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Research Article

Effect of doping on the optical properties of lanthanum-gallium tantalate

Evgeniya V. Zabelina[1], Nina S. Kozlova[1], Oleg A. Buzanov[2]

1 National University of Science and Technology "MISIS", 4-1 Leninsky Ave., Moscow 119049, Russian Federation

2 JSC Fomos-Materials, 16-1 Buzheninova Str., Moscow 107023, Russian Federation

Corresponding author: Evgeniya V. Zabelina (zabelina.ev@misis.ru)

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Abstract

Nominally pure lanthanum-gallium tantalate $La_3Ga_{5.5}Ta_{0.5}O_{14}$ crystals doped with aluminum, silicon and gallium oxide to above stoichiometric content have been grown by the Czochralski technique in iridium crucibles in argon and in agron with addition of oxygen atmospheres. The transmittance spectra of the crystals have been measured on a Cary-5000 UV-Vis-NIR spectrophotometer in the 200–800 nm range. Absorption spectra α(λ) have been plotted on the basis of the experimental data. The absorption spectra of the undoped crystals grown in an oxygen-free atmosphere have one weak absorption band at λ ~ 290 nm. The absorption spectra of the crystals grown in an agron with addition of oxygen have absorption bands at λ ~ 290, 360 and 480 nm. We show that for the crystals grown in an oxygen-free atmosphere, gallium doping to above stoichiometric content reduces the intensity of its only λ ~ 290 nm absorption band. Aluminum doping of the $La_3Ga_{5.5}Ta_{0.5}O_{14}$ crystals grown in an oxygen-free atmosphere significantly reduces the intensity of the λ ~ 290 nm absorption band and increases the intensity of the λ ~ 360 and 480 nm bands. Aluminum doping of the $La_3Ga_{5.5}Ta_{0.5}O_{14}$ crystals grown in an oxygen-containing atmosphere reduces the intensity of the λ ~ 360 and 480 nm bands and increases the intensity of the λ ~ 290 nm absorption band. Silicon doping of these crystals significantly reduces the intensity of the λ ~ 480 nm band and also reduces the intensity of the λ ~ 290 and 360 nm bands.

Keywords

single crystal, lanthanum-gallium tantalate, doping, optical properties, spectrophotometry, transmittance, absorption

1. Introduction

Lanthanum-gallium tantalate crystals ($La_3Ga_{5.5}Ta_{0.5}O_{14}$, LGT) pertain to the group of calcium-gallium germinate structured crystals, point symmetry 32. The structure of LGT can be represented by the chemical formula $A_3BC_3D_2O_{14}$. The *A* positions in the form of Thompson's twisted cubes are occupied by lanthanum ions La^{3+}. The octahedral *B* positions are occupied by gallium ions Ga^{3+} and tantalum ions Ta^{5+}. The bigger and smaller tetrahedral *C* and *D* positions are occupied by gallium ions Ga^{3+} [1–3]. LGT is successfully used in working elements of piezoelectric devices [4–7]. Those elements convert mechanical energy to electric one thus allowing the fabrication of pressure, temperature, vibration, weight, flowrate etc. sensors. Piezoelectric sensors are miniaturized and do not require external power sources. Optical LGT applications may be matrix for rare-earth and transition element doping [8–16], second harmonic generation [17–19] and electrooptical elements [20]. These applications require high and temporally stable quality of crystals for stable operation of devices based thereon. The growth of large-

sized high-quality calcium-gallium germanate structured crystals remains a complex task [6, 21]. Defect centers in the crystals can manifest on the transmittance spectra in the form of absorption bands. Crystal growth atmosphere was shown to have a prevailing effect on the transmittance spectra of LGT crystals [22]. The absorption spectra of crystals grown in an oxygen-free atmosphere have one weak absorption band at λ ~ 290 nm in the near-UV and visible regions. Oxygen addition to the growth atmosphere increases the intensity of that absorption band and produces two absorption bands at λ ~ 360 and 480 nm. The λ ~ 480 nm absorption band delivers the yellow-orange color of the crystals.

It was reported [23, 24] that gallium oxides evaporate during LGT crystal growth leading to high concentrations of gallium and oxygen vacancies in the as-grown crystals. Furthermore there are other processes that occur in the growth chamber. Part of oxygen is spent for the oxidation of crucible material (iridium) and for the complete oxidation of the charge since it can contain tracer amounts of underoxidized components. These processes increase the oxygen depletion of the system.

The nature of defect centers in LGT crystals has not yet been finally clarified. Experimental studies of the transmittance spectra of LGT crystals grown in different atmospheres and annealed in air and in vacuum, X-ray diffuse scattering structural studies of specimens as well as X-ray photoelectron spectroscopy were reported [25]. The results [25] and literary data on the high-temperature behavior of gallium oxides [26] showed that the visible region absorption band at λ ~ 480 nm is caused by F-center type defects ($V_o^{++} + 2e$) and their complexes in the crystals. The origins of the other two bands in the near-UV region at λ ~ 290 and 360 nm are still unknown.

The volatility of gallium oxides is quite sensitive to the oxygen partial pressure in the growth chamber [26], this dependence being nonlinear relative to oxygen percentage in the atmosphere. By adjusting the oxygen partial pressure in the growth chamber one can control gallium oxide evaporation and hence the preferential formation of specific types of defect complexes in the growing crystals. However the presence of oxygen in the growth chamber causes crucible oxidation [27].

Another method of overcoming gallium depletion in the as-grown crystals is adding gallium oxide to the charge in above-stoichiometric quantities.

It could be possible to dope LGT crystals with elements having ionic radii close to that of gallium but less volatile. Such elements can be aluminum and silicon. Gallium in LGT structure can occupy octahedral and tetrahedral positions. The ionic radius of Ga^{3+} in an octahedral position is 0.62 nm and that in a tetrahedral position, 0.47 nm, the ionic radii of Si^{4+} are 0.40 and 0.26, respectively, and those of $Al^{3+}$are 0.54 and 0.39 nm, respectively [28]. According to gallium, aluminum and silicon oxide evaporation data [26, 29, 30], silicon and aluminum oxides have lower evaporation rates than that of gallium under similar conditions.

The aim of this work is to determine the effect of crystal growth atmosphere on the optical properties of LGT crystals doped with aluminum, silicon and gallium to above the stoichiometric content.

2. Specimens and experimental methods

The LGT crystals were grown and the test specimens were prepared by JSC Fomos-Materials. The charge was produced by high-temperature solid state synthesis from the following raw components: tantalum pentoxide and at least 99.99% purity (4N) lanthanum and gallium oxides. The crystals were grown by the Czochralski technique in a modified Kristall-3M unit in iridium crucibles. The charge was melted and the crystals were grown in a pure argon gas protective atmosphere (Ar) and in an argon + 2 vol.% oxygen atmosphere ($Ar + O_2$). Argon gas atmosphere was used for growing nominally pure undoped crystals, crystals with gallium addition to above the stoichiometric content and aluminum doped crystals. $Ar + O_2$ gas atmosphere was used for growing nominally pure crystals and aluminum or silicon doped ones. All the as-grown crystals were transparent and had no cracks, other visible defects or scattering centers as seen in He–Ne laser light. The crystals were cut into specimens in the form of double-side polished 2 mm thick wafers.

The optical properties of the specimens were studied at the certified laboratory "Single Crystals and Stock on their Base" of the National University of Science and Technology "MISIS" (certificate No. ААЦ.Т.00038). The transmittance spectra $T(\lambda)$ of the specimens were recorded at room temperature on a Cary-5000 UV-Vis-NIR spectrophotometer in the 200–800 nm range. The $T(\lambda)$ measurement accuracy was not worse than 1%. Absorption spectra were calculated on the basis of the experimental data using the formula

$$\alpha = -\frac{1}{d} \ln T, \quad (1)$$

where d is the specimen thickness, mm.

3. Results and discussion

All the LGT crystals grown in an oxygen-free atmosphere were colorless regardless of doping. The specimens grown in an oxygen containing atmosphere had orange except for the silicon doped ones which were colorless.

The absorption spectra of the LGT specimens are shown in Fig. 1. The absorption spectra of the undoped LGT specimens grown in an argon gas atmosphere exhibit one weak absorption band at λ~290 nm (Fig. 1 *a*). The crystals grown in an argon + oxygen atmosphere exhibit absorption bands at λ ~ 290, 360 and 480 nm (Fig. 1 *b*).

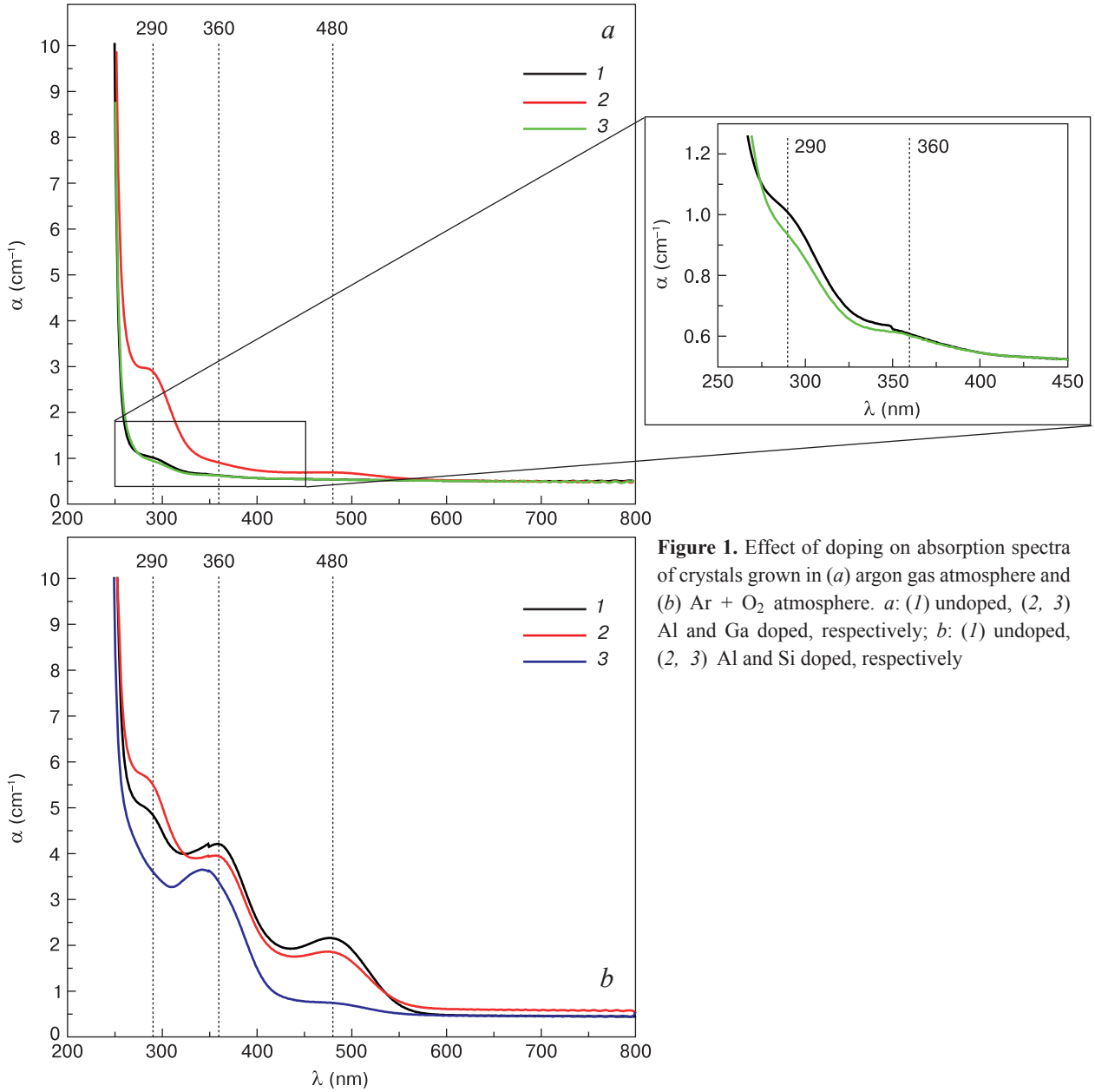

Figure 1. Effect of doping on absorption spectra of crystals grown in (*a*) argon gas atmosphere and (*b*) Ar + O_2 atmosphere. *a*: (*1*) undoped, (*2, 3*) Al and Ga doped, respectively; *b*: (*1*) undoped, (*2, 3*) Al and Si doped, respectively

Gallium oxide doping to above the stoichiometric content of the crystals grown in an argon gas atmosphere slightly reduces the intensity of the absorption band at λ ~ 290 nm (Fig. 1 *a*, callout).

Aluminum doping of the LGT crystals grown in an oxygen-free atmosphere significantly reduces the optical quality of the crystals, greatly increasing absorption near the λ ~ 290 nm band, increasing absorption at the λ ~ 360 nm and producing a band at λ ~ 480 nm (Fig. 1 *a*). The significant growth of the absorption intensity indicates a higher concentration of defect complexes.

Aluminum doping of the LGT crystals grown in an Ar + O_2 atmosphere significantly increases the λ ~ 290 nm absorption band intensity and slightly reduces the intensity of the λ ~ 360 and 480 nm absorption bands.

Silicon doping of the LGT crystals grown in an oxygen containing atmosphere increases spectral transmittance over the whole wavelength range studied. The most pronounced effect of doping is observed at λ ~ 490 nm: the intensity of that band decreases dramatically (Fig. 1 *b*).

Thus, the optical quality of the LGT crystals grown in an argon gas atmosphere is improved by gallium doping to above the stoichiometric content. For the crystals grown in an oxygen containing atmosphere, silicon doping reduces the intensity of all the three absorption bands, the reduction being the greatest near the λ ~ 490 nm absorption band.

4. Conclusion

Nominally pure LGT crystals and LGT crystals doped with aluminum, silicon and gallium to above stoichiometric content were grown in argon and Ar + O_2 atmospheres.

Spectrophotometric studies showed that the LGT crystals grown in an argon gas atmosphere have the highest optical quality. The transmittance spectra of these crystals have one absorption band at 290 nm. The LGT crystals grown in an Ar + O_2 atmosphere are less perfect: the transmittance spectra of those crystals contain clearly expressed bands at λ ~ 290, 360 and 480 nm.

Methods of reducing the intensity of the absorption bands in the transmittance spectra were found. For example, the intensity of the only absorption band at λ ~ 290 nm for the LGT crystals grown in an argon atmosphere can be reduced by gallium doping to above the stoichiometric content. For the LGT crystals grown in an Ar + O_2 atmosphere, silicon doping increases transmittance near all the three absorption bands and significantly reduces the absorption intensity near the λ ~ 490 nm band.

Aluminum doping reduces the optical quality of the LGT crystals grown in an oxygen-free atmosphere: the transmittance spectra exhibit a significant increase in the λ ~ 290 nm absorption band intensity, and bands at λ ~ 360 and 480 nm emerge. For the crystals grown in an Ar + O_2 atmosphere, aluminum doping also increases the λ ~ 290 nm absorption band intensity but reduces the intensity of the λ ~ 360 and 480 nm absorption bands.

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