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Complex Compounds of Phthalocyanines and Transition Metal Halogenides Applied as Nonlinear Filters for Ruby Lasers

Part I

Complex Compounds of Phthalocyanines and Aluminium Chloride

The applicability of the above complex compounds has been investigated, and the half-width of the monopulse duration determined.

A possible application of complex compounds of phthalocyanine and aluminium chloride as nonlinear filter for ruby lasers has been examined. The time half-width of the produced monopulses and their energy has been determined.

The duration of a light pulse emitted by solid-state lasers ranges from several μs to several ms. The pulse consists of a series of single shots (flares) of short life-time. The energy contained in such a pulse is distributed among the particular subpulses, while their power is relatively low, due to the long emission time.

However, there exists a possibility of a considerable reduction in the emission time to about 10^{-7} – 10^{-3} s, with a relatively small decrease in laser beam energy. The power of such a shortened laser pulse, which is commonly called a gigant pulse, may exceed that of a freely generated pulse by a factor of several millions.

In practice, the laser Q-switching technique is realized in various ways, e.g. by optical shutters (like Kerr cells or Pockles cells). Another method consists in applying mechanical shutters, like rotating prisms or disks (the latter being supplied with properly cut holes). The requirements imposed on the laser shutter operation are usually very high.

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They are expected to assure a rapid increase in Q-factor of the resonator and possibly small losses in energy after the shutter is opened.

It is well known that the laser action develops not earlier than in 20–80 ms after a high value of Q-factor in the resonator is achieved. Consequently, the time needed for a complete opening of the shutter should be less than 20 ns. A slower maximizing of Q-factor results in excitation of several consecutive pulses and the laser action ceases to be a single-pulse of gigant type [1].

An employment of the optical and mechanical shutters, mentioned above, is usually connected with all kind of technical difficulties. The mechanical shutters are especially troublesome in operation, due to the necessity of applying the suitable engines and synchronization systems, whereas, the electro-optic shutters must be driven by the corresponding generators.

In view of the above difficulties the use of shutters based on solutions of organic dyes appeared to be particularly convenient.

In ruby lasers the following substances are most commonly used as passive filters: solutions of cryptocyanines [2–5] and phthalocyanines of various metals [6–10] and glass filters doped with selenides and cadmium sulphides. A cuvette filled with the solution of the respective dye is placed between the active element of the laser and one of its mirrors.

The solution strongly absorbs the light of the wavelength emitted by the laser. The laser action may be developed when (as a result of the intense pumping) the population of the upper laser level becomes so numerous that the gain in the active medium exceeds the absorption loss in the dye solution. The laser action, though initially weak, is however, sufficient to a rapid bleaching of the dye, due to quick saturation of the absorption transitions, which in turn results in shifting of the absorption band beyond the spectrum of the emitted laser beam. The recovered high value of the Q -factor in the resonator enables a rapid development of the laser action and the whole energy accumulated in the active medium may be emitted in form of one or several light pulses. Thereafter, the dye molecules are quickly brought back to their initial state and the dye may be used anew.

The so far used cryptocyanine dyes, though simple in exploitation, exhibit one serious shortcoming — being instable chemically. Consequently, after each "shot" a part of the dye within the light beam region is destroyed. The passive cryptocyanine filters may not be used in whenever a good reproducibility of the results as well as a long durability of the filtering material are required.

The dyes of the phthalocyanine group characterized by a good chemical stability do not decompose due to laser irradiation, even of great power. Their only disadvantage is a poor solubility in the commonly used organic solvents. Consequently, the usage of such solvents like alcohols, ether, acetone or benzene is impossible, as the achievable concentrations range between 10^{-7} mol/l — 10^{-9} mol/l. To assure a proper transmission thick filtering layers ought to be used.

Nitrobenzene proved to be one of the best organic solvents for the phthalocyanine. The obtained concentrations range within 10^{-3} – 10^{-6} mol/l, depending on the type of phthalocyanine.

When looking for new chemical compounds to be applied as nonlinear filters for ruby lasers a series of complex compounds of phthalocyanine of p and d transition metal halogenides has been obtained. The molecule of phthalocyanine serves as an electron donor, while the transition metal halogenide plays a part of an electron acceptor. In the polar or anhydrous medium these compounds form complexes of ionic structure, this has been stated by spectroscopic examination as well as by measuring the electrolytic conductivity.

Thus, in the process of complexing some new chemical individuals appear, which because of their ionic structure exhibit a good solubility in the polar orga-

nic solvents, such as nitrobenzene, chlorobenzene, chloronitrobenzene and so on. The solubility increases by 2 to 4 orders of magnitude, depending on the type of the complex. This fact, enabling to obtain nonlinear filters of small thickness of the absorbing layer to 0.1 mm, seems to be important for the reduction in the losses of laser beam energy caused by inserting the filter into the resonator. so far, we have obtained tens of various complex compounds of phthalocyanine and different metal halogenide. E.g. the following, (among others) phthalocyanines were used as electron donors in our laboratory: non-metallic phthalocyanine (H_2Pc), sodium phthalocyanine (Na_2Pc), copper phthalocyanine ($CuPc$) chloroaluminium phthalocyanine ($AlClPc$), chloroferric phthalocyanine ($FeClPc$) chlorogallium phthalocyanine ($GaClPc$), hydroxychromium phthalocyanine ($CrOHPc$) and chlorovanadium phthalocyanine ($VClPc$). On the other hand, (as the electron acceptors) the following transition metal halogenides were employed: $AlCl_3$, $AlBr_3$, $GaCl_3$, VCl_3 , $SnCl_2$, $FeCl_3$, $SnCl_4$, $SbCl_5$ and others. The complex compounds obtained were spectroscopically examined in order to determine their chemical structure and to select the compounds of absorption bands overlapping the ruby laser line $\lambda_n = 694.3$ nm (Fig. 1). Results obtained from spectral data are given in [11–13].

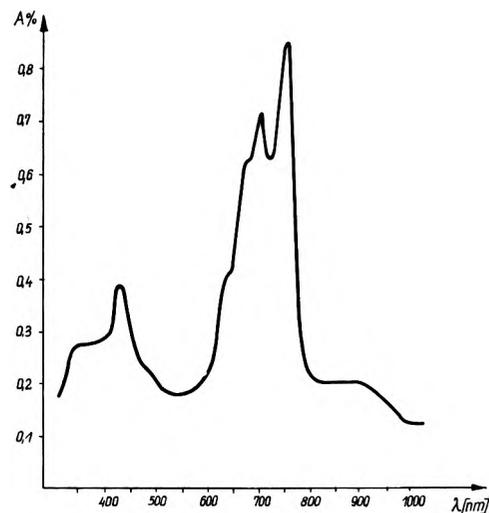


Fig. 1. Absorption spectrum of the $Na_2PcAlCl_3$ complex in nitrobenzene

The laser examinations of the complexes obtained in our Laboratory have not been accomplished yet. Hereafter, the results obtained for complex compounds of phthalocyanine and aluminium chloride are presented.

The laser measurements were performed with the help of a system shown in Fig. 2. Initially, we have examined the reproducibility of the laser energy

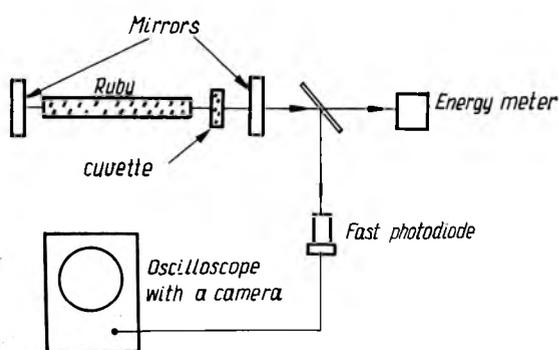


Fig. 2. Scheme of the measuring system for examination of non-linear filters

values under the free-generation condition in the course of 40 consecutive shots performed at a 5-minute intervals. It should be emphasized that the shot energy of a freely generating laser changed only slightly its value within the time interval between the first and the last shots.

The relations obtained are presented in Fig. 3. Further measurements were made with this type of laser. The cuvette of thickness $d = 1$ mm was filled with the nitrobenzene solution of the complex

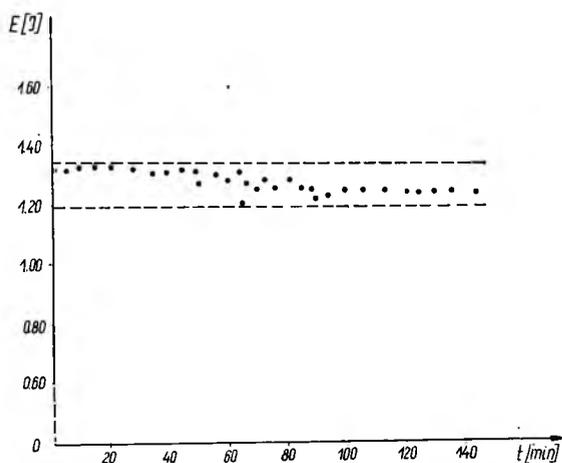


Fig. 3. Dependence of the free-generating laser energy upon the number of shots performed in the 5 min intervals

compound. The monopulse obtained was observed on an oscilloscope display, its photograph being simultaneously taken with the help of a camera. The half-width of the monoimpulse duration obtained by using the respective complex compounds as non-linear filters, and the monopulse energy have been given in Table.

Two series of measurements have been made: In the first one the complex compound concentration was maintained steady with various transmission values at $\lambda_{\max} = 695$ nm. In the second series the concentrations of the particular complexes were different, while the transmission value at $\lambda = 695$ nm was constant and equal to about 35%.

The results obtained during the first measurement series have allowed to state that the solutions of transmission not exceeding 30%, are difficult to bleach, and cannot work as passive values, unless sufficiently high pumping energy is used. Results of the second measurement series, where the tran-

Symbol of the compound	Donor-to-acceptor ratio	Transmission $\lambda = 695$ nm $d = 1$ mm	Average half-width duration of a monopulse ns	Average monopulse energy mJ
$H_2Pc \cdot AlCl_3$	1 : 100	0.355	30	162
$Na_2Pc \cdot AlCl_3$	„	0.361	24	154
$CuPc \cdot AlCl_3$	„	0.358	29	183
$AlClPc \cdot AlCl_3$	„	0.355	—	15
$CrOHpc \cdot AlCl_3$	„	0.350	22	138
$FeClPc \cdot AlCl_3$	„	0.355	—	20
$GaClPc \cdot AlCl_3$	„	0.356	48	167
$VClPc \cdot AlCl_3$	„	0.338	31	41

mission value was approximately constant and equal to 35%, could be better estimated. From Table it follows that almost all complex compounds of the phthalocyanine and the aluminium chloride may be used as nonlinear filters for ruby lasers.

Weak effects were obtained only for chloroaluminium and chloroferric phthalocyanines, for samples of transmission $T = 35\%$. These complex compounds cause high energy losses, as compared with the pulse energy in free generation, and very small amplitude of the monopulse. This effect may be explained by the fact that the absorption band of those complexes is shifted toward the longer wavelengths. The complex compounds of the phthalocyanine and the aluminium chloride reduce the laser beam energy by a factor, usually less, than 10^{-1} (as compared with the free-generation pulse energy) and in this respect are comparable with the R68 filters as well as with the solution of chlorophyll in benzene.

From the performed measurements it follows that the energy loss in laser beams caused by insertion of the nonlinear filter made of an organic dye, depends both on layer thickness and concentration of the solution. Detailed results will be given in a paper to follow. Nonlinear filters for ruby laser prepared of phthalocyanine complex solution being water sensitive should work in tightly closed cuvettes. On the other hand, they are resistant to the very high power laser-induced damage (including those of very high power lasers) and their chemical stability under waterless conditions — may last for years.

Complexes de phtalocyanines avec les halogénures des métaux de transition comme filtres non-linéaires pour un laser à rubis

Première partie — complexes: phtalocyanines-chlorure d'aluminium

On a étudié la possibilité de l'utilisation des complexes: phtalocyanines — chlorure d'aluminium comme filtres non-linéaires pour un laser à rubis. On a déterminé la demi-période de la durée des monoimpulsions obtenues.

Комплексы фталоцианинов с галогенидами переходных металлов в качестве нелинейных фильтров для рубинового лазера

Часть I. Комплексы фталоцианинов с хлористым алюминием

Исследована возможность применения комплексов фталоцианинов с хлористым алюминием в качестве нелинейных фильтров для рубинового лазера. Определена половинная продолжительность полученных моноимпульсов.

References

- [1] STANKOWSKI J., GRAJA A., *Wstęp do elektroniki kwantowej*, Warszawa 1972.
- [2] BASOV N. G., ZUYEV S., KRIUKOV P. G., *ZETF* **43**, 353 (1962).
- [3] SOFFER B. H., *J. App. Phys.* **35**, 2551 (1964).
- [4] MIKAELJAN A. L., ANTOMIANC V. J., DOLGICH V. A., TURKOV J. G., *Radio i elektron.* **10**, 1350 (1965).
- [5] BRET G., GIRES F., *Appl. Phys. Letters* **4**, 175 (1964).
- [6] ARMSTRONG J. A., *J. Appl. Phys.* **34** (8) 2346 (1963); **36** (2), 471 (1965).
- [7] SOROKIN P. P., LUZZI J. J., LANKARD J. R., PETTIT G. D. I.B.M., *J. Resch. Develop.* **8** (2), 182 (1964).
- [8] GRIAZNOV J. M., LEBEDEV O. L., CHASTOV A. A. *Opt. i Spectrosk.* **20** (3), 503 (1966).
- [9] KOSONOCKY W. F., HARRISON S. E., *J. Appl. Phys.*, **37** (13) 4789 (1966).
- [10] GULIANO C. R., HESS L. D., *IEEE, J. Qn. Electr.* **3** (8), 358 (1967).
- [11] GRACZYK A., SOBZYŃSKA J., RADOMSKA K., *J. Chem. phys.* (in print).
- [12] GRACZYK A., DOBKOWSKI J., *J. Chem. phys.* (in print).
- [13] LEIBLER K., GRACZYK A., BIAŁKOWSKA E. *J. Chem. phys.* (in print).

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