Physics of the Solid State, Vol. 46, No. 3, 2004, pp. 458–461. Translated from Fizika Tverdogo Tela, Vol. 46, No. 3, 2004, pp. 446–448.

Electromechanical Properties of $Pb_3Ga_2Ge_4O_{14}$ Piezoelectric Crystals Grown from Solution in a Melt

B. P. Sorokin*, D. A. Glushkov*, L. N. Bezmaternykh, V. L. Temerov**, I. A. Gudim**, and K. S. Aleksandrov****

** Krasnoyarsk State University, Svobodnyĭ pr. 79, Krasnoyarsk, 660041 Russia*
e-mail: bsorokin@lan.krasu.ru
*** Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

Received July 18, 2003

Abstract—Single crystals of lead gallium germanate $Pb_3Ga_2Ge_4O_{14}$ are grown from their own solution melts. The propagation of bulk acoustic waves is investigated, and the elastic, piezoelectric, and dielectric constants are calculated. The temperature dependences of the dielectric constants of this compound are analyzed. *© 2004 MAIK "Nauka/Interperiodica".*

1. Quartz, lithium niobate, germanosillenite, and silicosillenite are the crystals used in piezoelectric engineering and acoustoelectronics. Among these materials, only quartz crystals have found wide application owing to their thermally stable cuts suitable for propagating bulk and surface acoustic waves, even though quartz exhibits relatively small coefficients of piezoelectric coupling for both bulk and surface acoustic waves. One of the most important problems is the search for new crystalline materials that are characterized by large piezoelectric-coupling coefficients and slow attenuation of acoustic waves and that involve cuts providing thermal stability in devices based on these materials. Moreover, the cost of producing these crystals on a mass scale should be relatively low.

In recent years, considerable interest has been expressed by researchers in crystals that are isomorphic to calcium gallium germanate $Ca_3Ga_2Ge_4O_{14}$ and belong to the symmetry class 32. To date, over one hundred compounds of this family (including single crystals) have been synthesized [1]. In particular, this includes the langasite $La_3Ga_5SiO_{14}$, which substantially excels quartz in piezoelectric coupling and, consequently, has already successfully been used in acoustoelectronics and piezoelectric engineering. Although langasite and some other materials have been synthesized using the melting (Czochralski) technique, which was specially devised for growing large-sized single crystals, many problems concerning the crystal chemistry and technology of these materials, particularly those regarding the quality of single crystals, remain unsolved. As a result, the losses due to the propagation of high-frequency elastic waves occurring in these crystals are greater than those in piezoelectric quartz. This can be explained by the fact that virtually all single crystals with a langasite-like structure are considered to be structurally disordered, because one cation position in their structure can be occupied by atoms of two (or more) sorts [2]. However, the langasite family also involves crystals with an ordered structure [3]. These crystals are currently objects of intensive investigation.

2. The extreme members of this family are lead and barium gallium germanates ($Pb_3Ga_2Ge_4O_{14}$, $Ba_3Ga_2Ge_4O_{14}$), which have the largest sized cations and, hence, the largest unit cell parameters. According to extrapolation data, these crystals possess strong piezoelectric properties. However, upon melting, these compounds undergo decomposition and, therefore, cannot be prepared in the form of single crystals from a melt [1].

In this work, $Pb_3Ga_2Ge_4O_{14}$ isometric single crystals more than 1 cm^3 in volume were grown from both their own solution melts and solution melts diluted with lead fluoride [4].

3. The propagation of bulk acoustic waves in a $Pb_3Ga_2Ge_4O_{14}$ single crystal was studied using the pulsed ultrasonic method (30 MHz), which ensured an accuracy of better than $\pm 10^{-4}$ [5] in determining the velocity of bulk acoustic waves. As a rule, the determination of the electromechanical properties is based on measuring the velocities of bulk acoustic waves along particular directions. The velocity of bulk acoustic waves is related to the elastic moduli, piezoelectric constants, and dielectric constants (Table 1). The ultrasonic data were supplemented with the results of measuring the low-frequency permittivity $\varepsilon_{ij}^{\sigma}$ at a frequency of 1 kHz (the electric-bridge method). The measurements of the low-frequency permittivity $\varepsilon_{ij}^{\sigma}$ and the dielectric loss tangent $\tan\delta$ were carried out in the temperature range –100–150°C (Fig. 1). The piezoelectric activity

1063-7834/04/4603-0458$26.00

Table 1. Relationships between the velocities of bulk acoustic waves and piezoelectric-coupling constants for crystals of symmetry 32 and velocities of bulk acoustic waves in the $Pb_3Ga_2Ge_4O_{14}$ single crystal at 20°C

Mode no.	**N**	**U**	Wave type	Relationships for material constants	V_i, m/s
1	[001]	[001]	*L*	C_{33}	5128.1 ± 0.5
2	[001]		*S*	C_{44}	2743.5 ± 0.5
3	[100]	[100]	*L*	$C_{11}+\frac{e_{11}^2}{e_{11}^{\eta}}$	4618.0 ± 0.5
4	[100]		*SF*	$\frac{1}{2}(C_{44}+C_{66})+\frac{1}{2}\sqrt{(C_{44}-C_{66})^2+4C_{14}^2}$	2932.9 ± 0.5
5	[100]		*SS*	$\frac{1}{2}(C_{44}+C_{66})-\frac{1}{2}\sqrt{(C_{44}-C_{66})^2+4C_{14}^2}$	2257.3 ± 0.5
6	[010]	[100]	*S*	$C_{66}+\frac{e_{11}^2}{e_{11}^{\eta}}$	2413.4 ± 0.5
7	[010]		*QL*	$\frac{1}{2}(C_{44}+C_{11})+\frac{1}{2}\sqrt{(C_{11}-C_{44})^2+4C_{14}^2}$	4630.3 ± 0.5
8	[010]		*QS*	$\frac{1}{2}(C_{44}+C_{11})-\frac{1}{2}\sqrt{(C_{11}-C_{44})^2+4C_{14}^2}$	2713.1 ± 0.5
9	$\left[0\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right]$	[100]	*S*	$\frac{1}{2}(C_{44}+C_{66}+2C_{14})+\frac{1}{2}\frac{(e_{11}+e_{14})^2}{e_{11}^{\eta}+e_{33}^{\eta}}$	2284.2 ± 0.5
10	$\left[0\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right]$		*QL*	$\frac{1}{4}(C_{11}-2C_{14}+2C_{44}+C_{33})+\frac{1}{4}\sqrt{(2C_{14}-C_{11}+C_{33})^2+4(C_{13}+C_{44}-C_{14})^2}$	5107.9 ± 0.5
11	$\left[0\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right]$		*QS*	$\frac{1}{4}(C_{11}-2C_{14}+2C_{44}+C_{33})-\frac{1}{4}\sqrt{(2C_{14}-C_{11}+C_{33})^2+4(C_{13}+C_{44}-C_{14})^2}$	2604.6 ± 0.5
12	$\left[0-\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right]$	[100]	*S*	$\frac{1}{2}(C_{44}+C_{66}+2C_{14})+\frac{1}{2}\frac{(e_{11}-e_{14})^2}{e_{11}^{\eta}+e_{33}^{\eta}}$	2853.6 ± 0.5
13	$\left[0-\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right]$		*QL*	$\frac{1}{4}(C_{11}+2C_{14}+2C_{44}+C_{33})+\frac{1}{4}\sqrt{(2C_{14}+C_{11}-C_{33})^2+4(C_{13}+C_{44}+C_{14})^2}$	4830.5 ± 0.5
14	$\left[0-\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}}\right]$		*QS*	$\frac{1}{4}(C_{11}+2C_{14}+2C_{44}+C_{33})-\frac{1}{4}\sqrt{(2C_{14}+C_{11}-C_{33})^2+4(C_{13}+C_{44}+C_{14})^2}$	2556.8 ± 0.5

Note: **N** and **U** are the unit vectors of propagation and polarization of the bulk acoustic waves.

was also determined by measuring the longitudinal piezoelectric effect with the use of a V7-30 electrostatic voltmeter. The structure of the samples used in our experiments had point symmetry 32. For example, the ultrasonic measurements were performed using samples with the following characteristics. The linear dimensions of the samples fell in the range 4–7 mm, the samples were oriented using an x-ray diffractometer

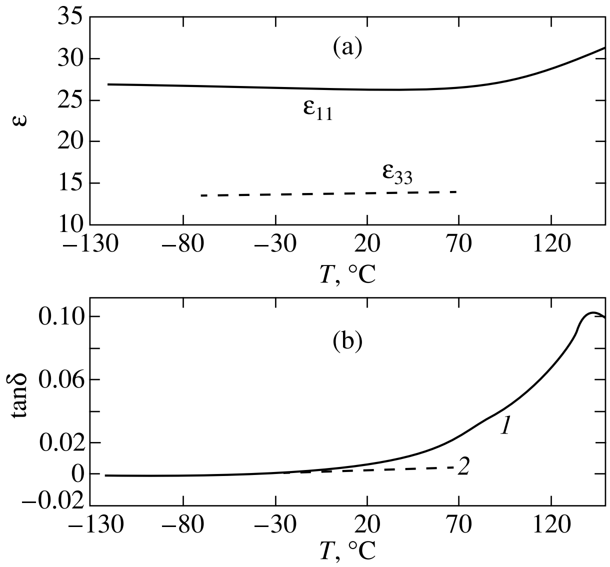

Fig. 1. Temperature dependences of (a) the low-frequency permittivity and (b) the dielectric loss tangent for the (*1*) *X* and (*2*) *Z* cuts of the $Pb_3Ga_2Ge_4O_{14}$ crystal.

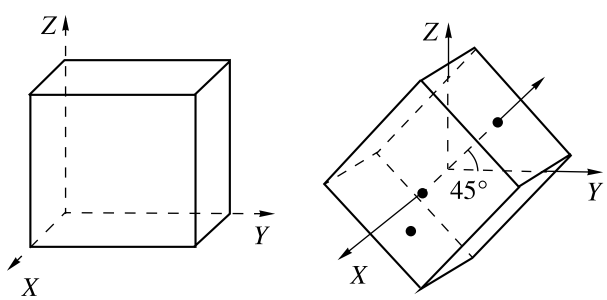

Fig. 2. Schematic representation of the orientation of samples used in ultrasonic investigations.

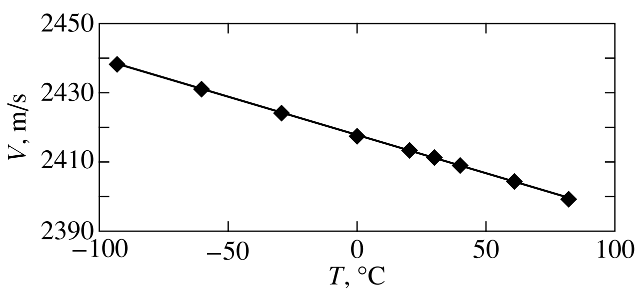

Fig. 3. Temperature dependence of the velocity of a pure shear wave propagating along the [010] direction (mode 6).

with an accuracy of better than ±3', and the deviations of the crystal facets from their plane-parallel orientation did not exceed ±1 μm/cm (Fig. 2). According to our earlier work [6], the $\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]$ and $\left[0\ -\frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]$ directions in crystals of this symmetry differ in terms of their elastic properties; in particular, the condition for the elastic constant $C_{14} < 0$ is satisfied along the direction $\left[0\ \frac{1}{\sqrt{2}}\ \frac{1}{\sqrt{2}}\right]$.

The low-frequency permittivities $\varepsilon_{ij}^{\sigma}$ (the case of a mechanically free sample) and ε_{ij}^{η} (the case of a mechanically fixed sample) of crystals with symmetry 32 are governed by the following relationships:

$$\varepsilon_{11}^{\eta} = \varepsilon_{11}^{\sigma} - \frac{e_{11}^2}{\varepsilon_0 C_{11}^E}, \quad \varepsilon_{33}^{\eta} = \varepsilon_{33}^{\sigma}. \qquad (1)$$

Here, e_{11} is the tensor component of the piezoelectric constants $e_{i\lambda}$, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of free space, and C_{11}^E is the tensor component of the elastic moduli measured in a dc electric field. The parameters involved in relationships (1) were used to calculate the low-frequency permittivities ε_{ij}^{η}.

Table 2 presents the electromechanical characteristics of the $Pb_3Ga_2Ge_4O_{14}$ crystals in comparison with the data obtained for langasite crystals [5]. These characteristics are calculated from the data presented in Table 1 and the results of dielectric measurements.

Analysis of the data presented in Table 2 shows that, despite the predictions based on the extrapolation data, the $Pb_3Ga_2Ge_4O_{14}$ crystals possess weak piezoelectric properties, because the piezoelectric-coupling coefficients are less than 10%. The elastic moduli of the $Pb_3Ga_2Ge_4O_{14}$ crystals are less than those of the langasite crystals. This indicates that the $Pb_3Ga_2Ge_4O_{14}$ crystal has a smaller hardness as compared to the langasite crystal. The temperature dependence of the velocity of bulk acoustic waves (mode 6), which is determined by the elastic constant C_{66}, exhibits normal behavior (Fig. 3). This suggests that the $Pb_3Ga_2Ge_4O_{14}$ crystal has no temperature-compensated directions or cuts suitable for propagating bulk and surface acoustic waves. The quantitative comparative estimations demonstrated that the attenuation of elastic waves in $Pb_3Ga_2Ge_4O_{14}$ is insignificant.

It is worth noting that the temperature dependences of the dielectric parameters of $Pb_3Ga_2Ge_4O_{14}$ differ from those of the majority of crystals with a langasite structure, for which the permittivity, as a rule, obeys the relationship $\varepsilon_{33}^{\sigma} > \varepsilon_{11}^{\sigma}$. For example, the temperature dependence of the permittivity $\varepsilon_{33}^{\sigma}$ of langasite crystals has the form $\varepsilon_{33}^{\sigma}(T) \sim T^{-1}$, which corresponds to the contribution of the dipole polarization. It should also be noted that the slope of the temperature dependence $\varepsilon_{11}^{\sigma}$ for the $Pb_3Ga_2Ge_4O_{14}$ crystal changes at room temperature. This correlates with the increase observed in the

Table 2. Elastic, piezoelectric, and dielectric properties of $Pb_3Ga_2Ge_4O_{14}$ and $La_3Ga_5SiO_{14}$ crystals at 20°C

	$Pb_3Ga_2Ge_4O_{14}$	$La_3Ga_5SiO_{14}$
	Density ρ, kg/m³ (calculation)	
	6884.8	5743
λμ	$C^E_{\lambda\mu}$, 10^{10} Pa	
11	14.65 ± 0.01	18.875
66	3.98 ± 0.01	4.2
33	18.12 ± 0.01	26.14
44	5.21 ± 0.01	5.35
14	–1.02 ± 0.01	–1.412
13	7.04 ± 0.01	9.59
*i*λ	$\|e_{i\lambda}\|$, C/m²	
11	0.26 ± 0.03	0.44
14	0.09 ± 0.03	0.1
ij	$\varepsilon^{\sigma}_{ij}$	
11	26.2 ± 0.5	18.92
33	13.9 ± 0.5	50.7
ij	ε^{η}_{ij}	
11	26.1 ± 0.5	
33	13.9 ± 0.5	
	Piezoelectric-coupling coefficients, %	
The piezoactive longitudinal wave propagating along the *X* direction (mode 3)*	4.7	8
The piezoactive pure shear wave propagating along the *Y* direction and polarized along the *X* direction (mode 7)*	9	16

* The mode numbering is the same as in Table 1.

dielectric loss tangent in this range and can be explained by the relaxation ionic polarization due to hopping conduction.

ACKNOWLEDGMENTS

This work was supported by the Russian Federal program "Integration" (project no. 67).

REFERENCES

1. B. V. Mill and Yu. V. Pisarevsky, in *Proceedings of the 2000 IEEE/EIA International Frequency Control Symposium and Exhibition* (Kansas-City, USA, 2000), p. 133.
2. A. A. Kaminskiĭ, S. É. Sarkisov, B. V. Mill', and G. G. Khodzhabagyan, Izv. Akad. Nauk SSSR, Neorg. Mater. **18**, 1396 (1982).
3. B. H. T. Chai, A. N. P. Bustamante, and M. C. Chou, in *Proceedings of the 2000 IEEE/EIA International Frequency Control Symposium and Exhibition* (Kansas-City, USA, 2000), p. 163.
4. L. N. Bezmaternykh, A. D. Vasil'ev, I. A. Gudim, and V. L. Temerov, in *Abstracts of the X National Conference on Crystal Growth* (Moscow, 2002).
5. E. L. Belokoneva, S. Yu. Stefanovich, Yu. V. Pisarevskiĭ, and A. V. Mosunov, Zh. Neorg. Khim. **45** (11), 1786 (2000).
6. B. P. Sorokin, P. P. Turchin, and D. A. Glushkov, Fiz. Tverd. Tela (St. Petersburg) **36** (10), 2907 (1994) [Phys. Solid State **36**, 1545 (1994)].

Translated by I. Volkov