ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2020, Vol. 84, No. 7, pp. 780–782. © Allerton Press, Inc., 2020.
Russian Text © The Author(s), 2020, published in Izvestiya Rossiiskoi Akademii Nauk, Seriya Fizicheskaya, 2020, Vol. 84, No. 7, pp. 948–950.

IR-to-THz Down Conversion in Nonlinear GaSe:Al Crystals

D. M. Lubenko[a, *], D. M. Ezhov[b], V. F. Losev[a], Yu. M. Andreev[c], and G. V. Lanskii[c]

[a] *Institute of High Current Electronics, Siberian Branch, Russian Academy of Sciences, Tomsk, 634055 Russia*

[b] *National Research Tomsk State University, Tomsk, 634050 Russia*

[c] *Institute of Monitoring of Climatic and Ecological Systems, Siberian Branch, Russian Academy of Sciences, Tomsk, 634055 Russia*

**e-mail: lubenkodm@gmail.com*

Received February 14, 2020; revised March 16, 2020; accepted March 27, 2020

Abstract—The optical properties and hardness of GaSe, GaSe:Al, GaSe:S:Al, and GaSe:Al:O crystals are studied to create effective terahertz radiation generators. Doped crystals differ from pure GaSe in high mechanical and optical properties at a optimum doping level. Oxygen doping allows wide ranging changes in birefringence in the terahertz range.

DOI: 10.3103/S1062873820070163

INTRODUCTION

All three type of crystals: pure and doped with isovalent impurities GaSe, as well as their solid solutions with acceptable mixing ratios, are typical representatives of III–VI compounds prone to the formation of crystal structures with point symmetry group $\bar{6}2m$ [1]. Having pronounced layering, they are characterized by a high anisotropy of optical properties [2] and have a birefringence value of $B = 0.34$ in the main transparency window of 0.62–20 μm. They are also transparent in a wide part of the terahertz (THz) range from 60 μm or more. Due to its unusually wide transmission region, high nonlinear coefficient of $d_{22} = 54$ pm V^{-1}, and strong birefringence, pure and doped GaSe crystals and their solid solutions are used to generate THz radiation using nonlinear crystal optics upon pumping from the near IR to the low-frequency part of the THz range [3–5]. However, the layered structure and extremely low cleavage of the layers result in poor mechanical properties and a strong tendency toward delamination and deformation, which limits the scope of their application to laboratory conditions.

Deep doping (the growth of solid solutions) with S, Te, and In isovalent impurities [6–8] allows us to control the range of transparency; linear [9, 10] and nonlinear properties (and thus phase matching conditions), but it also modifies mechanical properties slightly. Studies of the modification of properties (primarily mechanical) due to Al alloying revealed a wise scatter of data [11, 12]. The physical properties of crystals doped simultaneously with two chemical elements of different groups of the periodic table have not yet been studied.

Aluminum [13] and oxygen do not form solid solutions with GaSe and GaSe:S and can be only minor dopants. We therefore studied the optical properties of GaSe:Al, GaSe:S:Al, and GaSe:Al:O crystals as promising materials for frequency converters from the main transmission window to the THz range.

ALUMINUM-DOPED GaSe CRYSTALS

Samples of GaSe:Al crystals from the same boules as in [11, 12, 14] were used in this work. Their optical properties were studied with state-of-the-art equipment: an Agilent Cary 5000 spectrophotometer (spectral range 175–3300 nm), a Simex FT-801 Fourier spectrometer (Russia; spectral range 470–5700 cm^{-1} (or 21–1.8 μm); resolution, 0.5 cm^{-1}; signal-to-noise ratio, no less than 40000 (in the range of 2000–2200 cm^{-1}); and a Zomega Z-3 time-domain spectrometer (Zomega, United States; spectral range 0.1–3.5 THz).

Our studies confirmed that Al doping increases the hardness of crystals by as much as 400%; i.e., it virtually eliminates their main drawback. This is due to the formation of a metal bond between small Al atoms upon introducing them into the interstitial sites of GaSe structures. At optimum doping, the established drop in the optical loss coefficient is due to the formation of strong Al–Al bonds of a chain type reducing the number of structural defects. At optimum doping, we would expect an increase in the efficiency of frequency conversion, due to an improvement in optical quality.

We also found that an increase in doping rapidly leads to degradation of the optical quality of GaSe. We

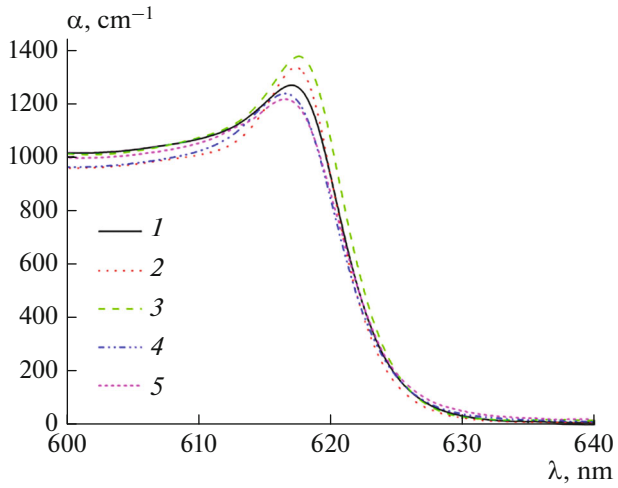

Fig. 1. Determination of the optical quality of crystals using the maximal steepness of the short-wavelength boundary of the transmission spectrum: (*1*) GaSe, (*2*) GaSe:Al (0.01 at %), (*3*) GaSe:Al (0.05 at %), (*4*) GaSe:Al (0.2 at %), and (*5*) GaSe:Al (0.5 at %).

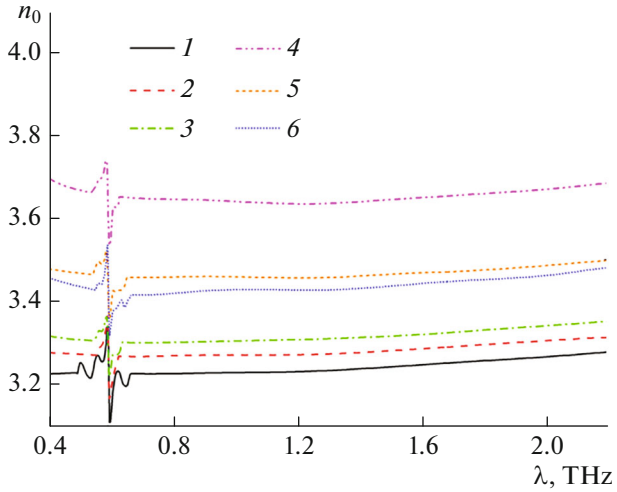

Fig. 2. Phonon absorption spectra of GaSe:Al:O crystals: (*1*) GaSe, (*2*) GaSe:Al 0.01%, (*3*) GaSe:Al 0.02%, (*4*) GaSe:Al 0.5%:O, (*5*) GaSe:Al 0.5%, and (*6*) GaSe:Al 0.01%:O.

believe the reason for this is the absence in nature of the AlSe compound isostructural to GaSe [13] and thus the emergence of a large number of Al precipitates [12].

Using a variety of growth technologies, Huang et al. [15] obtained relatively high-quality GaSe:Al samples at a Al content of no more than 0.5 at % at starting charge. Considerable precipitation of Al precipitates in the crystal and a corresponding degradation of quality were observed in the 0.37 to 2 at % at starting charge range of the concentration [15]. Note that the question of the actual Al impurity content remains open, due to the limited accuracy of the measuring equipment that were used, and the obtained results are rather qualitative. Using the Bridgman approach with rotation of the thermal field, a GaSe:Al crystal homogeneous in structure and composition (0.27 at %) and 2.6 times harder than a pure GaSe crystal was obtained in [15]. The crystal could be cut in any direction and polished. The coefficient of absorption of a sample 5.5 mm thick does not exceed 0.1 cm^{-1} in the range of 0.83–14 μm, testifying to its high optical quality.

Our analysis showed that the level of Al doping that does not lower optical quality relative to pure crystals (or even slightly improves it) is no more than 0.01 at %. Since determining differences in the coefficients of absorption in the main transmission window is complicated by the Al content's proximity to the threshold of the measured values, the optimum Al content was measured by several means for the sake of clarity. Measuring the time required to establish the stationary temperature of the crystal placed in an evacuated chamber was used in particular. Control measurements were made and crystals with the smallest optical losses were chosen by estimating the absorption peaks outside the range of maximum transparency (i.e., the exciton (Fig. 1) and phonon (Fig. 2) absorption peaks for samples 50 μm thick).

Crystals with the maximum steepness of the boundary between the UV and visible ranges were found to have the best optical quality. The control determination of the best crystal quality was performed according to the minimum time needed to establish the stationary temperature of a crystal irradiated with a radiation intensity-stabilized beam. The coefficient of absorption was in this case calculated using the time required for the stationary temperature to be established. Using these indirect means, the optimum doping level of GaSe crystals for the generation of THz radiation was found to lie in the range from 0.002 to 0.01 at %.

Note that a low level of Al doping does not affect nonlinear properties, but it does increase the resistivity of GaSe crystal, reducing optical losses. The resistivity of crystal samples lies in the range of 10^5–10^7 Ω cm, which is 3–5 orders of magnitude higher than that of undoped crystals. The concentration of free charge carriers and the anisotropy of conductivity along and orthogonal to the growth layers determine the contribution from plasmon absorption to the optical properties of pure and doped nonlinear GaSe crystals in the THz range and their strong anisotropy, primarily in the long-wavelength part of the THz range. Upon an increase in the concentration of charge carriers, the boundary of their transmission spectrum shifts to the region of short wavelengths while losses in the THz range increase. For example, Al doping at the level of hundredths–thousandths of an atomic percent is able to change the concentration of free charge carriers within 5–7 orders of magnitude, which increases the

refractive index for an normal wave and the birefringence in the THz range by as much as 50%. Based on this, we propose a way of controlling the dispersion properties for waves of ordinary polarization and birefringence in the THz range. The latter is virtually independent of the properties in the main transparency window, where the optical losses remain relatively low for such a content of free charge carriers, at least in the thin samples used for the frequency conversion of ultrashort radiation pulses. The aim of the proposed approach is to control the concentration of free charge carriers and their contribution to dielectric properties by controlling the level of Al doping.

GaSe DOPED WITH TWO CHEMICAL ELEMENTS

There is a strong change in the properties of a GaSe crystal upon double doping with aluminum and oxygen (GaSe:Al:O). The optical losses in this case rise sharply in the THz range at the optimum Al content and an oxygen excess of more than 0.01 at %, which is typical of oxygen-containing crystals. However, the rise in losses may not have a noticeable effect on the efficiency of generating ultrashort THz radiation pulses when crystals with submillimeter thicknesses are used. More important is the substantial increase in nonlinear properties during double doping when one of the additives is oxygen.

Among GaSe crystals doped with two elements, the GaSe:S (2.5 mass %):Al (0.002 at %) crystal was found to have the highest radiation resistance and efficiency. It simultaneously displayed a 75% increase in hardness, a 2–3 times reduction in the loss coefficient, and a 3–5 times increase in the efficiency of THz radiation generation.

CONCLUSIONS

We studied the optical properties and hardness of pure and Al-doped nonlinear GaSe, GaSe:S:Al, and GaSe:Al:O crystals. In terms of improving the optical and mechanical properties, the optimum level of GaSe doping with aluminum was found to be within 0.002–0.01 at %. The optimum level of GaSe crystal doping with sulfur and aluminum is GaSe:S (2.5 mass %):Al (0.002–0.01 at %). When doped with aluminum and oxygen, it is GaSe:Al (0.002–0.01 at %): O (0.01 at %).

FUNDING

This work was supported by the Russian Science Foundation, project no. 19-19-00241.

REFERENCES

1. Palik, E.D., in *Handbook of Optical Constants of Solids*, San Diego: Academic, 1997, p. 473.
2. Fernelius, N.C., *Prog. Cryst. Growth Charact. Mater.*, 1994, vol. 28, no. 4, p. 275.
3. Huber, R., Brodschelm, A., Tauser, F., and Leitenstorfer, A., *Appl. Phys. Lett.*, 2000, vol. 76, no. 22, p. 3191.
4. Shi, W., Ding, Y.J., Fernelius, N., and Vodopyanov, K., *Opt. Lett.*, 2002, vol. 27, no. 16, p. 1454.
5. Tochitsky, S.Y., Sung, C., Trubnick, S.E., et al., *J. Opt. Soc. Am. B*, 2007, vol. 24, no. 9, p. 2509.
6. Allakhverdiev, K.R., Guliev, R.I., Salaev, E.Yu., and Smirnov, V.V., *Sov. J. Quantum Electron.*, 1982, vol. 12, no. 7, p. 947.
7. Shigetomi, S. and Ikari, T., *J. Appl. Phys.*, 2004, vol. 95, no. 11, p. 6480.
8. Suhre, D.R., Singh, N.B., Balakrishna, V., et al., *Opt. Lett.*, 1997, vol. 22, no. 11, p. 775.
9. Zhang, H.-Z., Kang, Z.-H., Jiang, Y., et al., *Opt. Express*, 2008, vol. 16, no. 13, p. 9951.
10. Feng, Z.-S., Kang, Z.-H., Wu, F.-G., et al., *Opt. Express*, 2008, vol. 16, no. 13, p. 9978.
11. Zhang, Y.-F., Wang, R., Kang, Z.-H., et al., *Opt. Commun.*, 2011, vol. 284, no. 6, p. 1677.
12. Guo, J., Xie, J.-J., Zhang, L.-M., et al., *Cryst. Eng. Commun.*, 2013, vol. 15, no. 32, p. 6323.
13. Howe, J.M., *Bull. Alloy Phase Diagrams*, 1989, vol. 10, no. 6, p. 650.
14. Guo, J., Xie, J.-J., Zhang, L.-M., et al., *J. Mater. Sci. Mater. Electron.*, 2014, vol. 25, no. 4, p. 1757.
15. Huang, C.B., Mao, M.S., Wu, H.X., et al., *J. Cryst. Growth*, 2018, vol. 483, p. 318.

Translated by A. Ivanov