On growth and dielectric properties of $Ca_4GdO(BO_3)_3$ single crystals

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ABSTRACT

Single crystals of $Ca_4GdO(BO_3)_3$ (CGBO) have been grown from a melt by the Czochralski pulling method making use [010] seed orientation. Defects, like dislocation were investigated. Chemical methods were developed on various planes of crystals, in order to reveal the nature and the distribution of these defects. Dielectric measurements in frequency range 20Hz – 13 MHz in three main crystallographic directions were curried out. The values of elastic and piezoelectric coefficients were calculated for the first mode of piezoelectric vibration in each direction.

Keywords: Oxides, growth, defects, dielectric.

1. INTRODUCTION

In the recent years there has been a great interest in non-linear optical materials that allow producing a visible laser beam by second harmonic generation (SHG).

Calcium gadolinium oxoborate $Ca_4GdO(BO_3)_3$ (CGBO) is a new efficient non-linear optical crystal[1,2] , belonging to the rare earth calcium borate group with general composition $Ca_4RB_3O_{10}$ (R = La – Lu, Y). The compound melts congruently at 1480^0C [1] and the crystal has high hardness (6.5), is nonhydroscopic, chemically stable and easy to polish. Additionally, it exhibits large transparency region and high damage threshold [3] .

1.1. Crystal structure

Norrestam et al.[4] synthesised a series of calcium oxoborate compounds with R = La, Nd. Sm, Gd, Y by high - temperature solid state reaction. Iliukhin et al.[5] grow crystals by the flux method with R = Gd, Tb, Lu ions and measured the crystal structure of $LnCa_4O(BO_3)_3$ by X-ray diffraction methods. CGBO structure is related to the fluoroborate and fluoroapatite. The unit cell parameters are a = 0.8104(1), b= 1 6030(3), c = 0.35584(3) nm and β = 101.250°. The space group is monoclinic noncentrosymetric Cm. The CGBO crystal is biaxial what means that the optical axis (X,Y,Z) are not in coincidence with the crystallographic axis (a, b, c). There are two types of Ca^{2+} ion occupy distorted octahedral sites. All octahedra share corners with BO_3 triangles to form a three-dimensional network. There are two kinds of boron site, B(1) and B(2), with threefold coordination. Three planar borate units lie approximately parallel to the (001) plane. The Gd^{3+} ions are located in the crystallographic mirror plane. The environment of Gd^{3+} is a distorted octahedron with Cs site symmetry. Four oxygen ions are shared with the BO_3 groups. The existence of a probable disorder between calcium and gadolinium atoms in the two octahedral positions is expected [5] .

2. GROWTH OF CGBO SINGLE CRYSTALS

The CGBO compound was prepared by solid state reaction, with $CaCO_3$ of 4N purity and Gd_2O_3 and B_2O_3 of 5N purity. B_2O_3 was prepared in the special way to III-V technology and contains water no higher than 70 ppm. The mixture was heated at 950 °C, cooled and ground, and then heated again at 1150 °C, for 20 h, respectively.

Crystals were grown by the Czochralski method. The synthesised charge was melted in iridium crucible and the seed of orientation [010] was introduced into crucible, at the top, and kept in contact with the melt. The growth processes were computers monitored by a weight-and-diameter system and without the computer system by visual diameter control. A nitrogen atmosphere was provided during growth. The typical growth rate was about 1 mm/h and crystal was rotated at 10-25 rpm. The crystals obtained in this way are colourless, with a good optical quality, not hygroscope, and chemically stable. The CGBO single crystal presents good mechanical properties, permitting easy polishing.

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3. CHEMICAL ETCHING

To investigate a quality of CGBO single crystals chemical etch methods were developed on planes of cube cut out along the three monoclinic axes [010] from three regions of crystal (top, central and bottom). The dislocations were detected on all planes of cube, however, they were observed very well on (100) and (010) planes (see Fig.1) and less on (001) flat. The dislocations were revealed by etching in 4% HCl at room temperature.

The (010) oriented plates showed similar amount of etches pits at the outer part of plates. Etch pits density decrease from $6 \cdot 10^4 cm^{-2}$ at the top of the crystal to $8 \cdot 10^3 cm^{-2}$ at the central part of the cone. However at the inner part of the crystal the etch pits density is about $1 \cdot 10^3 cm^{-2}$.

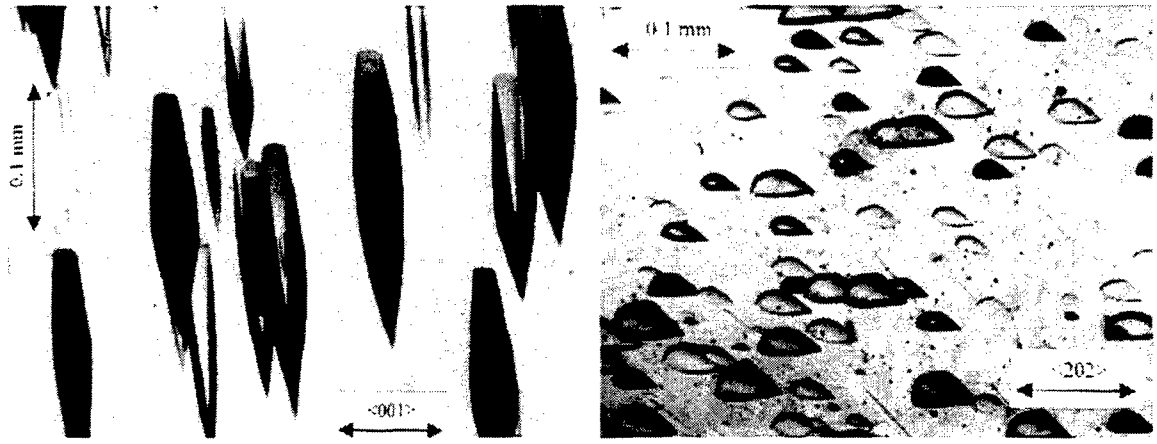

Fig.1. Etch pits pattern developed on the (100) plane (left) and (010) plane (right).

4. DIELECTRIC MEASUREMENTS

The dielectric measurements in frequency from 20 Hz to 13 MHz range were carried out using a HP4284A RCL meter and HP4192A impedance analyser. The temperature was stabilised in the range from 10K to 450K using an Oxford Instruments cryostat CF 1204.

The measurements were performed for samples cut out in the three main crystallographic directions [100], [010], [001]. The temperature dependence of permittivity and dielectric losses is show in the Fig.2. From this one can conclude that the crystal is very good isolator with maximum electric permittivity along the monoclinic axis [010] ($\varepsilon' = 12$) and a very small dielectric losses ($tg\delta \leq 0{,}01$).

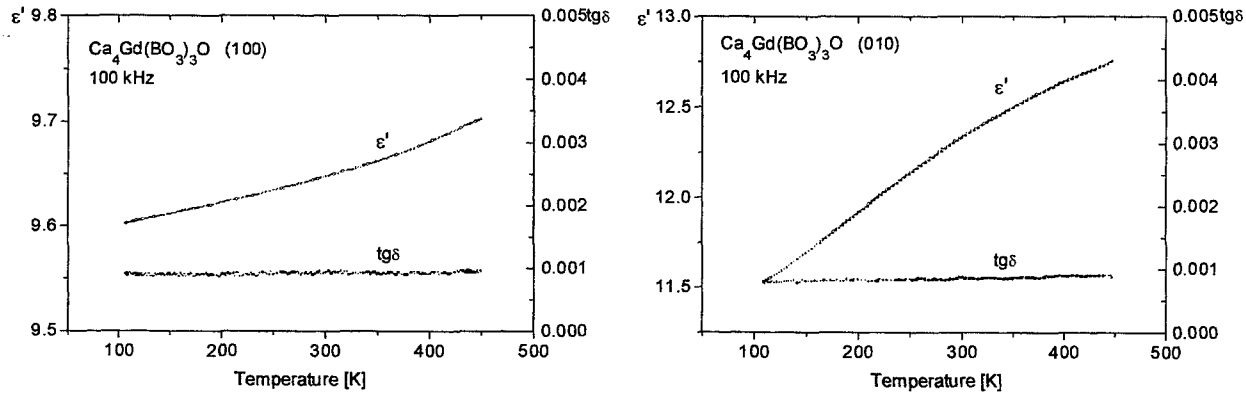

Fig.2. The temperature dependence of permittivity and dielectric losses in two main crystallographic directions.

In the Fig.3 the frequency dependencies of both parts ε' and ε" of the permittivity are shown. Resonance dependencies are observed at frequencies near 1MHz. The number of resonance peaks reflects the number of piezoelectric vibration modes of the sample. In the (100) oriented sample e.g. a tripled of basic modes is observed. The experimental points for basic tripled can be well fitted with dielectric function for the sum of three harmonic oscillators:

$$\varepsilon^*(f) = \sum_i \frac{A_i f_{ri}^{\ 2}}{f_{ri}^{\ 2} - f^2 - jf\Gamma_i}, \qquad (1)$$

where f denotes measuring frequency, A_i, f_{ri} and Γ_i - amplitude, resonance frequency and damping constant of the i-th oscillator, respectively. The values of parameters A, f_r, and Γ obtained from the fit are also given in the Fig.3c.
Moreover, at higher frequencies non-odd harmonic vibrations can be observed. The ratios of the harmonic/basic frequencies amount ..., 5, 3, 1, as expected in the case of piezoelectric resonance (see Fig. 3d).

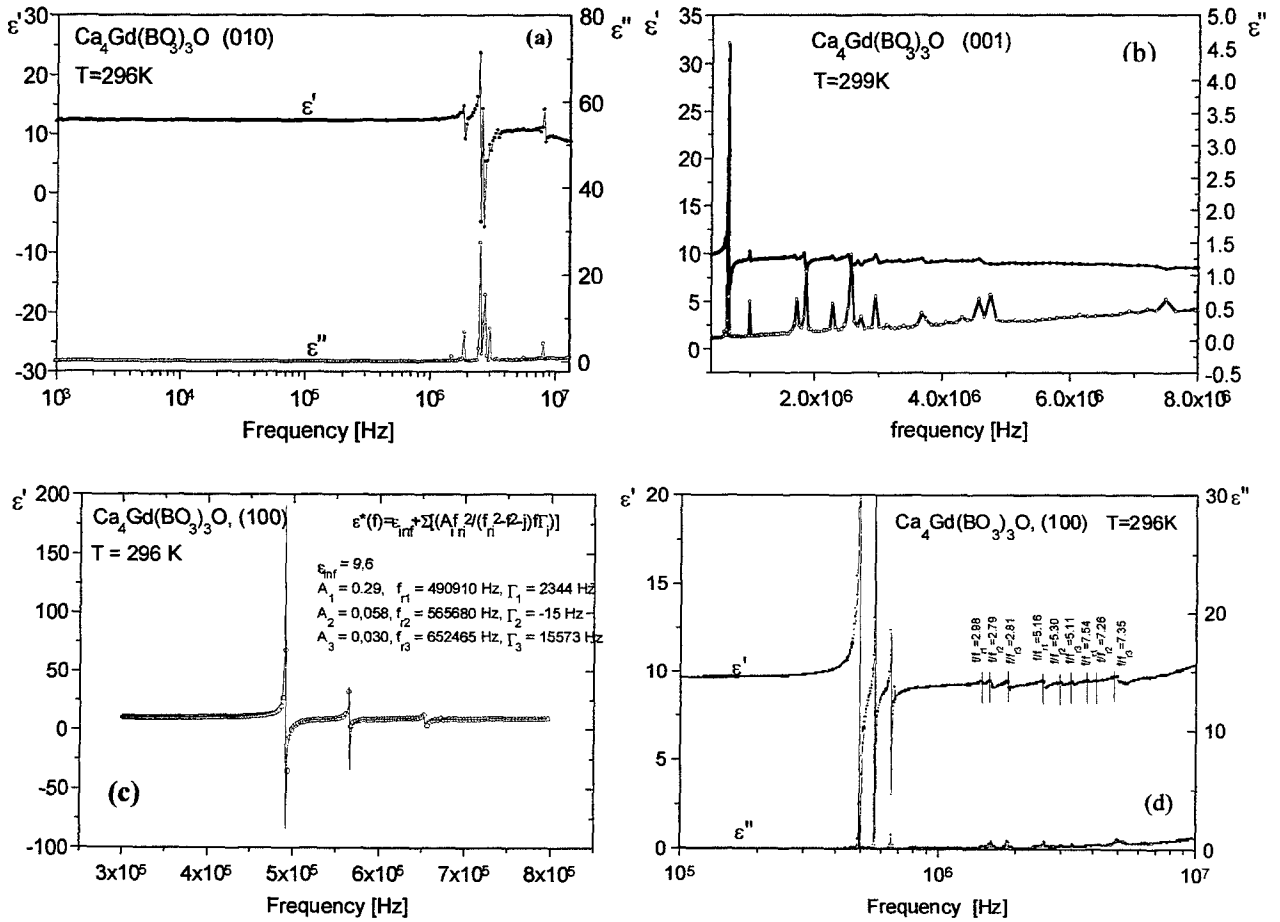

Fig.3. The frequency dependencies of the permittivity in the three crystallographic directions.

The electric equivalent circuit method [6] was used to calculate elastic and piezoelectric coefficients. The circuit is given in Fig. 4.

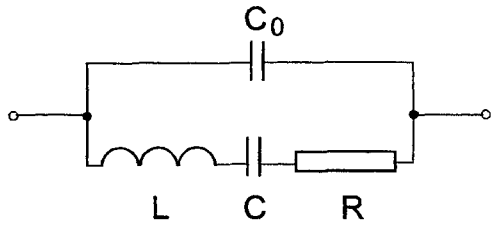

Fig. 4. The $RLCC_0$ electric equivalent circuit.

The R, L, C and C_0 values are associated with the above coefficients [7,8] in the following way:

electromechanical coupling factor k_{ij}:

$$k_{ij}^2 = \frac{1}{8}\pi^2 \frac{C}{C_0} \tag{2}$$

dielectric permittivity under constant tension ε_{ij}^T:

$$\varepsilon_{ij}^T = \frac{C_0 t}{A} \tag{3}$$

where: A is the area of the sample,
t is the thickness of the sample

elastic compliance coefficient under constant field s_{ij}^E:

$$\frac{1}{s_{ij}^E} = \frac{1}{\pi^2} t^2 \varpi_s^2 \rho \tag{4}$$

piezoelectric coefficient d_{ij}:

$$d_{ij}^2 = k_{ij} \varepsilon_{ij}^T s_{ij}^E \tag{5}$$

The values of above coefficients were calculated for the first mode of piezoelectric vibration in each direction. They are summarised in the Table 1. The measurement results showed that CGOB crystals exhibit the best piezoelectric properties along the monoclinic axis [010]. The piezoelectric coefficients along this axis shows 1.6 - 2 time more value than along the others. Elastic compliance of CGOB crystal is the least one related to the monoclinic axis because the reciprocal of the elastic compliance coefficient under constant field $\frac{1}{s_{22}^E}$ reaches the largest value.

Table1. Elastic and piezoelectric coefficients.

parameter	value	unit
$\varepsilon_{11}^{T}/\varepsilon_0$	8.92	
$\varepsilon_{22}^{T}/\varepsilon_0$	5.18	
$\varepsilon_{33}^{T}/\varepsilon_0$	10.92	
$\frac{1}{s_{11}^{E}}$	1.76×10^{9}	N/m^2
$\frac{1}{s_{22}^{E}}$	55.37×10^{9}	N/m^2
$\frac{1}{s_{33}^{E}}$	3.14×10^{9}	N/m^2
d_{11}	3.84×10^{-11}	C/N
d_{22}	6.32×10^{-12}	C/N
d_{33}	3.04×10^{-11}	C/N

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5. CONCLUSIONS

CGOB single crystals obtained by the Czochralski method are colourless, with a good optical quality. The investigated crystals were partially defected showing dislocations and stacking faults along the crystal growth direction [010]. The etch pits density at the central part of crystal on the {010} face was $1\cdot10^{3}cm^{-2}$.

Dielectric measurements carried out in frequency range 20 Hz - 13 MHz and in temperature range up to 450K in the three main crystallographic directions [100], [010], [001] showed, that CGBO crystal is a very good isolator with dielectric losses $tg\delta<0{,}01$ stable with temperature and frequency. Resonance dependency was found at frequencies near 1MHz. CGBO single crystal exhibits the best piezoelectric properties along the monoclinic [010] axis.

ACKNOWLEDGEMENTS

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