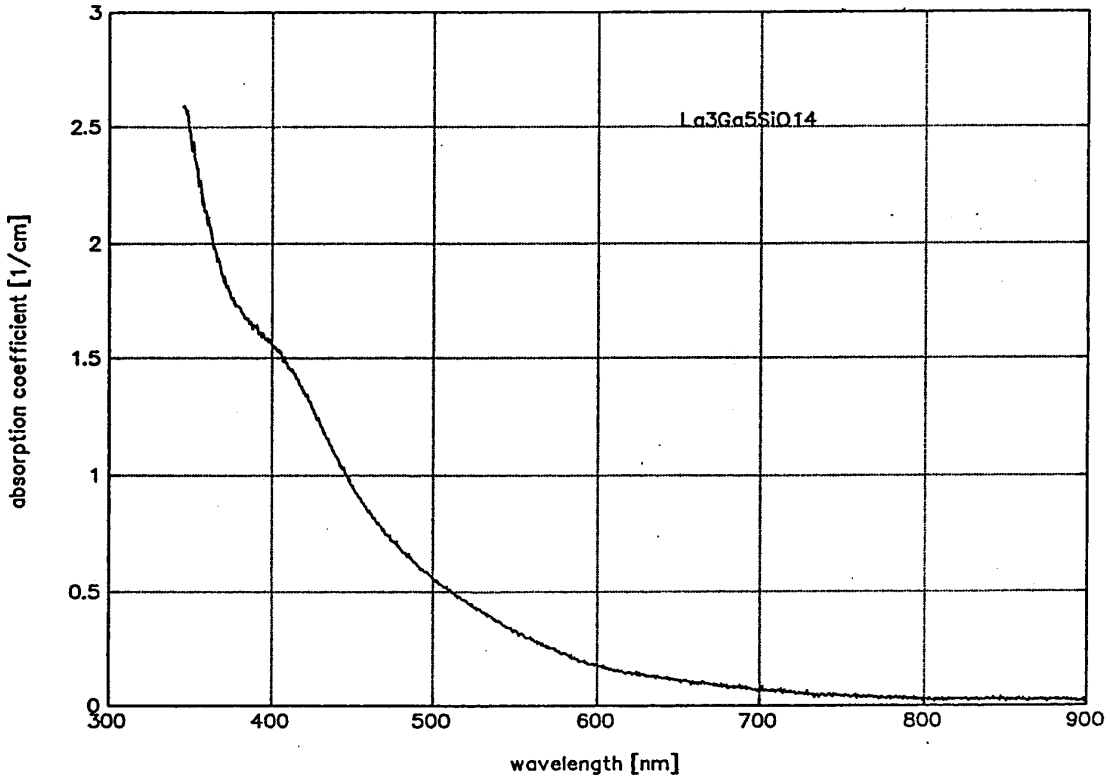

Fig. 3. Absorption spectrum measurement over the wavelenght range of 350-2400 nm before annealing

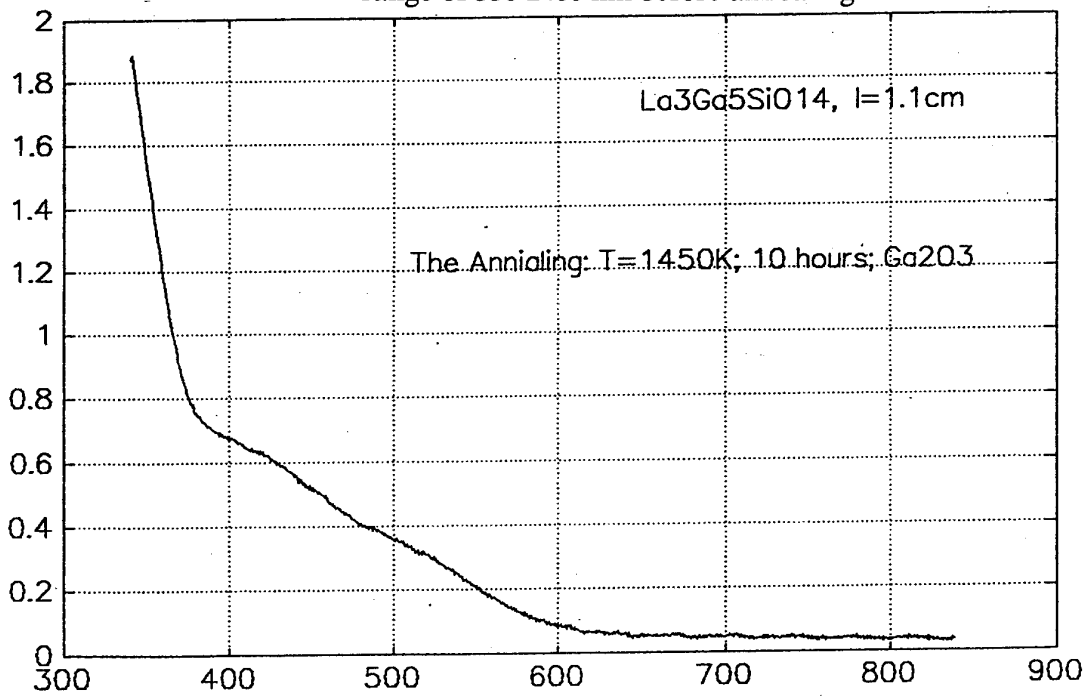

Fig. 4. Absorption spectrum measurement over the wavelenght range of 350-2400 nm after annealing

In order to move equilibrium process to the left, i.e. to reduce gallium oxide evaporation and platinum oxidation, we have used an inert atmosphere at the stage of synthesis and charge melting. Two crystal growth run have been made. Crystals grown up under these conditions had a more pale color. The minimum evaporation of gallium oxide has been obtained in the inert atmosphere of nitrogen with the additive of 2-5 % of oxygen. However, no significant influence on the quality and Q-factor of crystals has been noficed at this stage of investigation.

Influence of purity and quality of initial materials

For charge obtaining we have used the following reactives as initial materials: lanthanum oxide (La_2O_3) with the purity of 99.9%, silicium oxide (SiO_2) - 99.9% and gallium oxide (Ga_2O_3) - 99.9%. The impurity contents in these reactives are given in tables 1,2,3.

Table 1

Impurity in lanthanum oxide reactive (*)

Impurity designation	Mass percent (not over)
CeO_2	0.001
Pr_2O_3	0.0005
V	0.00005
Fe	0.0001
Ca	0.01
Co	0.00003
Mn	0.00005
Cu	0.00001
Ni	0.00005
Ti	0.00005
Cr	0.00001

Table 2
Impurity content in silicium oxide reactive (*)

Impurity designation	Mass percent (not over)
Weight losses after annealing	1.5
Non-volative substances with HF	0.2
NO_3	0.002
Fe	0.002
Cl	0.002
SO_4	0.001
Pb	0.003

Table 3
Impurity content in gallium oxide reactive (*)

Impurity designation	Mass percent (not over)
NO_3	$5x10^{-3}$
SO_4	$5x10^{-3}$
Cl	$5x10^{-3}$
Al	$5x10^{-4}$
Fe	$5x10^{-4}$
In	$1x10^{-4}$
Co	$1x10^{-4}$
Cd	$5x10^{-5}$
Mn	$1x10^{-4}$
Cu	$1x10^{-4}$
Ni	$1x10^{-4}$
Sn	$1x10^{-4}$
P	$1x10^{-4}$
Ag	$5x10^{-5}$
Cr	$1x10^{-4}$

(*) As specified by the manufacturer

The quality of charge components was calculated by reaction equation

$$3La_2O_3 + 5Ga_2O_3 + 2SiO_2 => 2La_3Ga_5SiO_{14}$$

The reactives have been preliminary annealed in a muffle furnace at the temperature of 1000 °C up to a constant weight. Weight losses obtained are given in table 4.

Table 4

Reactives used, volatile components content in them (Δ) and annealing temperature

Reactive	Δ	t, °C
Ga_2O_3	0.0040	1000
La_2O_3	0.0750	1000
SiO_2	0.0200	1000

Calculation of each charge component weight has been made taking into account weight losses.

After annealing, the reactives were weighted by using a balance with the accuracy of 0.01 g, placed in a glass container and mixed in a roll mill during 24 hours with a periodic shaking.

The charge was then placed into a platinum crucible for melting it into inductor of the station "Kristall" at the temperature of 1470 °C. Charge synthesis was effected directly in the melt, for which the melt was held in the atmosphere of pure nitrogen during 4-6 hours at a temperature, which was 20 °C higher than the melting temperature. The temperature was then lowered and the seeding process began. Crystals have been grown by using constant technological regimes.

"As grown" crystals were tested for the impurity content. The nature of impurity distribution in the crystal was investigated. Impurity quantity was determined by direct atomic-emission analysis and spectrum excitation in d.c. arc with recording by DCC-8 spectrometer with the reticule of 600 lines/mm. Table 5 gives the data on impurity content in the melt before growth (Sample № 1), after the growth (Sample № 2) and in two crystal samples grown up from this melt (Samples № 3, 4)

Table 5

Investigation results for impurity content in the melt and in LGS-crystals

Impurity	Sample № 1	Sample № 2	Sample № 3	Sample № 4
Al_2O_3	2.8×10^{-2}	5.7×10^{-2}	2×10^{-2}	5.5×10^{-3}
TiO_2	1.4×10^{-3}	2.2×10^{-3}	1.4×10^{-4}	1.7×10^{-4}
Fe_2O_3	8.4×10^{-3}	1.7×10^{-2}	3.2×10^{-3}	2.2×10^{-3}
CaO	5.6×10^{-3}	8.4×10^{-3}	1.4×10^{-3}	$< 1.4\times10^{-3}$
CeO_2	$< 1\times10^{-2}$	$< 1\times10^{-2}$	$< 1\times10^{-2}$	$< 1\times10^{-2}$
PtO_2	$< 3\times10^{-4}$	$< 3\times10^{-4}$	$< 3\times10^{-4}$	$< 3\times10^{-4}$

As one can see from the data listed in the table, the impurities are being concentrated in the melt during the growth process (ferrum oxide content increases two times, especially). Apparently, due to this the rests of the melt used have a dark brown color. Samples № 3 and № 4 differed by the pulling rate: 3 and 1.5 mm/h, respectively. As it is evident, sample № 4 has a lesser impurity content. Judging by the results obtained, the impurity distribution coefficients for sample № 4 are the following:

$K_{Al_2O_3} = 0.196$ $K_{TiO_2} = 0.121$ $K_{Fe_2O_3} = 0.262$

5 MHz resonators have been fabricated from samples № 3 and № 4 by using technological process and design described below. The quality factor Q of resonators fabricated from sample № 3 did not exceed $(12\text{-}15)\text{x}10^3$, and the quality factor Q of resonator fabricated from sample № 4 was $(25\text{-}30)\text{x}10^3$.

Crystals grown during the last five runs were tested for their general composition by using spectrophotometer Link 10000 and impurity content by Camebax SX-50.

The following results have been obtained:

A. The impurity content in crystals was the following:

Al < 0.015 % weight
Zr < 0.01%
Fe < 0.01 - 0.0005 %
Ce was not observed
Nd < 0.005 %
Pt < 0.003 %

B. Crystals grown up from the charge of stoichiometric composition can differ considerably from the stoichiometry of the composition. It was discovered that langasite has a sufficiently wide region of homogeneity. For example, a single crystal of composition $La_{3.27}Ga_{4.9}Si_{0.87}O_{14}$ has been grown up. This fact explains the existence of non-homogeneous region (Fig. 5). It is caused by impurity phases present in the melt, which are trapped by a growing crystal. This trapping of impurity phases increases at poor melt mixing. It is therefore necessary to test more thoroughly the ratio of components at the stage of charge preparing and after charge melting aimed at melt composition correction. It was observed that during crystal growing from a non-stoichiometric composition (deviation of 3 weight %) concentration of impurity phases in the melt and deterioration of crystal quality, can occur (Table 6).

Table 6

Homogeneity region test results at 1400°C

Composition, mol % La_2O_3 : Ga_2O_3 : SiO_2			Impurity phases
30	50	20	-
28	51.5	20,5	$Ga_2O_3 + La_2Si_2O_7$
29	49	22	$Ga_2O_3 + La_2Si_2O_7$
30	48	22	$La_2Si_2O_7$
31.7	48.3	20	$LaGaO_3 + La_{14}Si_9O_{39}$
30	52	18	$LaGaO_3$

Fig. 5. Central non-homogeneous region in langasite crystals

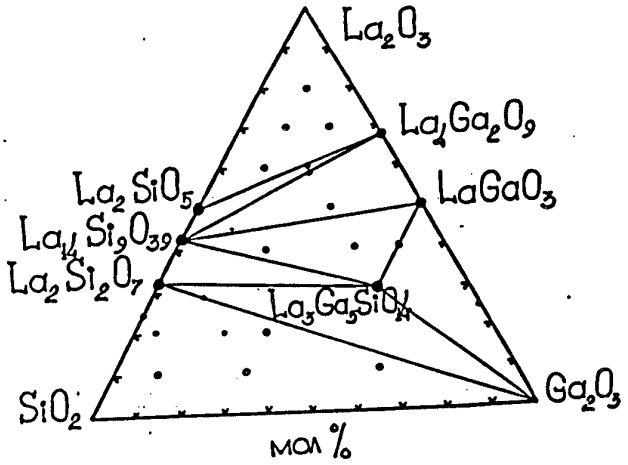

Fig. 6. Phase diagram in the system La_2O_3-Ga_2O_3-SiO_2

These works could not be completed due to a lack of time, because the problem is very broad and no sufficient time was available for its thorough investigation. The study is continuing. It is also necessary to study the influence of deviations from stoichiometric composition on the varation of piezoelectric characteristics of resonators.

C. A new additional crystal phase with greater Ga content has been discovered for the first time. It appears sometimes as a small white thin coating at the crystal surface at a place of tearing off crystal from the melt and is presumably present in the melt. By using Link 10000 instrument, this crystal phase has been identified as $La_{2.56}\ Ga_{5.8}\ Si_{0.72}\ O_{14}$. Up to now langasite was considered to be a unique triple compound in the phase system La_2O_3-Ga_2O_3-SiO_2 (Fig. 6). Therefore, LGS-phase diagramme needs to be investigated in more detail.

We have also tested the charge produced at the plant GIREDMET (Podolsk), obtained by using the method of self-distributing high-temperature synthesis (SHS). The charge has been synthetisized at 15% of metal gallium ignition, contained in the mixture of gallium, silicium and lanthanum oxides. However, it also differed from the stoichiometry in Ga content, its general composition corresponded to the formula $La_{3.05}\ Ga_{4.75}\ Si_{1.18}\ O_{14}$ and it contained a large number of impurities (Fig. 7, 8):

Fe $\approx$ 0.1 % weight
Ca $\approx$ 0.02
Zr $\approx$ 0.01
Y $\approx$ 0.005

Therefore we had refused to use it and began development of our technology with testing at all stages up to growing crystal. We have also refused to use a charge obtained as a result of recrystallization because it is difficult to control stoichiometric composition. Inforfunately, these works are not yet completed.

Determination of main defect types by chemical etch method

For chemical etching the solvents described below were used. Real structure elements - main macro- and microdefects have been identified which can be inherent to langasite crystal [1].

The main macrodefects are:
- sectorial non-homogeneity,
- striation along the crystal length,
- growth column or stressed centre,
- knags and microcracks on the conical part of crystal.

The main microdefects are:
- dislocation slipbands,
- places of dislocation exit at the surface of Y- and Z-cut plates,
- inclined dislocations,
- screw dislocations,
- platinum inclusions,
- point defects.

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[1] A.N. Gotalskaja, D.I. Dresin , G.N. Cherpoukhina, V.V. Bezdelkin, "Aspects of growing langasite crystal and properties", Journal de physique IV, Colloque C2, supplément au Journal de Physique III, Volume 4, février 1994

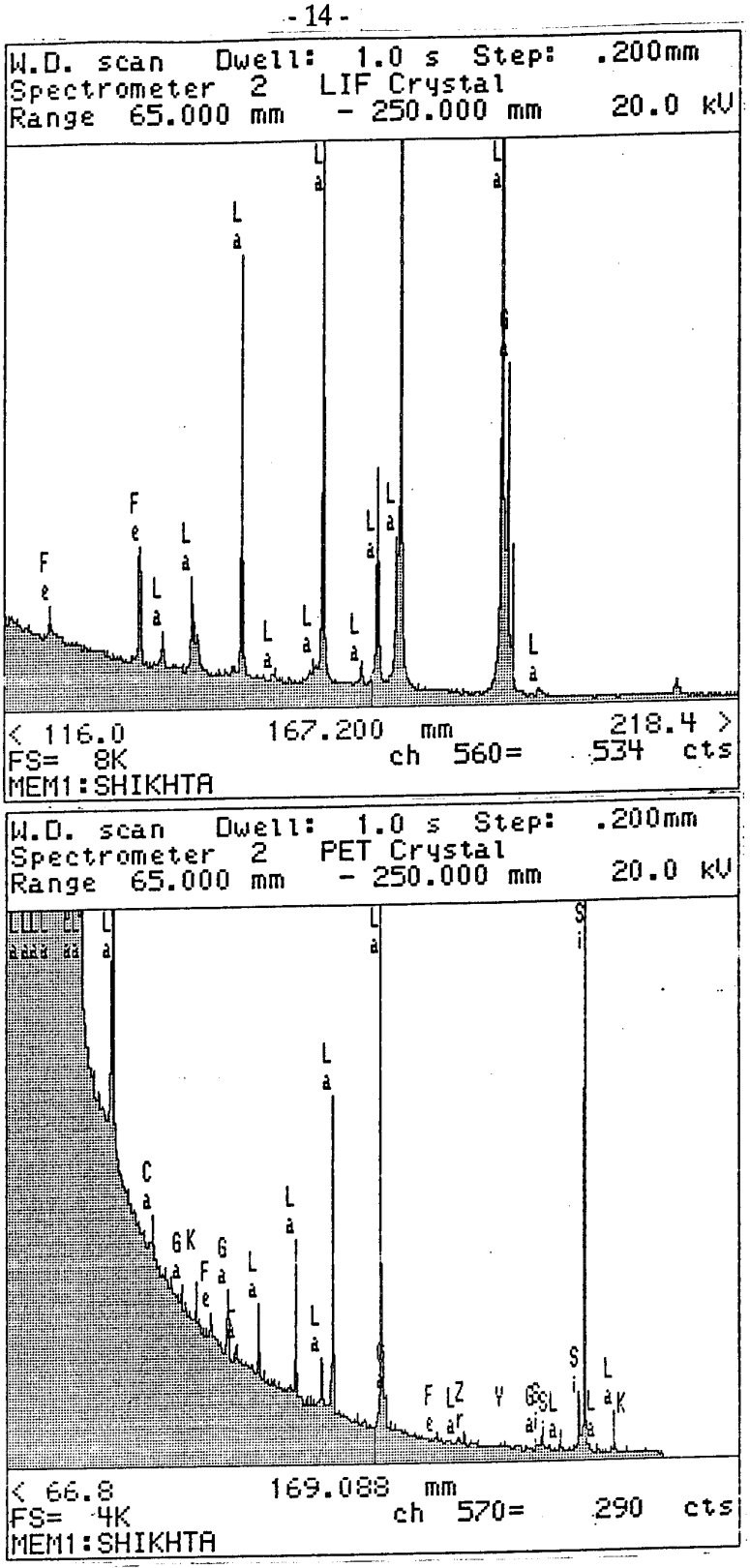


Fig. 7 , 8. Test results the charge produced at the plant GIREDMET (Podolsk)

Elementary cell parameter influence on the quality factor

From crystal grown up under different technological regimes Z-cut plates have been sawn with the thickness of 10 mm and Y- and Z-planes oriented with the accuracy of 10'. Measurements of these parameters have been made by X-ray goniometer "DRON-3". Crystal grown with pulling rates above 3 mm/h had a-parameter — spread of $1x10^{-4}$Å, but greater spread in c-parameter $1x10^{-3}$Å. These c-parameters values increased along the crystal length. Plates cut from less defective regions of crystal grown with pulling rate 1.5-2 mm/h had the following cell parameters:

$a=8.1684\pm1x10^{-4}$Å and $c=5.0975\pm1x10^{-4}$Å.

Resonators have been later manufactured of these plates.

DESIGN AND TECHNOLOGY INVESTIGATIONS OF LANGASITE RESONATORS FOR CRYSTAL MATERIAL QUALITY FACTOR EVALUATION

The parameter most completely characterizing resonator quality is its quality factor Q. We have manufactured evacuated langasite resonators with plano-convex piezoelectric elements of Y-cut operating at 5 MHz, 3rd overtone.

Langasite resonators were manufactured analogously (in technology) to precision quartz crystal units but taking into account langasite features.

Due to drastical difference of langasite from quartz in major physical-chemical properties: hardness, chemical resistance to acids and alkalis, chemical activity of the surface etc., manufacturing processes commonly used for quartz resonators required improvement for langasite resonators taking into account these properties.

Peculiarities of langasite resonator manufacturing technology

Electrical parameters and quality factor Q, in particular, of piezoelectric resonators, depend to a considerable extent on the quality of mechanical surface treatment of crystal elements (CE).

Crystal cutting was carried out by a diamond wheel (with external cutting edge) of 0.6 mm thickness and 100 mm in diameter, the feed force of 2.5-3.5 kg and cutting speed of 5 mm/min in a lubricating-cooling fluid based on kerosene. Non-observance of these regimes causes appearance of deep cracks at the cut crystal surface and does not allow to cut blocks thinner than 3 mm.

Manufacturing process of langasite plates of yxl/ -cut consisted of several stages. First, Z-cut blocks of necessary height were manufactured. Then these blocks were pasted with their basal face at the support and were cut into X-sections of necessary dimensions. Before cutting plates of desired orientation out of X-section, the positive direction of the X-axis was determined in the section. For this purpose the measurement method of direct piezoelectric effect by means of microvoltmeter was used. The positive direction X-axis can be determined by means of X-ray method by the intensity of X-ray beam reflected from 0.1 3 plane or by asterism figures after long-term crystal etching in hydrofluoric acid; these two last methods are more complicated and less productive.

X-ray method of angular parameters control of atomic planes, shown in table 7 for CuK - radiation was used during crystal cutting process.

Table 7

Angular parameters of langasite atomic planes measured by X-ray method

Cut	Atomic plane indices, hkl	Detector angle	Sample angle
X	11.0	21°45'	$g_1=g_2+g_3+g_4=-2°27'$
Y	02.0	25°08'	$g_1+g_2+g_3=g_4=21°08'$
Z	00.2	35°12'	$g_1=G_2+g_3+g_4=4°17'$
yxl/+4°	02.0	25°08'	$g_1=-4°44'$ $g_2=3°16$ $g_3=g_4=-0°44'$

Manufacturing accuracy of control cuts was not worse than ±10'

Plates lapping

Technological process of mechanical plate treatment should ensure minimum surface structure destruction.

As it is known, mechanical quartz treatment one can conditionally distinguish in three types of disturbed layers located one under another: the upper one strongly destructed layer with abrasive inclusions, middle destructed layer with microcracks and block structure and weekly disturbed layer with distorted crystal lattice. The depth of each layer is gouverned by preceding ones and depends on the grain size of abrasive powder. Experiments have shown that langasite is more sensitive to mechanical treatment compared to quartz. Table 8 gives results of surface roughness Ra measurements for langasite and quartz after identical mechanical treatment at the flat cast iron disk.

Table 8

Abrasive powder type	Mean grain size of micropowder μm	Mean surface roughness R_a ($R_a \approx 0.2R_z$) Langasite	AT-cut quartz
M28	28-20	0.69	0.28
M14	14-10	0.37	0.18
M10	10-7	0.31	0.14
M7	7-5	0.26	0.12
M5	5-3	0.18	0.10

It is shown that the rate of langasite material removal and the mean surface roughness after lapping is 2-3 times greater compared to quartz.

This peculiarity makes it possible to consider langasite as a softer material compared to quartz. Therefore lapping by micropowders with the grain size M28 and more has not been used for langasite lapping and for complete removal of disturbed layer.

For example, with one-sided lapping of langasite plates by micropowders M14, M10 and M7 the thickness layer to be removed, was 0.25, 0.06 and 0.04 mm, respectively. With double-sided lapping plates with the rate of 80 rev/min and the pressure at the crystal

element of 115 kg/cm^2 by micropowders M7 and M5, the thickness of the layers to be removed was 0.03 and 0.02 mm, respectively, from each side. It was further found that langasite plate lapping should be made at glass disks by micropowder M14 and at brass disks by micropowders M7 and M5.

Crystal element surface polishing

The application of quartz crystal polishing technology with crocus for langasite polishing caused defects at the plate surface which had the appearance of "orange peel". For elimination of this and other defects such as scratches and splits off, the method of asymptotic polishing by means of water slurry of diamond micropowders at a soft polisher were used.

Lapped langasite plates were polished at disks or in brass cups with a soft pasted overlay of felt, analogously those used for SAW substrates polishing. Experimentally chosen polishing regimes enabled us to obtain langasite plate surface with minimum mechanical distortions. Polishing was effected in three ways:

— polishing at a tissue stretched over a glass disk of 150-200 mm in diameter with M3 micropowder by removing not less than 0.03 mm of material from one side, the disk rotation rate being not over 30 rev/min;

— polishing at a coating of felt type with diamond powder ACM 3/2 in the mixture of glycerine, alcohol and water by removing not less than 0.003 mm per one side, and ACM 1/0 in the same mixture — not less than 0.002 mm per one side, the disk rotation rate being not over 30 rev/min.

Chemical etching and cleaning of langasite crystal elements

In the quartz crystal technology chemical etching of crystal elements in water solutions of HF is used for removing abrasive grains, small crystal fragments and other mechanical impregnations originating from the plate lapping and also for removal of plate surfaces, destructed as a result of mechanical treatment.

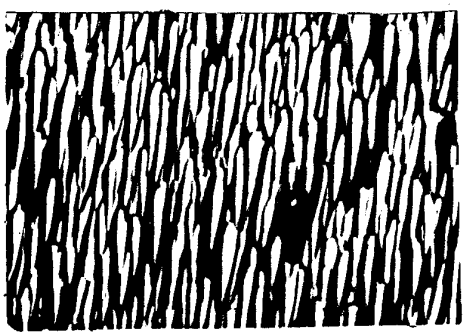
For removal of layer of disturbed by mechanical treatment a method of deep chemical etching to the depth of about 15 μm was used. Chemical etching process of langasite crystal elements is obligatory between lapping and polishing processes. However, the application of quartz etching technology in HF solutions to langasite leads to formation of white loose deposit at its surface, necessitates the use of new etchants.

For choosing possible compositions of etching solutions for langasite it is convenient to consider the langasite as a solid solution of lanthanum — and gallium oxides with the additive of silicium oxide: $3La_2O_3 + 5Ga_2O_3 + 2SiO_2$. It is well known that lanthanum — and gallium oxides are highly reacting and are easily solved in most acids. This circumstance facilitates etching process of langasite plates but causes difficulties during their chemical cleaning. Therefore the chemical etching process is often combined with the process of fine chemical adjustment of crystal element frequency.

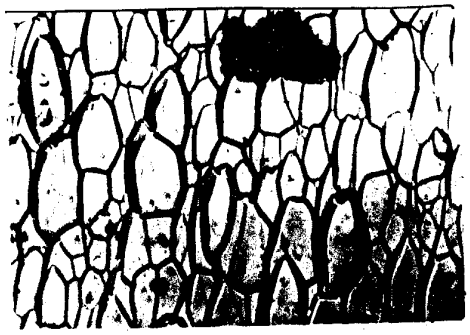
It is also known that lanthanum and gallium salts: fluorides, chlorides, carbonates, phosphates, oxalates etc. are poorly water-soluble and therefore they can form deposits at langasite surface treated by corresponding acids under ordinary conditions. At the same time during treatment of langasite surface by hot acids these deposits are not formed. This allows to consider hydrochloric, nitric and sulfuric acids and their waters solutions as perspective components of etching solvent.

It is obvious that every etching reagent will possess its characteristic features at different temperatures, the most important of which are in our case, etching rate and surface finish (roughness) of plate after etching (Fig.9).

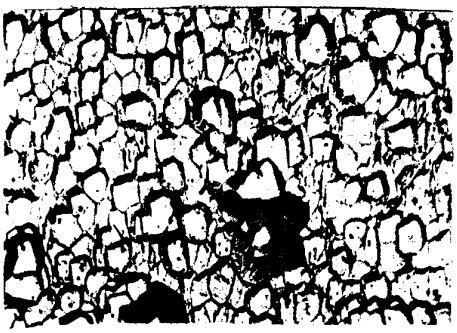
Langasite plates lapped by M10 abrasive were subjected to chemical etching treatment. The calculated value of disturbed surface depth after mechanical treatment of the plate was equal to 15 μm (calculation was made by using the formula



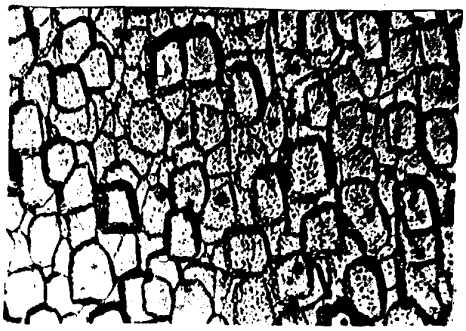
$HNO_3 : H_2O = 1:2$



$HCl : H_2O = 1:2$



$HCl : HNO_3 : H_2SO_4 = 1:1:1$



$HNO_3 : CH_3COOH = 2:3$

$HCl : HNO_3 = 3:1$

$HNO_3 : H_2SO_4 : H_2O = 1:1:1$

Fig. 9 Chemical etch figures of langasite plates obtained in different solutions at temperatures near to boiling point (magnification x 300)

$T_{dish} \approx 5R_y \approx 5R_{pm}$, known for quartz plates). Therefore investigations were carried out by etching off the layer considerably exceeding 15 μm per one side. As etchants hydrofluoric acid (HF) and ammonium bifluorure (NH_4F+HF) commonly used in quartz etching technology have been applied and also solutions based on sulfuric, nitric, hydrochloric, hydrofluoric, oxalic and orthophosphorous acids.

The influence of the these compositions on deposit formation at the plate surface, on etch rate and surface roughness was tested.

The use of HF, H_2SO_4, NH_4F + HF and also of the solution $K_2Cr_2O_7$ in H_2SO_4 for langasite etching causes chemical reaction with lanthanum and gallium and formation of a white deposit at langasite surface. This deposit is easily scraped, by uncovering smooth surface of a langasite plate. For example, langasite etching at the room temperature during 10 min causes formation of non-solid thin deposit layer at the surface of plates. Heating of solution up to 60-80°C causes formation of a thick loose deposit layer at the surface of a plate during the same period of time. These reactions were particularly well observed at the surface of polished plates.

Langasite dissolves in solutions on the basis of HCl, HF and HNO_3 without deposits. This is explained by a good solubility of La- and Ga-fluorides in these acids. Etch rate, surface quality (roughness after etching) and shape of etch figures change depending on the composition and concentration of such solutions.

Most quickly, approximately 2-3 μm/min, langasite dissolves in hot solutions of HCl and in solutions with HF content not over 6-8%. Surface quality of plates becomes worse and microrelief reminds "cobble-stone" structure, which is characteristic for solutions, containing HCl.

Langasite etch rate in HNO_3 is approximately three times less, than in HCl the surface quality degrades considerably less and microrelief reminds narrow long wedges, stretched along the Z-axis. Addition to HNO_3 even of a small quantity of HF leads to formation of a deposit at the crystal plate surface. Addition of HF to HNO_3 causes etch rate increase, but deteriorates the surface quality.

Addition of H_2SO_4 to the compositions described above causes usually microrelief deterioration of the surface. Mixtures of nitric and acetic acids possess polishing properties.

In Table 9 etch rates and surface quality evaluations are given after etching in several solutions in the vicinity of their boiling point.

Table 9

Solution composition	Mean etch rate μm/min	Microrelief better (+) worse (-)
$HCl : H_2O = 1 : 2$	2-3	- -
HCl + 5%HF	5-6	-
$HNO_3 : H_2O = 1:2$	0.6-0.7	+
$HNO_3 : HCL = 1:3$	1-2	-
$HNO_3 : CH_3COOH = 2:1$	0.1-0.2	+ +

For deep etching of langasite resonator elements a water solution of HCl was used at the temperature near to the boiling one. The mixing rate (rotation rate of magazine with crystal elements) was 10-12 rev/min with 3 reverses.

Chemical cleaning before metallization was made in hot 20% KOH solution during 15-20 min. Then resonator elements were treated in ultrasonic installation with hot solution of peroxide-ammoniac and in hot deionized water.

Electrode evaporation

Silver film electrodes of 0.3 μm thickness were vacuum evaporated at a cold substrate. Crystal elements were placed in metal magazines and subjected to preliminary ion cleaning.

Mounting piezoelectric element into package

Langasite piezoelectric elements were mounted into package by two methods: by using conducting glue with temperature stability of 300°C and by sealing. The conductive glue was prepared by using quartz crystal technology. It consisted of 85% of small particle size silver powder and light flux based on 81% PbO+15% H_3BO_3+ 4% SiO_2. Contact firing was effected at a temperature of ≈500 °C during 1-1.5 h. Adhesion strength of the contact was 0.8-1.2 kg at the diameter of 1.2 mm.

Hermetical sealing

Resonators were hermetically sealed in glass enclosure by high-frequency welding method in vacuum with a residual pressure ≈$5x10^{-3}$ mm Hg.

Design of piezoelectric element for langasite resonators

Initial data for the choice of resonator design are operating frequency and maximum permissible diameter of piezoelectric element for a specified package.

Taking into account a substantial difference of langasite frequency coefficient from that of quartz it was impossible to realize PE design recommended by the IEC for quartz. Langasite resonators operating at 5 MHz, 3rd overtone have been manufactured using plano-couvex design represented in Fig. 10, 11. In accordance with the calculated data and frequency coefficient of langasite for PE diameter of 15 mm and the edge height of 0.2-0.3 mm, optimum radius of sphere is 100 mm.

Optimum electrode diameters calculated were taken 5-8 mm. Due to the fact that no reliable theory exists on calculation of single frequency resonators with suppressed anharmonics, samples with different electrode dimensions have been fabricated. Parameter measurements of these resonators allowed us to find out that resonators with electrode diameter of 5 mm have maximum quality factor Q. The main resonator parameters are represented in Table 10 and Fig. 12.

Table 10

Langasite resonator parameters

Resonance frequency f_r (Hz)	5002838
Quality factor Q, 10^3	115
Motional resistance R_1 (Ω)	77.8
Motional inductance L_1 (H)	$2.83x10^{-1}$
Motional capacitance C_1 (pF)	$3.57x10^{-3}$
Static capacitance C_0 (pF)	6.35
Capacitance ratio C_0/C_1	$1.779x10^3$
Dissipation power P_{diss} (μW)	9.92

In spite of the fact that the works on improvement langasite crystal quality are not yet completed, rather good characteristics of langasite resonators have been obtained.

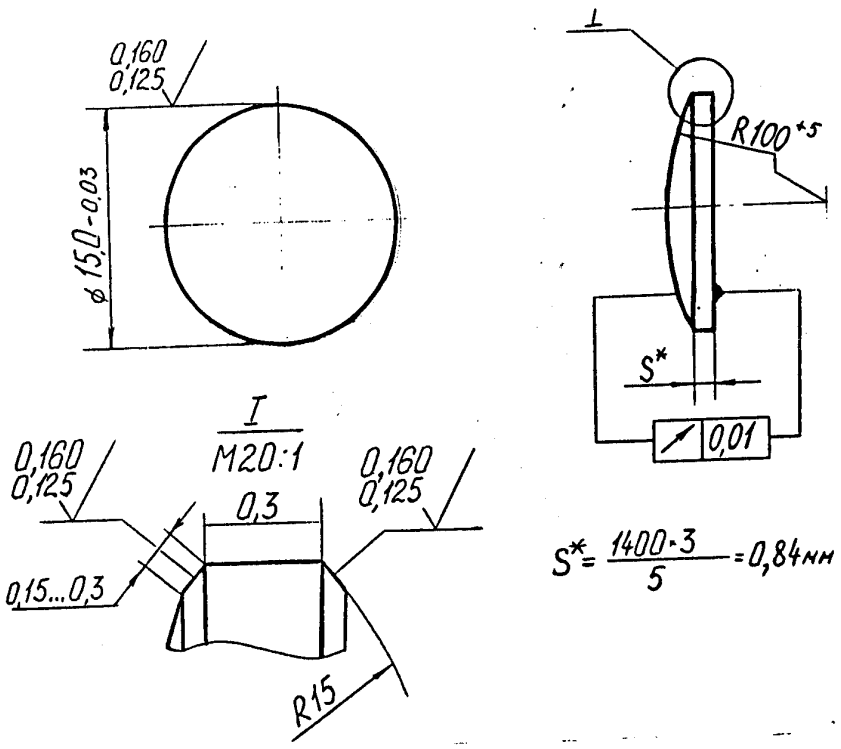


Fig. 10. Geometric dimensions of langasite piezoelectric element for resonator

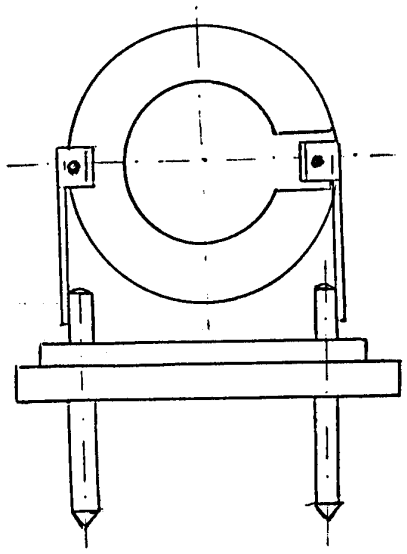


Fig. 11. Langasite resonator assembly

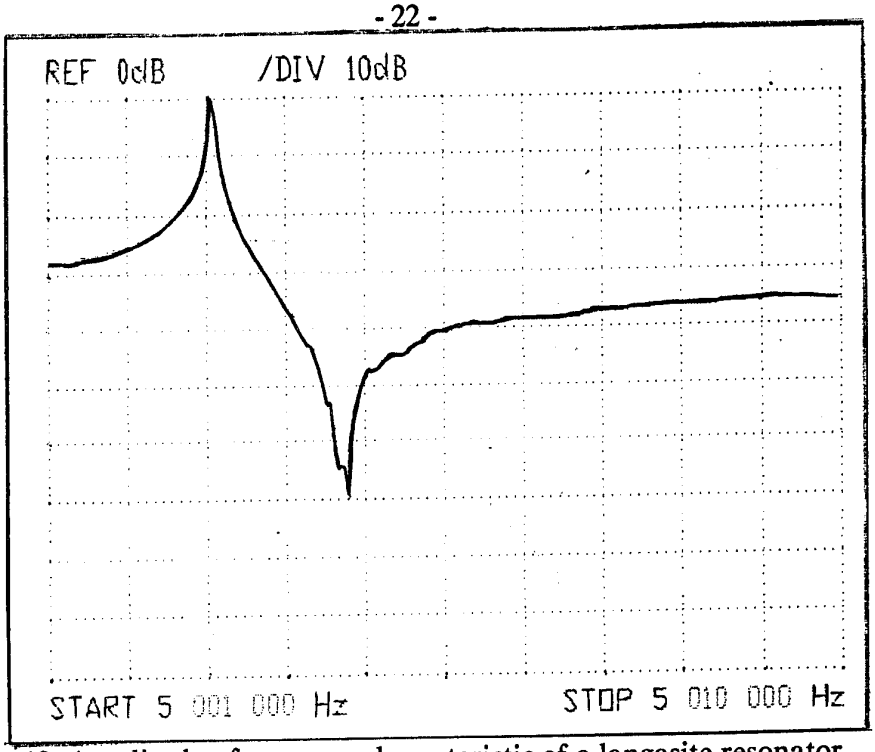


Fig. 12 Amplitude - frequency characterictic of a langasite resonator

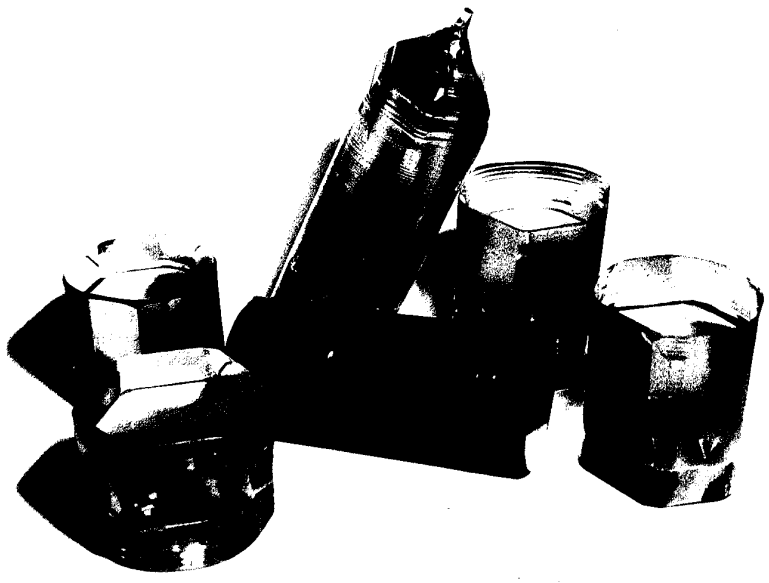


Fig. 13 "As grown" langasite crystals

CONCLUSIONS

In the process of work 28 langasite growth runs have been made. 26 crystals have been grown up, 6 of which have been sent to the U.S.A. Government, the rest — used for investigations (Fig. 13). In the course of the work the following has been made:

1. Distribution of temperature fields vs heat assembly design has been studied. It has been found that optimum values of axial temperature gradient are 15-20°/cm.
2. Optimization of pulling and rotation rates (1.5-2 min/h and 19 rev/min, respectively) has been investigated. Optimization of the rates allowed us to reduce impurity content in crystals by 1.5 times and to reduce c-parameter spread of the crystal lattice.
3. Composition of charge and technology of its manufacturing has been studied. It has been found, that langasite has a wide range of homogeneity. This can cause strong discrepancy from a stoichiometric composition, which requires rigid composition tests at all stages of charge preparing.
4. A new crystal phase of triple composition at the crystal surface has been discovered, which evidences of the necessity to make phase diagram more exact.
5. Crystal annealing regimes have been studied both in the growth and additional annealing processes. It has been found that for eliminating tempering stresses and more regular stress distribution along the crystal radius, this additional annealing process at 1300°C during 10 h is sufficient.
6. It has been found that at this stage of investigations the composition of gaseous medium during the growth process has no influence on the quality factor of resonators.
7. The main defect types of LGS-crystals have been determined and identified.
8. The influence of elementary cell parameters on resonator quality factor has been investigated.
9. Langasite resonator design at 5 MHz, 3rd overtone has been developed. Maximum quality factor Q obtained at this stage of investigation was 1.15×10^5. The works in this area need to be continued, because this Q-value is not a limit one.

In spite of the fact, that it has not been managed to obtain desirable crystal quality at this stage of the work rather high Q-value of langasite resonators is achieved, which evidences of perspectiveness of this material and expediency of its further investigation.

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