Influence of growth atmosphere on Ca$_3$TaGa$_3$Si$_2$O$_{14}$ single crystals optical properties

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Abstract. Ca$_3$TaGa$_3$Si$_2$O$_{14}$ crystals were grown by the Czochralski technique in different atmospheres. Crystal grown in pure Ar was colourless and in N$_2$+(1-3)%O$_2$ – yellowish coloured. In the absorption spectra of yellowish CTGS we observed anisotropy: no significant absorption bands are observed in Z direction, but in X direction we observe absorption bands at 360 nm and at (470-480) nm. In case of colourless CTGS we observed extremely low intensity of the absorption band at ~500 nm, in near UV we observed anisotropy of absorption and absorption band at ~290 nm for X direction. Dichroism degree intensity is extremely low for these crystals, with maximum connected with coloration at 470 nm for yellow crystal and in case of colourless CTGS the main extrema are observed in near UV.

1. Introduction

Structure and properties of the crystals with Ca-gallogermanate structure (Ca$_3$Ga$_2$Ge$_4$O$_{14}$, La$_3$Ga$_5$SiO$_{14}$, La$_3$Ga$_{5.5}$Ta$_{0.5}$O$_{14}$ etc.) with point group of symmetry (PGS) 32 are investigated for more than 20$^{th}$ years since the moment of synthesis of the first representatives of this group in the beginning of 80$^{th}$ of XX century [1, 2], but still new details are being clarified or discovered. For example, the structure of Ca$_3$Ga$_2$Ge$_4$O$_{14}$ was reported in 80$^{th}$ [2] but specified in 2013 [3].

The most investigated and widely used in practice crystals with this structure are La$_3$Ga$_5$SiO$_{14}$ (LGS, langasite) and La$_3$Ga$_{5.5}$Ta$_{0.5}$O$_{14}$ (LGT, langatate). It was determined that growth atmosphere significantly influences optical properties of LGS and LGT [4 - 11], so authors of recent manuscript on Ca-gallogermanate family obligatory point out growth conditions. Origin of color centers in these crystals still remains undefined [11]. The defect centers in oxide crystals are studied for many years and trends in their behavior are determined reliably. However, the response of Ca - gallogermanate crystals on certain external treatments differs from other oxide crystals: for instance, annealing of colored LGT or LGS in vacuum leads to bleaching while opposite behavior is generally observed in other oxide crystal [5, 9, 10].

Recently a new effect was observed in colored LGT – dichroism phenomenon [11]. If dichroism is allowed by the structure of the colored crystal then it will manifest itself by the modification of color or color intensity when the crystal is rotated. This effect is more pronounced when observed in the linearly polarized light. In the crystals with PGS 32 the most dichroic direction is along axis 2 of point group of symmetry. Dichroism is studied by the methods of optical spectroscopy and may be observed for
absorption bands both in visible and UV or IR regions. This phenomenon may be a slight or pronounced, for example, in LGT difference between two transmission spectra obtained in the same direction with the rotation of the sample at 90° reaches about 11% at the absorption band ~480 nm. [12] Thus, dichroism may be quite significant effect and should be taken into account.

Nowadays more and more compounds with Ca-gallogermanate structure are synthesized. One of them, Ca$_3$TaGa$_3$Si$_2$O$_{14}$ (CTGS, catangasite) is very perspective for both high-temperature piezoelectric applications and non-linear optics [13, 14]. At 500 °C CTGS possess high resistivity with value over 10$^8$ Ω·cm and its $R\cdot C$ ($R$ – electrical resistance, $C$ – capacitance) is 2.36, that is approximately by two orders of magnitude higher than that of LGS [13]. These characteristics together with high thermal stability of dielectric and piezoelectric properties reinforces CTGS potential for high temperature and low frequency applications [13]. Moreover, CTGS is a new laser frequency-doubling crystal [14] that may enrich very limited number of multi-functional self-frequency doubling nonlinear laser crystals and expand areas of their applications.

Compounds with Ca-gallogermanate structure crystallize in the P321 space group with formulae A$_3$B$_i$C$_j$D$_k$O$_{14}$, where A is decahedron position, B – octahedral position, symmetry C and D – large and small tetrahedral positions [2]. The crystal structure is characterized by the presence of two layers, which are perpendicular to the axis of 3 order. One layer contains the decahedral and octahedral positions, another – two types of tetrahedral positions.

Ca-gallogermanate compounds are divided into ordered, when all structurally distinct sites are occupied by dissimilar atoms, and disordered, when one type of position is statistically shared by two types of atoms [15]. LGT and LGS are referred to disordered type, and CGTS to ordered one (table 1).

Table 1. Occupancy of the positions by the elements in LGT, LGS and CTGS.

| Crystal           | Type      | Elements’ Positions |
|-------------------|-----------|---------------------|
| La$_3$Ga$_{5.5}$Ta$_{0.5}$O$_{14}$ [16] | disordered | La$^{3+}$ | $\frac{1}{2}$ Ga$^{3+}$ | $\frac{1}{2}$ Ta$^{5+}$ | Ga$^{3+}$ | Ga$^{3+}$ |
| La$_3$Ga$_2$SiO$_{14}$ [2]          | disordered | La$^{3+}$ | Ga$^{3+}$ | Ga$^{3+}$ | $\frac{1}{2}$ Si$^{4+}$ | $\frac{1}{2}$ Ga$^{3+}$ |
| Ca$_3$TaGa$_3$Si$_2$O$_{14}$ [17]   | ordered   | Ca$^{2+}$ | Ta$^{5+}$ | Ga$^{3+}$ | Si$^{4+}$ |

Since LGS, LGT and CTGS belong to different structure types the origin of the defect centers in this crystals may also differ.

For successful optical application of CTGS it’s important to obtain values of crystals optical characteristics with high accuracy. Also exact studies of CTGS optical properties are important to clarify the origin of defect structure and mechanisms of its formation. This will be helpful both for piezo- and optical applications.

Here we present the results of our studies of the optical characteristics of CTGS crystals, grown in different atmospheres taking into account the dichroism effect.

2. Materials and methods

CTGS crystals were grown by the Czochralski technique in an atmosphere of pure Ar or in N$_2$ with the addition of oxygen (1-3)%. The studied samples were in the form of cubes or rectangular parallelepiped, with two faces oriented perpendicular to the crystallographic X-axis (the axis of order 2) and Z-axis (the axis of order 3). Crystal grown in Ar was colorless, in N$_2$+(1-3)%O$_2$ – yellowish colored. All studied crystals were transparent without cracks or visible inclusions.

The samples were measured in the Accredited testing laboratory “Single Crystals and Stock on their Base” (“SCSB”) of the National University of Science and Technology “MISiS” Moscow, Russia, by spectrophotometry in the wavelength range of 250–800 nm using the spectrophotometer “Cary 5000” (“Agilent Technologies”) with the automatic universal measurement accessory (UMA).

3. Influence of the growth conditions on the optical properties
The effect of the growth atmosphere on the color and transmission spectra of LGS, LGT and CTGS crystals was reported [5-7, 11, 13, 14]. First of all it is necessary to describe how growth conditions influence on the coloration of these crystals.

LGT is usually grown in pure Ar, Ar with admixture of O₂, or in air [5, 11], CTGS in N₂ with admixture of O₂ or also in air [13, 14, 18] and LGS is grown in Ar or N₂ with admixture of O₂, in air [6, 7, 19, 20] in Pt or Ir crucibles.

According to [5, 11] LGT coloration enhances with increase of oxygen concentration in growth atmosphere (from colorless at Ar):

\[(\text{Ar, Ir}) \rightarrow (\text{Ar} + (0.5-1)\% \text{O}_2, \text{Ir}) \rightarrow (\text{air} \sim (20\% \text{O}_2), \text{Pt}) \rightarrow (\text{Ar} + 2\% \text{O}_2, \text{Ir})\]  \hfill (1)

As for LGS it’s difficult to create equation similar to (1) because the exact oxygen concentration wasn’t specified in the papers, never the less authors state [6, 7] that oxygen concentration influences color of LGS as well.

Though in [13] authors approve that CTGS color doesn’t depend on growth atmosphere (pure Ar or N₂, N₂+1%O₂) and occurs only due to the material of crucible - yellow in Ir and colorless in Pt. However according to the photos of crystals presented in [13, 14] the color of CTGS gets more intensive as follows (from almost colorless in air, Pt):

\[\text{air, Pt} \rightarrow \text{N}_2^+ + (1-5)\% \text{O}_2, \text{Ir} \rightarrow \text{N}_2^+1\% \text{O}_2, \text{Ir}\]  \hfill (2)

Data on absorption bands in these crystals in connection with crucible material allow to create a table 2 [11, 13, 14].

**Table 2.** LGT, LGS and CTGS absorption bands in connection with the crucible material.

| Effect             | Object      | Wavelength, nm | Ref. |
|--------------------|-------------|----------------|------|
| Induce (OH) bands  | Ir, Ir⁴⁺    | 200-458        |      |
| Observed bands     | LGS         |                | 2920 | [11] |
|                    | P     |                | 290-290 | 1860 | 2920 | SCSB |
|                    | Pt     |                | 290-290 | 370-370 | n/r | 1840 | n/r | 2920 | SCSB |
| CTGS               | Ir     | 340            | 450  | 1790 | - | - | - | - | [13, 14, 18] |
|                    | Pt     | -              | - | - | - | - | - | - | - | [13] |

- a – not observed or not reported in literature date as far as we know
- b – not revealed in laboratory SCSB
- c – absorption band in this wave-length region that is responsible for colour

One can see (table 2) that in case of LGT and LGS the material of the crucible is not the main reason for the coloration. It’s interesting that band at 1798 nm that may be induced by Ir⁴⁺ or Ir⁴⁺ wasn’t reported in LGT or LGS as far as we know, but it was revealed in CTGS. Connections between coloration of CTGS and crucible material probably make sense to be investigated more explicitly.

Transmission spectra of CTGS were presented in [13, 14, 18]. In [13] authors report no absorption bands for CTGS, grown in Pt crucible, and three absorption bands for CTGS, grown in Ir crucible (340, 450, 1790 nm).

The anisotropy of transmission spectra of CTGS was presented in [18]: authors observed no bands in Z direction and one absorption band at 477 nm in X direction. However, the shape of the transmission curves in this work indicates that the thicknesses of the sample in X and Z directions were different.
In our opinion, it is better to present absorption spectra instead of transmission spectra, since absorption spectra take into account the thickness of the sample. Absorption coefficient is calculated by the Burger-Lambert law [21]:

\[ I = I_0 \cdot e^{-\alpha d}, \]

where \( I_0 \) – intensity of incident light, \( I \) - intensity of light transmitted through the sample, \( d \) – sample thickness.

According to [11] in polar X direction dichroism should be taken into account. This means that the sample should be installed into the sample holder in the way so that the light will propagate along the crystallographic axis X (position (1)), and then the sample is rotated by 90° around the axis of propagation of light (position (2)). For each position (figure 1), the transmission spectrum was recorded.

Absorption spectra of CTGS grown in \( \text{N}_2+(1-3)\%\text{O}_2 \) are presented in figure 2. Crystal is almost colourless (Figure 2, a) - the intensity of absorption band at visible wave-range is low.

In the Z axis no absorption bands are observed as well as no dichroism. In the X axis two absorption bands were observed – weak band at \( \sim 360 \) nm and more pronounced at 470-480 nm. These results are in agreement with [18]. The shift of the absorption band maximum with rotation of the sample from \( \sim 470 \) nm at position (1) to \( \sim 480 \) nm at position (2) indicates dichroism.

CTGS grown in \( \text{Ar} \) is colourless (Figure 3) with extremely low absorption band at \( \sim 500 \) nm. In near UV we observe anisotropy of absorption and absorption band at \( \sim 290 \) nm for X direction.

**Figure 1.** Scheme of dichroism study: left – position (1); right – position (2).

**Figure 2.** Absorption spectra of CTGS grown in \( \text{N}_2+(1-3)\%\text{O}_2 \) in the wave-range 250-700 (a) and 300-540 (b): position (1) X "—", Z "—"; position (2) X "- - - -", Z "- - - -".
We used a usual mathematical formula to gain contrast obtained at the two variations of absorption in positions when light propagates along X direction to calculate the degree of dichroism $\Delta$ [22]:

$$\Delta = \frac{D_2 - D_1}{D_2 + D_1}$$

where $D_1$ is the optical density of the light transmitted through the sample in the position (1); $D_2$ - in the position (2).

Dichroism spectra of CTGS are presented in figure 4.

Dichroism degree intensity is extremely low, and it is normal for nearly colorless crystals, though maximum connected with coloration is still at 470 for CTGS grown in N$_2$+(1-3)%O$_2$ and in case of CTGS grown Ar the main extrema are observed in near UV.

Dichroism indicates the anisotropy of colour centres.

4. Conclusions

CTGS crystals were grown in N$_2$+(1-3)%O$_2$ and Ar atmospheres. Crystal grown in pure Ar was colourless and in N$_2$+(1-3)%O$_2$ – yellowish coloured. In the absorption spectra of CTGS grown in N$_2$+(1-3)%O$_2$ the anisotropy was observed: no significant absorption bands were observed in Z direction, but in X direction absorption bands at 360 nm and (470-480) nm were observed. In case of
CTGS grown in Ar atmosphere the absorption band at ~500 nm with extremely low intensity was observed, which was accompanied by the anisotropic absorption band at ~290 nm for X direction.

Dichroism degree intensity is extremely low for these crystals, with maximum connected with coloration at 470 nm for N$_2+(1-3)$%O$_2$ CTGS crystal and in case of Ar CTGS crystal the main extrema are observed in near UV region.

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