Optica Applicata Vol. X, No. 4, 1980

The effect of imperfections on thermoluminescence and lasing of ruby crystals

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The presence of mosaic blocks in ruby crystals has a negative effect on lasing of the rods studied. It has been also found that the low-temperature maximum $CT_m = 420$ K) observed in the samples diffuses when mosaic blocks or strains appear in a crystal. The results also allow to expect that the thermoluminescence can be successfuly used in evaluation of the quality of ruby crystals utilized in laser technology.

Introduction

The properties of the ruby single crystal which decide on its applicability in laser technology, depend mainly upon the method of crystal growing and the technical parameters of the crystallization process.

As a result of the temperature gradient in the crystallization chamber during the crystal growth (Verneuil method) there appear some optical heterogeneities, like: structure defects, concretion planes, gas bubbles, doppings of strange materials, and uneven distribution of chromium ions in the matrix.

It follows from the earlier studies [1-3] that the structure defects in ruby crystals are most often of three types: the block limits, slip lines, and single dislocations. Most of the ruby crystals obtained by Verneuil method have a mosaic structure. The mosaic consists of the stones of single crystals called blocks, the orientations of which differ by certain angle. The blocks are limited by the conglomeration of dislocations which are responsible for the strains observed in those areas.

The studies [2, 3, 11, 15-18] have been for several years oriented toward the elaboration of a method for evaluation of the quality of ruby crystals. However, the results obtained so far provide only rough information as to the usefulness of the crystal in the laser technology.

It is also known from the literature [4-9] that the thermoluminescence is strongly effected by the strange dopings as well as by the structural defects arising during the growth of the crystal and its thermal treatment. From [10-14] it follows also that the defects deteriorate optical properties of crystal and, consequently, have negative effect on the lasing action.

High intensivity light (from flash-lamps, for example) or the ionizing radiation causes the change in colour of a simple from pink into orange.

This change of colour should be associated with the colour centres [7, 8, 19-21] produced in ruby crystals by the above mentioned factors. For example, from the absorption measurements of the crystals X-ray coloured [21] it results that there appear four additional bands with the maxima at 473, 379, 289 and 216 nm. Similar results were obtained for ruby crystals coloured by γ rays [7]. Extra colouring can be removed by heating a sample. This is accompanied by a strong thermoluminescence in the range of R-lines. The termoluminescence curve for ruby crystals (e.g. of concentration $3\cdot10^{-2}\%$ Cr_2O_3 in Al_2O_3) coloured by X-rays exhibits two evident maxima [9]: one at about 430 K, and the other at 605 K.

Considering the above mentioned facts the attempt has been made to apply the thermoluminescence as a method for foreseing the lasing properties of a ruby crystal sample.

Sample preparation

The samples used were grown by Verneuil method in the Research Institute at Aluminium Works in Skawina, Poland. The measurements were taken with the approximate orientation of C axis and concentration of 0.05% Cr_2O_3 in Al_2O_3. The rate of crystallization was taken as a variable, since it was presumed that this parameter could strongly influence the crystal quality. The rate of growth varied from 7.6 to 18 mm/h. Before the lasing properties were measured the mosaic blocks of the studied samples had to be identified macroscopically. To this end the polarized light was used. The samples, in form of a rod or disc, were cut from the half of a crystal which did not undergo the strain-relief process.

The thermoluminescence curves were recorded for 0.15 mm thick discs with radius of 0.6 cm. The lasing properties were studied for the rods 9 cm long and 0.8 cm in diameter. Parallelity of the side walls was assured with certainty of 10′. The two types of studies were done for five samples.

The experimental setup

The lasing properties were examined in a quadru-eliptical head air-cooled at 284 K. A special electronic system secured the temperature stabilization in the head. The setup is shown in fig. 1.

The ruby rod was pumped by means of the four flash lamps (Presler G-340). The laser beam went through the head directed by the dielectrical mirror of 35% transmission. The energy has been measured with the use of the "rat nest" type meter. The laser worked in the free generation mode.

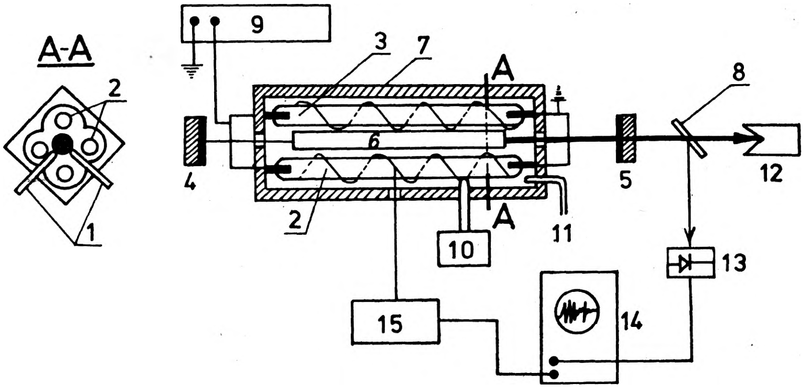

Fig. 1. Setup for studies of lasering properties of ruby

1 – micrometers; 2, 3 – flash lights; 4, 5 – mirrors; 6 – ruby rod; 7 – quadru-elliptical head; 8 – beam splitter; 9 – high voltage power supply; 10 – thermocouple with temperature control system; 11 – inlet of cold compressed air; 12 – power meter, a "rat's nest"; 13 – photodiode; 14 – oscilloscope 15 – trigger

The setup for the thermoluminescence curve

The whole arrangement for the thermoluminescence curve studies is shown in fig. 2. There are two main parts: the heating system and the recording system. A small oven was used for heating the sample. The hot plate temperature has been controlled by means of specially arranged 650 Unipan thermo-controller. Heating rate used in the measurements was equal to 0.8 deg/s. The temperature of the system ranged from 300 to 700 K. It was measured by a resistance thermometer Resemouth 2100S.

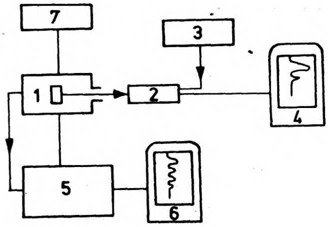

Fig. 2. Setup for the luminescence studies

1 – crystal; 2 – photomultiplier; 3 – high voltage power supply; 4 – recorder; 5 – temperature controller – 650 Unipan; 6 – recorder; 7 – programmer

The recording system consisted of the photomultiplier FEU-38 and the recorder GBI of Carl Zeiss, Jena. Optical colouring was done by means of Presler G-430 flash lamps with flashes lasting for 500 μs. The crystals were coloured in the laser head. The constant electric power supplied to the lamps was 120 kJ.

Results

The thermoluminescence measurements were done for the five samples cut from the ruby crystal and numbered 1-5.

It follows from the measurements that the *I* (*T*) curve had two maxima, similarly as in the case when the crystals were X-ray coloured [9].

The first, low-temperature maximum, has been observed at 420 K, and the second, i.e. high-temperature maximum, at 620 K. It should be underlined that the high-temperature maximum was recorded for all the studied samples, while the low-temperature maximum was clearly cutlined for some samples only. Fig. 3 shows two different curves *I*(*T*) registered in the vicinity of the low-temperature maximum: a — for the sample No. 1, and b — for the sample No. 2.

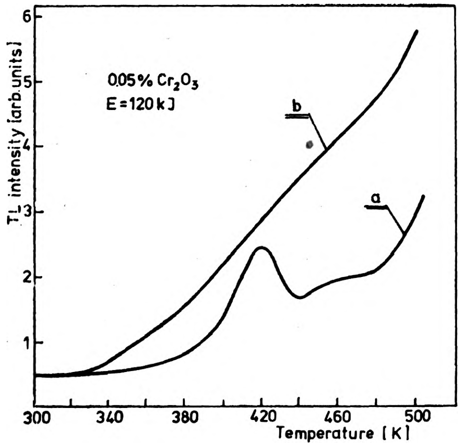

Fig. 3. Thermoluminescence curves of ruby crystal coloured by means of the flash light
a — crystal No. 1, b — crystal No. 2

Similar recordings for the samples 3, 4 and 5 have shown distinct low-temperature maxima for the samples cut from the crystals 3 and 5, the maximum for the sample 4 being hardly noticeable.

For the studied crystals the macroscopic identification of the block structure has also been made. The studies have shown that in some of the crystals the mosaic blocks are clearly seen. The mosaic blocks in ruby crystal are observed when there exist the regions of different crystallographic orientations, at the same time local strains are observed at the block limits. Therefore, the mosaic blocks affect the type and number of defects in a crystal.

Considering these facts the thermoluminescence curves have been correlated with the block structure of the corresponding crystals. The results are listed in table.

Table

Crystal number	Cristallization rate mm/h	Maximum TL 420K	Threshold energy kJ	Beam energy from 1 cm^3	Remarks
1	18.4	very distinct	1.6	0.27	hardly seen
2	10.4	weak	2.1	0.06	blocks distinct
3	7.6	distinct	1.8	0.24	hardly seen
4	17	weak	1.9	0.06	blocks distinct
5	12	very distinct	1.6	0.27	hardly seen

The analysis led to the conclusion that a very weak maximum is observed in crystals having great number of mosaic blocks and a very distinct maximum in crystals with relatively few mosaic blocks. It follows from the studies that the strains and the mosaic blocks strongly affect the $I(T)$ curves in the region of the low-temperature maximum and do not influence its high-temperature part. In other words, the low-temperature maximum is "sensitive" to the appearance of the mosaic blocks and accompanying defects in a ruby crystal.

One of the ways by which the defect number in a crystal sample can be changed is the tehrmal treatment. It seemed to be interesting to record the thermoluminescence curves before and after the thermal treatment of the sample. To this end, the samples of $3\cdot 10^{-2}\%$ Cr_2O_3 concentration in Al_2O_3 were heated in the oven for 2 hours until they reached the temperature of about 2073 K, and then cooled to the room temperature. Two hours after the oven was switched off the temperature dropped to 773 K, and after next 3.5 hours the cooling was finished. The crystals were heated and cooled in the atmosphere of hydrogen. Such a treatment should result in increase of the defect number in ruby.

Typical $I(T)$ curves recorded for a sample before and after treatment are shown in fig. 4: a — before the treatment, and b — after the treatment. While comparing the two curves it can be seen that the treatment had caused a very distinct diffusion of the curve in the vicinity of low-temperature maximum. This effect, observed in crystals with very distinct mosaic blocks after their thermal treatment, is most probably due to the change in position of the trap levels being located at different depts with respect to the $E = 1.1$ eV level. The electron traps at 1.1 eV below the conduction band seem to be responsible for non-diffused maximum [9].

For the studied samples the curves of radiation energy of the laser beam were also measured as a function of the energy of pumping. The

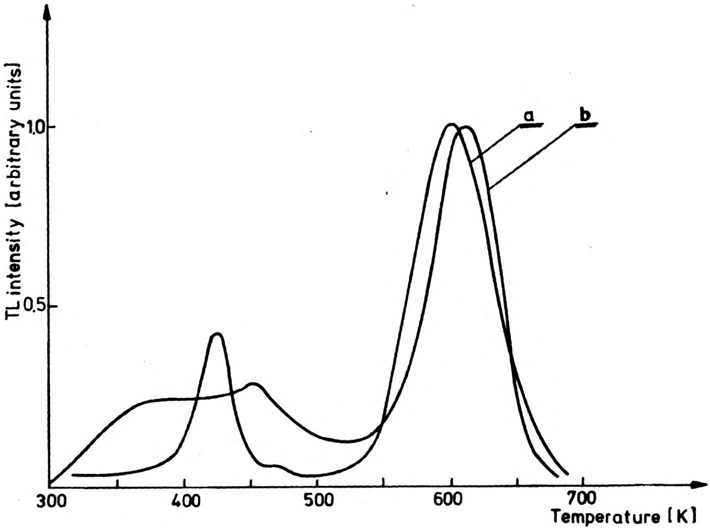

Fig. 4. Thermoluminescence curves for X-ray coloured ruby
a — before thermal treatment, b — after thermal treatment

results are listed in table. Typical curves for the samples with different numbers of the mosaic blocks are shown in figs. 5 and 6. From comparison of the curves it follows that the lasing of rod cut from crystal No. 2 is much worse than that of sample No. 1. These two rods display, moreover, large differences in threshold energy and radiating energy from 1 cm^3 (see table).

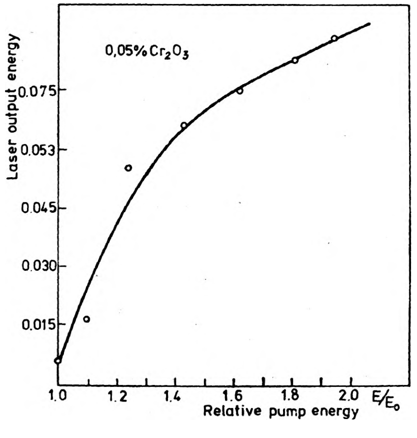

Fig. 5. Radiation energy of laser beam as a function of the relative pumping energy E/E_0 for the rod No. 2

By comparing the $I(T)$ curves with the above mentioned ones and making use of the results listed in table the following can be stated:

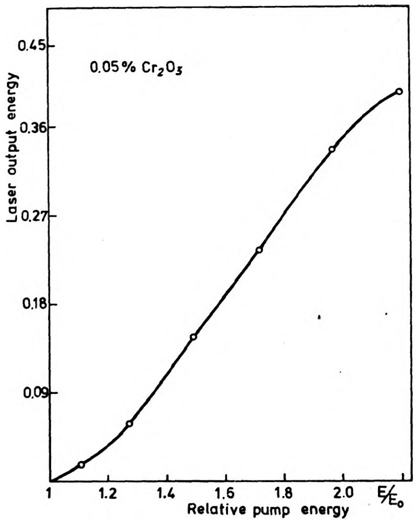

Fig. 6. Radiation energy of laser beam as a function of the relative pumping energy E/E_0 for the rod No. 1

— large number of the mosaic blocks worsens the lasing properties, rises the generation threshold and causes diffusion of the low-temperature maximum,

— small number of the mosaic blocks or their absence improves the lasing properties, lowers the generation threshold and gives distinct TL maximum.

In addition, the rods cut from the crystals with distinct low-temperature maximum are characterized by better collimation of the beam as compared to that of the rods with diffused maximum.

Conclusions

It follows from the measurements that the presence of the mosaic blocks and strains in ruby has negative effect on the lasing. Mosaic blocks and strains observed in the samples examined affect also the thermoluminescence curve.

The diffusion of the thermoluminescence maximum is most probably caused by the change in the number of electrons in the trap levels positioned at different depths with respect to $E = 1.1$ eV level. The traps which are at 1.1 eV are made responsible for the distinct maximum.

Hence, it follows that the thermoluminescence can be useful in evaluation of the equality of ruby crystals. The samples, for which $I(T)$ curve has a distinct maximum at about 420 K, should perform well the role of laser rods.

Acknowledgments — The authors take the opportunity to express their thankfulness to Prof. B. Sujak from Physics Institute of Wrocław University, for his valuable remarks and discussions.

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Received January 30, 1980

Влияние дефектов на термолюминесценцию и лазерирующие свойства кристаллов рубина

Наличие в кристаллах рубина блоков мозаики неблагоприятно влияет на лазерирующие свойства испытываемых стержней. Было выявлено, что низкотемпературный максимум (T_m = 420 K), какой наблюдался для испытываемых рубинов, подвергается размытию, когда в кристалле выступают блоки мозаики и напряжения. Полученные результаты позволяют судить, что термолюминесценция может оказаться пригодной для оценки качества кристаллов рубина, используемых в лазерной технике.