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Research Article

Luminescence in lanthanum-gallium tantalate

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Abstract

The optical and luminescent properties of undoped $La_3Ga_{5.5}Ta_{0.5}O_{14}$ lanthanum- gallium tantalate crystals grown in different atmospheres of pure argon gas and argon gas with different oxygen percentages have been studied. The optical absorption α(λ) spectra that characterize integral absorption and reflection have been measured in the 250–700 nm region. The spectral absorption functions have been calculated from the measured α(λ) spectra using the Kubelka–Munk formula. Luminescence has been observed in all the test specimens over a wide spectral region (375 to 650 nm) at 95 and 300 K. The luminescence spectra of the test crystals have a fine dispersed pattern represented by low-intensity discrete luminescence peaks. The 95 K luminescence peak maxima are more pronounced and shifted towards shorter wavelengths by ~16 nm (~0.1 eV) relative to the respective room temperature peaks. The crystal growth atmosphere has been demonstrated to largely affect the luminescent properties of the crystals: the higher the oxygen concentration in the growth atmosphere, the lower the luminescence intensity due to concentration quenching, the luminescence peak maxima shifting towards longer wavelengths. The positions of discrete luminescence peaks have been shown to correlate with the main 420 and 480 nm absorption bands with the respective ~20 nm (~0.2 eV) Stokes shift for crystals grown in different atmospheres. The luminescence in lanthanum-gallium tantalate crystals is a complex process involving several luminescence mechanisms.

Keywords

langatate, lanthanum-gallium tantalate, luminescence, optical properties

1. Introduction

$La_3Ga_{5.5}Ta_{0.5}O_{14}$ lanthanum-gallium tantalate (langatate, **LGT**) is a synthesized crystalline material having a calcium-gallium germanate structure which is a promising crystal matrix for the fabrication of active laser components [1, 2]. A number of crystals having this structure have been synthesized, with LGT being the best studied ones along with $La_3Ga_5SiO_{14}$ lanthanum-gallium silicate. Initially the synthesis conditions for these crystals did not provide for high optical quality thus limiting their laser applications. Furthermore it was impossible for a long time to obtain luminescence parameters of single crystal LGT specimens either by thermal activation or using any other activation methods.

However the quality of crystals having a calcium-gallium germanate structure has been significantly improved by now [3, 4], and the effect of growth conditions on the optical properties and homogeneity of these crystals has been described [4–11]. The defect formation and color center generation model proposed for LGT [12] can become the starting point for a new cycle of research toward

potential LGT applications as active media for lasers and hence studies of the luminescent properties of these crystals are of a special interest. Luminescence has now been obtained in rare-earth element doped langatate crystals e.g. Ho, Eu, Sm, Er, Yb [13–21]. However, the luminescent properties of the undoped LGT crystal matrix and the effect of crystal synthesis conditions on these properties have yet been studied insufficiently.

The aim of this work is to study the luminescence in langatate crystals, assess the effect of growth atmosphere on the luminescent properties of the crystals and analyze the effect of excitation parameters on the luminescence spectra.

2. Experimental

The absorption and diffuse reflection spectra were measured on a Cary 5000 spectrometer (Varian, Australia) with a DRA 2500 photometric sphere attachment (Labsphere, USA) [22–24]. The luminescence spectra excited by the YAG : Nd^{3+} laser third harmonic (λ_{ex} = 355 nm) were studied with an MDR23 indexer-driven monochromator, a 1200-II mm^{-1} diffraction grating and a FEU-79 signal receiver. The basic diagram of the experimental setup is shown in Fig. 1. The pulse frequency and duration were 10 Hz and 5 ms, the measurements being carried out at 95 and 300 K.

The spectra were taken from the flat-parallel surface of the $\{10\bar{1}0\}$ polar cut LGT crystals grown in different atmospheres. The crystals were grown by the Czochralski method at JSC Fomos-Materials in iridium crucibles in Ar, Ar + 0.5 % O_2 and Ar + 2 % O_2 gas atmospheres.

3. Results and discussion

The luminescence spectra of the LGT crystals grown in different atmospheres at T = 95 and 300 K are shown in Fig. 2.

Room temperature luminescence was observed over a wide spectral region, i.e., 375 to 650 nm (3.2 to 2 eV), the luminescence maximum being near 440 nm (2.8 eV). At least five luminescence peaks were observed at 380, 420, 440, 460 and 500 nm which are quite weak at room temperature presumably due to temperature quenching. These luminescence peaks were observed for all the studied crystals. However, the luminescence peaks shifted towards longer wavelengths by ~6 nm (~0.04 eV) with increasing oxygen concentration in the growth atmosphere.

LN temperature luminescence in the crystals was observed in the same wide spectral region, i.e., 375 to 650 nm, but the luminescence peak maxima were more pronounced and shifted towards shorter wavelengths by ~16 nm (~0.1 eV) relative to the respective room temperature peaks. The intensity of both the 300 and 95 K luminescence peaks decreased with increasing oxygen con-

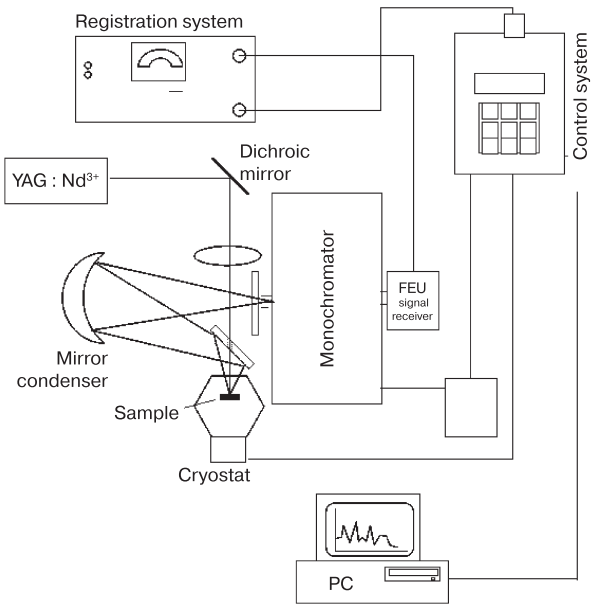

Figure 1. Schematic of luminescence spectrum measurement setup.

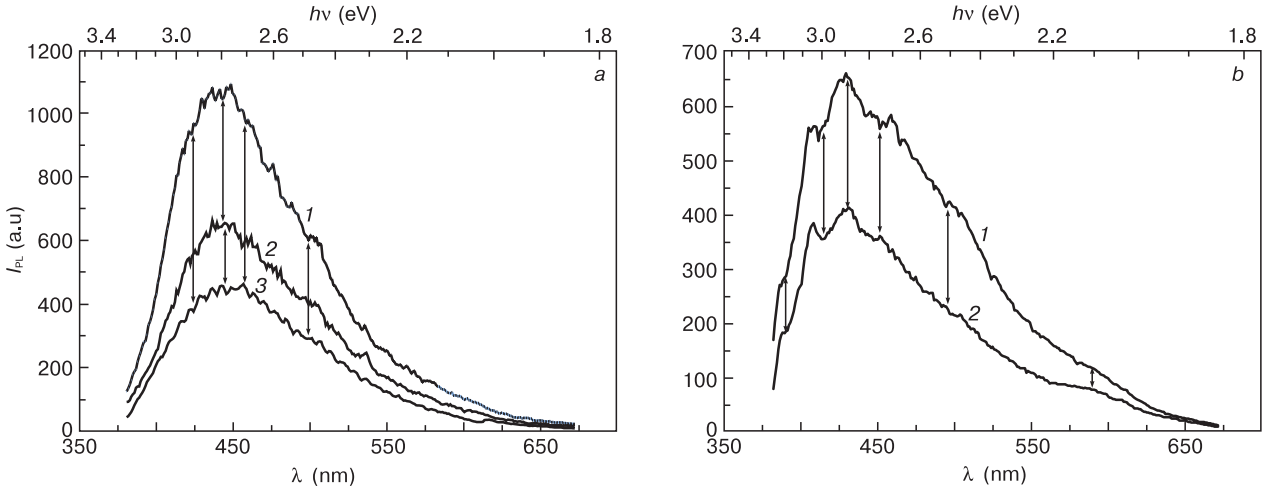

Figure 2. λ_{ex} = 355 nm luminescence spectra of LGT crystals grown in different atmospheres for (*a*) 300 and (*b*) 95 K. *a*: (*1*) Ar; (*2*) Ar + 0.5 % O_2; (*3*) Ar + 2 % O_2; *b*: (*1*) Ar; (*2*) Ar + 2 % O_2.

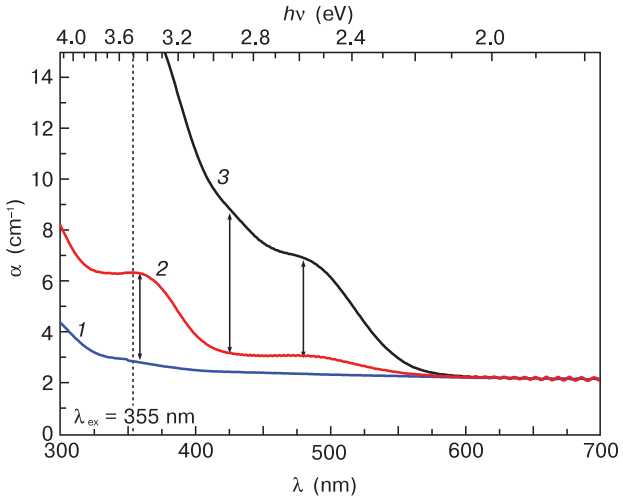

Figure 3. Luminescence spectra of LGT crystals grown in different atmospheres: (*1*) Ar; (*2*) Ar + 0.5 % O_2; (*3*) Ar + 2 % O_2.

centration in the growth atmosphere. This is probably due to the oxygen concentration quenching of luminescence.

This phenomenon is quite similar to the optical absorption in LGT crystals [10]. The intensity of the absorption bands observed in LGT crystals at 360, 420 and 480 nm grew with increasing oxygen concentration in the growth atmosphere (Fig. 3). These bands were attributed to defect structure formation in the LGT crystals, more specifically, to the formation of color centers.

Since α(λ) optical absorption spectra give an integral characterization of absorption and reflection we calculated the absorption spectra using the Kubelka–Munk formula $F(R)$ (Eq. (1)) from the experimental diffuse reflection spectra [23]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{a}{s}, \qquad (1)$$

where R is the diffuse reflection coefficient, R is the absorption coefficient and s is the light scattering coefficient.

These absorption spectra have a higher resolution in the entire experimental frequency range and provide more accurate interband electron transition energies [25].

Figure 4 shows absorption, luminescence and diffuse reflection spectra suggesting that the positions of discrete luminescence peaks correlate with the main 420 and 480 nm absorption bands with the respective ~20 nm (~0.2 eV) Stokes shift for crystals grown in different atmospheres.

A specific feature of the luminescence spectra for all the abovementioned crystals is their fine dispersed pattern represented by low-intensity discrete luminescence peaks spaced from one another by 0.03 eV on average. A similar spectral pattern was observed for the absorption spectra recalculated using the Kubelka–Munk formula. The discreteness of these peaks suggests that they are generated by exciton pairs.

Results of Gauss analysis with maximum position calculation for each of the spectra are shown in Table 1.

An increase in the oxygen concentration in the growth atmosphere regardless of the excitation parameters caused the luminescence peak maxima to shift towards longer wavelengths, i.e., the state of the luminescence generating centers changed.

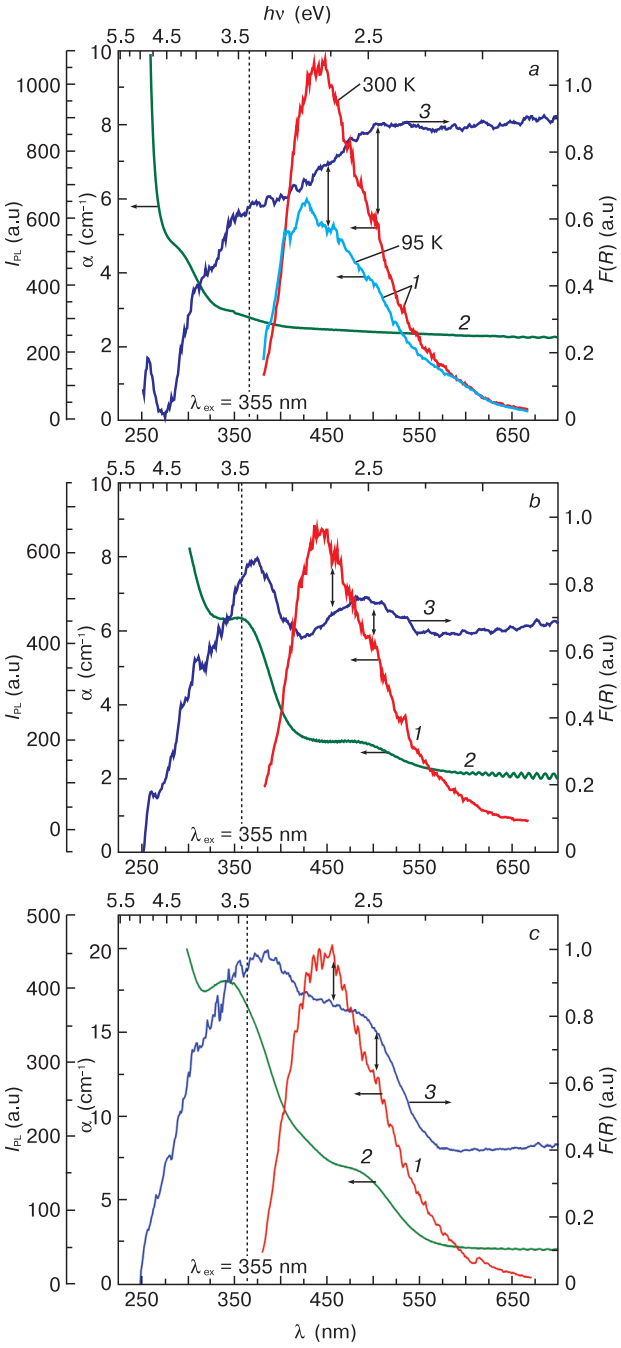

Figure 4. (*1*) I_{PL} luminescence, (*2*) absorption R and (3) Kubelka–Munk function $F(R)$ spectra for LGT crystals grown in different atmospheres: (*a*) Ar; (*b*) Ar + 0.5 % O_2; (*c*) Ar + 2 % O_2.

Table 1. Positions of luminescence spectra maxima depending on growth atmosphere and excitation temperature.

Growth atmosphere	λ, nm	
	300 K	95 K
Ar	439	428
Ar + 0.5 % O_2	442	429
Ar + 2 % O_2	445	430

The 300 K luminescence spectra are not elementary (Fig. 2*a*) and can be decomposed into three Gaussian components. The positions of their maxima (*C*) and halfwidths (Δ) are shown in Table 2. The presence of three Gaussian components suggests that there are three mechanisms responsible for luminescence. The Gaussian peaks for the crystals grown in Ar + 0.5 % O_2 atmosphere are shifted towards longer wavelengths compared to the crystal grown in argon atmosphere, the peak halfwidths decreasing. An increase in the oxygen content in the growth atmosphere to 2 % causes Gaussian maxima shifting towards shorter wavelengths, their halfwidths decreasing dramatically.

The LN temperature luminescence peaks resolve six Gaussian peaks. Unlike for the room temperature peaks increasing the oxygen content in the growth atmosphere to 2 % at LN temperature leads to Gaussian maxima shifting towards longer wavelengths (Table 3), the halfwidths of most peaks decreasing significantly.

These results suggest that the luminescence in lanthanum-gallium tantalate occurs by multiple mechanisms which require a more detailed study.

Table 2. Positions of maxima and halfwidths of Gaussian luminescence peaks depending on growth atmosphere for 300 K excitation temperature.

No. peaks	*C*, nm	Δ, nm	*C*, nm	Δ, nm	*C*, nm	Δ, nm
	Ar		Ar + 0.5 % O_2		Ar + 2 % O_2	
1	428	48	471	71	534	115
2	433	45	485	65	541	97
3	414	32	444	53	487	98

Table 3. Positions of maxima and halfwidths of discrete luminescence peaks depending on growth atmosphere for 95 K excitation temperature.

No. peaks	*C*, nm	Δ, nm	*C*, nm	Δ, nm
	Ar		Ar + 2 % O_2	
1	386	14	414	8
2	402	14	411	25
3	421	25	431	9
4	449	39	451	31
5	489	55	492	115
6	541	107	589	54

4. Conclusion

Luminescence parameters were for the first time obtained for langatate single crystals grown in different atmospheres. The luminescent and optical properties of lanthanum-gallium tantalate crystals were studied at 95 and 300 K for different growth atmosphere.

Growth atmosphere was found to dramatically affect the luminescence intensity: with increasing oxygen concentration in the growth atmosphere the luminescence intensity decreased as a result of concentration quenching.

We stated that a specific feature of the luminescence centers in the test crystals is their fine dispersed pattern consisting of low-intensity discrete luminescence peaks spaced from one another by 0.03 eV on average and presumably attributed to the exciton structure of the luminescence centers.

Gauss analysis showed that with increasing oxygen concentration in the langatate growth atmosphere the luminescence peak maxima of these crystals shift towards longer wavelengths. The luminescence in lanthanum-gallium tantalate crystals is a complex process involving several radiation mechanisms which require a more detailed study.

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