Bull. Mater. Sci., Vol. 30, No. 2, April 2007, pp. 101–104. © Indian Academy of Sciences.

Piezoelectric properties of $Sr_3Ga_2Ge_4O_{14}$ single crystals

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MS received 26 December 2006

Abstract. **A new piezoelectric single crystal, $Sr_3Ga_2Ge_4O_{14}$ (SGG), has been grown successfully by the vertical Bridgman method with crucible-sealing technique. SGG crystal up to 2″ in diameter has been obtained. The relative dielectric constants, the piezoelectric strain constants, elastic compliance constants and electromechanical coupling factors have been determined with resonance and anti-resonance frequencies method by using the impedance analyzer (Agilent 4294A). The results show that the piezoelectric strain constants and electromechanical coupling factors of SGG single crystal are higher than those of LGS single crystals making it a potential substrate material for surface-acoustic wave applications.**

Keywords. **$Sr_3Ga_2Ge_4O_{14}$; piezoelectric materials; piezoelectric constants.**

1. Introduction

Recently, langasite (LGS, $La_3Ga_5SiO_{14}$) structure family single crystals, have been considered to be the most promising piezoelectric materials for bulk acoustic wave (BAW) and surface acoustic wave (SAW) devices. LGS crystal wafers have been fabricated by using small size intermediate frequency SAW filter in a new mobile communication system, wide-band-code division multiple access (WCDMA) (Shimamura *et al* 1996). Langasite family structure crystals have a trigonal structure which belongs to point group 32, space group *P*321. There are four types of cation sites in this structure, which is represented by $A_3BC_3D_2O_{14}$. Since the cation positions may be occupied or substituted by various aliovalent ions, to date a large number of compounds belonging to the steadily growing LGS structural family such as LGS, $Sr_3Ga_2Ge_4O_{14}$ (SGG), $La_3Ga_{5.5}Nb_{0.5}O_{14}$, $La_3Ga_{5.5}Ta_{0.5}O_{14}$, $Ca_3NbGa_3Si_2O_{14}$, $Ca_3TaGa_3Si_2O_{14}$, $Sr_3NbGa_3Si_2O_{14}$ and $Sr_3TaGa_3Si_2O_{14}$ etc (Karki *et al* 2004) have been prepared. Among these homologous compounds, SGG crystal attracted our attention due to its superior piezoelectric properties and lower growth temperature, and ϕ2″ SGG crystals have been grown successfully by our group with the modified Bridgman method (Wu *et al* 2005).

Piezoelectric SGG crystals were first grown by the Fukuda group in 1997 (Kochurikhin *et al* 1997), however, only some piezoelectric parameters of SGG crystals were measured due to the limits of the crystal size and quality. We have grown SGG crystals with the modified Bridgman method since 2002, and ϕ2″ SGG crystals can be grown reproducibly now. The details of Bridgman growth of piezoelectric SGG crystals have been published earlier (Wu *et al* 2005). This paper deals with the systematic piezoelectric properties which include relative dielectric constants, piezoelectric strain constants, elastic compliance constants and electromechanical coupling factors.

2. Determination of crystal densities

The piezoelectric strain constants of the material can be derived from the resonance frequencies by using the impedance analyser. For this, the densities of the crystals must be known in advance. The crystal densities were obtained by two methods. First, the lattice parameters *a* and *c* (hexagonal setting) were determined on powdered samples of the as-grown materials using X-ray powder diffraction. From the lattice parameters and the formula masses of SGG crystal, the densities, ρ_X (so-called X-ray densities), were calculated. Hence, the density ρ_X, used in the calculations below, may be considered as an intrinsic one.

For comparison, experimental density, ρ_e, was determined by measuring the masses and the geometrical volumes of bar-shaped samples of ~$10 \times 10 \times 5$ mm^3 size. As usual, these densities, $\rho_e = 5.068$ g/cm^3, are somewhat smaller (about 0·4%) than the X-ray densities, $\rho_X = 5.087$ g/cm^3.

3. Piezoelectric properties measurement

The investigations of piezoelectric properties were carried out with the specimens fabricated from SGG crystals of high internal perfection. In resonance and anti-resonance frequencies method, and for the dielectric permeability, study bars ($10 \times 2 \times 0.5$ mm^3) and plates ($10 \times 10 \times 0.5$ mm^3)

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were used, the shape and orientation of which are shown in figure 1. At opposite surfaces of these specimens, gold electrodes were deposited by vacuum evaporation. During the fabrication of all specimens, an X-ray goniometer YX-1 type was used, which permitted to keep their orientation with the accuracy not worse than 5′. In these experiments, corresponding specimens of crystalline SiO_2 were also used.

3.1 *Dielectric permeability*

The dielectric permeability can be denoted as the relative dielectric constants, ε_{ii}, which have the structure of a second tensor. For symmetry reasons, there are two independent components, ε_{11} and ε_{33}, in SGG crystals with $\varepsilon_{11} = \varepsilon_{22}$. The measurements of the relative dielectric constants were carried out on oriented [100] and [001] crystal plates (*g* and *h* plates in figure 1) by means of a Hewlett Packard LCR meter. The electric capacities of oriented [100] and [001] crystal plates were measured and the relative dielectric constants were computed through the following equation:

$$\varepsilon / \varepsilon_0 = \frac{C \cdot t}{A \cdot \varepsilon_0}, \tag{1}$$

where A is the area of crystal plate, t the thickness of crystal plate, and $\varepsilon_0 = 8{\cdot}85 \times 10^{-12}$ F/M, which is the vacuum dielectric constant.

The measurements were performed at frequencies of 1 kHz and 1 MHz, which are far below and above the resonance frequencies, therefore, the dielectric constants at constant mechanical tension (ε^{T}) and constant strain (ε^{S}) were computed, respectively. Table 1 shows the dielectric constants and dielectric losses of SGG crystal at room temperature.

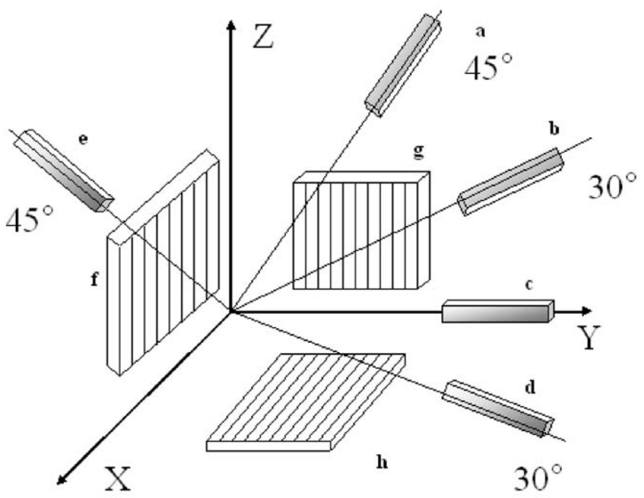

Figure 1. Shapes and orientations of SGG crystal for investigations of piezoelectric properties by resonance method.

3.2 *Elastic property*

The elastic properties of an anisotropic crystal can be completely described by the elastic stiffness constants, c_{ij}, as well as the elastic compliance constants, S_{ij} (Voigt notation, cf. Wu *et al* 2005). Both are fourth rank tensors and inversely related to each other. In the crystal class 32, there are, for reasons of symmetry, only six independent c_{ij}, usually denoted by c_{11}, c_{12}, c_{13}, c_{14}, c_{33} and c_{44}. The complete stiffness tensor consists of 18 non-vanishing components that can be written in a symmetrical 6×6 matrix form with $c_{66} = (c_{11}-c_{12})/2$. The reciprocal *s*-matrix of the elastic compliances has an identical form. However, deviating from the *c*-matrix, the components, $s_{56} = s_{65} = 2s_{14}$ and $s_{66} = 2(s_{11} - s_{12})$, appear. For the elastic stiffness constants, c_{ij}, as well as the elastic compliance constants, s_{ij}, the letters E and D denote the measurements performed under constant electric field and constant displacement, respectively. In this work, all the independent elastic compliance constants, s^{E}_{ij}, were determined.

The elastic compliance constants, s_{ij}, can be obtained through experimentally measuring resonance frequencies of the specimens. In these measurements, the resonance frequencies of all the bar specimens (figure 1) were determined in the length-extensional mode; s^{E}_{11} can be calculated through (2) based on the resonance frequency of (XYtwl)-0°/0°/0°-bar.

$$s^{\mathrm{E}}_{22} = s^{\mathrm{E}}_{11} = \frac{1}{4\rho l^2 f_{\mathrm{r}}^2}, \tag{2}$$

where ρ is the density of SGG crystal, l the length of the specimen. Compared to (XYtwl)-0°/0°/0°-bar, other bar specimens have a rotated angle, θ, around the thickness direction, accordingly, the relations between θ and the values of the elastic compliance tensor components can be described as follows:

$$s^{\mathrm{E}}_{22}(\theta) = s^{\mathrm{E}}_{11}\cos^4\theta + (2s^{\mathrm{E}}_{13} + s^{\mathrm{E}}_{44})\sin^2\theta\cos^2\theta - 2s^{\mathrm{E}}_{14}\sin\theta\cos^3\theta + s^{\mathrm{E}}_{33}\sin^4\theta. \tag{3}$$

Thus, the values of s^{E}_{11}, s^{E}_{14}, s^{E}_{33} and $2s^{\mathrm{E}}_{13} + s^{\mathrm{E}}_{44}$ can be calculated using these data and (2) and (3). The calculation of s^{E}_{44} was performed on the data of shear-contour vibrations of the Y-cut plate (seen as the calculation of k_{c} in the next section), the equation describing the relation between s^{E}_{44} and vibrations was written as:

$$s^{\mathrm{E}}_{44} = \frac{1}{4\rho l^2 f_{\mathrm{r}}^2} \bullet F^2, \tag{4}$$

$$F = 1{\cdot}289 - 0{\cdot}0469\sqrt{(s^{\mathrm{E}}_{11} + s^{\mathrm{E}}_{33})/s^{E}_{44}}. \tag{5}$$

To calculate s^{E}_{66} in addition, the following relations are given

Table 1. Dielectric constants and dielectric losses of SGG crystal at room temperature.

Frequency	1 K		1 M	
Dielectric constants and losses	$\varepsilon_{11}^{T} = 13{\cdot}61$	$tg\delta = 8{\cdot}7 \times 10^{-3}$	$\varepsilon_{11}^{S} = 14{\cdot}30$	$tg\delta = 2{\cdot}8 \times 10^{-3}$
	$\varepsilon_{33}^{T} = 18{\cdot}18$	$tg\delta = 1{\cdot}8 \times 10^{-3}$	$\varepsilon_{33}^{S} = 18{\cdot}15$	$tg\delta = 4{\cdot}4 \times 10^{-4}$

Table 2. Elastic characteristics describing vibrations of resonators made of SGG crystals.

Mode of vibration, measured specimen (figure 1)	Values s_{ik}^{E} and c_{ik}^{D} determined
Length-extensional mode of bar	
(XYtwl)-0°/0°/0°-bar (c)	$s_{22}^{E} = s_{11}^{E}$
(XYtwl)- –30°/0°/0°-bar (d)	$0{\cdot}063(9s_{11}^{E} + s_{33}^{E} + 10{\cdot}39s_{14}^{E} + 6s_{13}^{E} + 3s_{44}^{E})$
(XYtwl)-30°/0°/0°-bar (b)	$0{\cdot}063(9s_{11}^{E} + s_{33}^{E} - 10{\cdot}39s_{14}^{E} + 6s_{13}^{E} + 3s_{44}^{E})$
(XYtwl)-45°/0°/0°-bar (a)	$0{\cdot}25(s_{11}^{E} + s_{33}^{E} - 2s_{14}^{E} + 2s_{13}^{E} + 2s_{44}^{E})$
(YZtwl)-45°/0°/0°-bar (e)	$0{\cdot}25(s_{11}^{E} + s_{33}^{E} + 2s_{13}^{E} + 2s_{44}^{E})$
Shear-thickness mode, Y-cut plate (f)	c_{66}^{D}
Shear-contour mode, Y-cut plate (f)	s_{44}^{E}

$$c_{66}^{D} = 4\rho(tf_{r})^{2}, \tag{6}$$

$$c_{66}^{E} = c_{66}^{D}(1 - K_{26}^{2}), \tag{7}$$

$$s_{66}^{E} = (c_{66}^{E})^{-1} + 4(s_{14}^{E})^{2}(s_{44}^{E})^{-1}. \tag{8}$$

The calculation of the elastic stiffness constants, c_{66}^{D}, was performed on the resonance frequency of the Y-cut plate in the shear-thickness mode (seen as the calculation of k_{26} in the next section), where t is the thickness of the plate. Thus s_{12}^{E} can be calculated from the equation:

$$S_{66} = 2(s_{11} - s_{12}).$$

Thus, the elastic characteristics describing vibrations of the resonators made of SGG crystals are shown in table 2. From the data of the resonance frequencies, we derived a set of elastic compliance constants for SGG: $s_{11}^{E} = 96{\cdot}89 \times 10^{-13}$ m² N⁻¹, $s_{12}^{E} = -73{\cdot}02 \times 10^{-13}$ m² N⁻¹, $s_{13}^{E} = -33{\cdot}19 \times 10^{-13}$ m² N⁻¹, $s_{14}^{E} = -35{\cdot}46 \times 10^{-13}$ m² N⁻¹, $s_{33}^{E} = 78{\cdot}18 \times 10^{-13}$ m² N⁻¹, $s_{44}^{E} = 220{\cdot}37 \times 10^{-13}$ m² N⁻¹.

3.3 *Electromechanical property*

The electromechanical properties of a crystal can be described by their electromechanical coupling factors, k_{em}. The values of electromechanical coupling factors k_{12}, k_{26} and k_t were often determined in the trigonal crystal class 32 to which the LGS structure belongs. The resonator bars cut off from the SGG single crystals (seen in figure 1) were single-frequency ones, the values of electromechanical coupling factors, k_{12}, k_{23} and k_c (contour electromechanical coupling factor), were computed by

$$\frac{k_{12,23,c}^{2}}{k_{12,23,c}^{2} - 1} = \frac{\pi f_{ar}}{2f_{r}} ctg\left(\frac{\pi f_{ar}}{2f_{r}}\right), \tag{9}$$

where f_r and f_{ar} are the resonance and antiresonance frequencies, respectively. To measure the factors, k_t (thickness electromechanical coupling factor) and k_{26}, the thickness vibration modes of plates (figure 1) were performed. Due to the fact that the resonator plates were multi-frequency ones, not only the frequencies of the main resonances but also of some of their harmonics, we must determine the frequencies of the main signal for the plates first, then compute k_t and k_{26} by using the following equation:

$$K_{26,t}^{2} = \frac{\pi}{2}\frac{f_{r}}{f_{a}}\tan\left[\frac{\pi}{2}\frac{(f_{a} - f_{r})}{f_{a}}\right]. \tag{10}$$

All calculation results are shown in table 3.

3.4 *Piezoelectric constant*

The piezoelectric properties of a (non-centrosymmetric) crystal may be described by their piezoelectric constants (piezoelectric moduli, piezoelectric strain constants) d_{ij} (Voigt notation, cf. Bohm *et al* (2000)). The coefficients have the structure of a third rank tensor and can be written in a 6 × 3 matrix form with five non-vanishing components in the trigonal crystal class 32 to which the LGS structure belongs. For symmetry reasons only two components are independent, usually denoted as d_{11} and d_{14}.

From the obtained values, s_{ij}^{E} and the measured dielectric permittivity constants (ε_{ii}^{T}), the values of piezoelectric constants, d_{11} and d_{14}, can be determined according to the relations

$$d_{12} = -d_{11} = k_{12}(s_{11}^{E}\varepsilon_{11}^{T})^{1/2}, \tag{11}$$

$$d_{14} = 2k_{23}(s_{33}^{E}\varepsilon_{11}^{T})^{1/2}. \tag{12}$$

Table 3. Electromechanical properties of SGG crystals.

Mode of vibration, measured specimen (figure 1)	f_r (Hz)	f_{ar} (Hz)	k_{em} (10^{-2})
Length-extensional mode, (XYtwl)-0°/0°/0°-bar (c)	181·11 k	184·77 k	21·7
Length-extensional mode, (YZtwl)-45°/0°/0°-bar (e)	186·85 k	187·84 k	10·8
Shear-contour mode, Y-cut plate (f)	120·03 k	120·99 k	13·5
Thickness-extensional mode, X-cut plate (g)	1·461 M	1·467 M	10·1
Shear-thickness mode, Y-cut plate (f)	1·229 M	1·264 M	25·8

Table 4. Piezoelectric constants, d_{ij} (10^{-12} CN^{-1}), electromechanical coupling factors, k_{em} and dielectric permittivity constants, ε_{ii}^{T} of SGG and LGS crystals.

Piezoelectric properties	SGG (this work)	SGG (Kaminskii *et al* 1984)	SGG (Kochurikhin *et al* 1997)	LGS (Kaminskii *et al* 1983)
d_{11}	–7·41	–9·12	–6·43	–6·16
d_{14}	7·05	6·96	–	5·36
k_{26}	0·258	0·257	0·287	0·134
k_t	0·101	0·13	–	0·08
k_{23}	0·108	0·1095	–	0·075
k_c	0·135	–	–	0·084
k_{12}	0·217	0·258	0·18	0·16
ε_{11}^{T}	13·61	13·8	–	18·99
ε_{33}^{T}	18·18	18·21	–	49·32

Thus the piezoelectric constants of SGG crystal are determined as $d_{11} = -7{\cdot}41 \times 10^{-12}$ CN^{-1} and $d_{14} = 7{\cdot}05 \times 10^{-12}$ CN^{-1}.

Table 4 shows results of piezoelectric measurements of SGG crystals. For comparison, the piezoelectric properties of SGG (Kaminsky *et al* 1984; Kochurikhin *et al* 1997) and LGS crystals (Kaminsky *et al* 1983) grown by Czochralski method are given too. The measured piezoelectric constants, electromechanical coupling factors and dielectric permittivity constants of SGG crystals in this work were similar to the results of Russian and Japanese scientists, while all these properties of SGG crystals surpass those of LGS crystals.

4. Conclusions

Langasite-type single crystal, $Sr_3Ga_2Ge_4O_{14}$, has been grown successfully by the vertical Bridgman method. The relative dielectric constants, piezoelectric strain constants, elastic compliance constants and electromechanical coupling factors have been determined using the resonance and anti-resonance frequencies method. Compared with LGS crystal, SGG crystal has high piezoelectric strain constants, high electromechanical coupling factors and low dielectric constants. In general, all the necessary parameters of SGG crystals for bulk and surface acoustic wave applications were determined here, and the piezoelectric properties of SGG crystal obviously excelled than those of LGS crystals, therefore, SGG crystal is a potential substrate material for surface–acoustic wave applications.

Acknowledgements

The authors would like to acknowledge the financial support provided by the National Natural Science Foundation of China (50672110).

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