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Aspects of growing langasite crystals and their properties

A.N. GOTALSKAJA, D.I. DREZIN, G.N. CHERPOUKHINA, V.V. BEZDELKIN and
S.N. SCHEGOLKOVA

Scientific Research Institute "Fonon", 105023 Moscow, Krasnobogatyrskaya str. 44, Russia

Synthesis technology and growing langasite crystal are described. The real structure and main types of defects are defined. Fundamental physical and piezoelectric properties of langasite in comparison with properties of other piezoelectrics are given. The application of these crystals in resonators and filters is mentioned.

For designing VCXOs, TCXOs and filters with a wide pass band while maintaining high stability and small insertion attenuation of these devices, the necessity arose in discovering new piezoelectric crystals, having intermediate properties between those of quartz and lithium tantalate. They are berlinite and langasite. Growing berlinite crystals and its analogues, however, is connected with technological difficulties and with twinning problem [1]. Technological process of growing langasite crystals is simpler. It is grown up by Czochralsky method in an air atmosphere at a temperature of 1470°C. Langasite has no phase transitions up to the melting point and it does not need monodomenization compared with lithium niobate and lithium tantalate.

Langasite belongs to the group of compositions with the structure of calcium-gallium-germanium garnet (CGGG) and crystallizes in the same acentric group as quartz [2,3]. Langasite crystal is a dielectric.

The purpose of our work was to develop mass production technology of synthesis and growing langasite crystals. Due to design of heat assembly of crystallization chamber we could grow up langasite crystals

with the diagonal diameter of 62 mm and the weight up to 2,0 kg (fig.1). The crystals were grown along the Z-axis by employing equipment with the diameter control with the cylindrical part length up to 150 mm. The crystal yield obtained was 60%.

The charge was prepared from oxides by using solid-state phase reaction via an intermediate composition - perovskite at a temperature of 1300°C . Based on the result obtained by differential thermal gravimetric analysis it was found that langasite phase appears over the temperature range above 1000°C .

The features of langasite crystallization process are dissociation presence and evaporation of gallium oxide, crystallization front (CF) inversion and facial growth.

Gallium oxide evaporation causes distortion of stoichiometric composition of the melt and deterioration of crystal quality. Gallium oxide dissociation contributes to platinum oxidation, its transfer to the melt and entering into the crystal as inclusions.

The most important condition for growing perfect crystals is obtaining a flat crystallisation front. Crystallization front inversion was observed in the process of conical part growth of the crystal. This causes excessive defect formation in the conical part of the crystal. It is recommended to choose such a rotation rate that CF inversion takes place at the end of the conical part formation of a boule.

For langasite crystals a facial growth is characteristic. Crystals grown along the Z-axis have well developed six prism faces at its lateral surface.

It is necessary to consider the real structure and main defect types which can be inherent to a langasite crystal.

1. Sectorial inhomogeneity can occur when the crystallization front constitutes a complicated surface, consisting of regions of normal and of a facial growth. The crystals with sectorial structure showed that facial growth regions have greater elementary cell parameter $\Delta Q = 0,007\text{\AA}$. For this reason residual stress can appear in the crystal.

2. Short-term temperature fluctuations in the vicinity of the CF can cause striation along the crystal length (i.e. regions with different color, refraction index and other characteristics).

3. Langasite crystals grown with low rotation rates have a growth column, a macrodefect, along the crystal, consisting of gaseous

inclusions and microcracks. When natural convection predominates in the melt, voids (knags) can be formed within the conical part of the growing crystal.

The crystallographic investigation results of langasite crystals connected with correction of Wolf-Bragg-angular parameters of atomic planes in this material were also received. The finally obtained parameter values are: $a = 8,1783 \text{ \AA}$ and $c = 5.1014 \text{ \AA}$ [4].

We have studied micro defects of grown langasite crystals by chemical etch method. Structural defects of langasite are: dislocation slipbands, places of dislocation exit at the surface of Y- and Z-cut plates. Differently inclined dislocations, screw dislocations, platinum inclusions, point defects have been also observed (fig.2-10).

Langasite crystals can be successfully used in resonators and filters for covering the pass band of 0,4-0,8% over a wide frequency range. Frequency-temperature characteristics of langasite resonators and filters have a form of a quadratic parabola with extremum in the region of the room temperature for zero-cut, at which the maximum value of electromechanical coupling factor is 18%. Their change in the vicinity of zero cut has a gently sloping character. This evidences of the small compared with quartz crystal units dependence of FTC inflection point, of electromechanical coupling coefficient and frequency constant (N) on the angle of cut α . This fact simplifies manufacturing technology of langasite products. The steepness coefficient of FTC branches is $-7 \cdot 10^{-8} \text{ }^{\circ}\text{C}^{-2}$. Thus, as far as thermal stability of frequency is concerned, langasite resonators and filters are twice more stable than those of lithium tantalate.

The mean resonance spacing value for langasite resonators is equal to 0,8%, i.e. it is 3-4 times broader compared with that of the AT-cut quartz crystal units. The frequency coefficient value is 1380 kHz, which is 1,2 times smaller in comparison with AT-cut quartz crystal units. It is important to note, that parameters of langasite resonators and filters can be improved by employing optimum design and technology. From the data given it follows that these crystals have advantageous intermediate characteristics between those of quartz crystal units and lithium tantalate resonators (table 1).

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Table 1 . Physical and piezoelectric properties of langasite crystals in comparison with quartz and lithium tantalate

Property	Quartz	Langasite	Lithium tantalate
Symmetry class	32	32	3m
Melting temperature, °C	1710	1470	1650
Transition temperature, °C	573,5	-	660
Density, g/cm ³	2,65	5,75	7,45
Mohs hardness	7	6,5-7,0	6,7
Linear thermal expansion coefficient, $\times 10^{-6}$			
α_{11}	7,10	5,11	22,0
α_{33}	13,24	3,61	1,20
Electromechanical coupling factor, %			
k_{12}	0,14	16	44
k_{26}	0,098	13	19
Dielectric constant			
ϵ_{11}/ϵ_0	4,52	18,99	51
ϵ_{33}/ϵ_0	4,64	49,32	45
BAW propagation direction	AT	Y	X
Temperature characteristics, ppm/°C	0	1-2	25

Fig. 1. "As grown" langasite boules

Fig. 2. Etch pits at places of dislocations and dislocation slipband exit at the surface of Z-cut plate
(magnification $\times 90$)

Fig. 3. Etch pit at the place of dislocation exit at the surface of Z-cut plate (under very strong magnification)

Fig. 4. Etch pits at places of dislocations with different inclination angle and screw (Burgers) dislocations exit at the surface of Z-cut plate (magnification $\times 90$)

Fig. 5. Etch pit at the place of screw dislocation exit at the surface of Z-cut plate (magnification $\times 90$)

Fig. 6. Etch pit having a form of a groove (beak-shaped) at the place of inclusion etching out at the surface of Z-cut plate (magnification $\times 90$)

Fig. 7. Etch pits at places of different inclination angle dislocations (slipbands) at the surface of plate Z-cut (magnification $\times 90$)

Fig. 8. Etch pits at place of dislocation and point defects (smaller ones) exit at the surface of Z-cut plate (magnification $\times 90$)

Fig. 9. Etch pits at the place of dislocation slipband exit at the surface of Y-cut plate (magnification $\times 90$)-

Fig. 10. Etch pits at places of dislocations exit at the surface of Y-cut plate (magnification $\times 90$)