# PHYSICS

Corresponding Member of the Academy of Sciences of the USSR L. F. VERESHCHAGIN,

1964

SovietRxiv

**Abstract**

**Full Text**

# PHYSICS

Corresponding Member of the Academy of Sciences of the USSR L. F. VERESHCHAGIN,
Academician of the Academy of Sciences of the Uzbek SSR S. V. STARODUBTSEV, M. S. YUNUSOV

# COLORATION AND LUMINESCENCE OF SYNTHETIC RUBY IRRADIATED WITH $Co^{60}$ GAMMA RAYS

As is known, the coloration of corundum crystals is due to the presence in them of small amounts of foreign impurities that enter isomorphously into the spatial lattice. Chromium, manganese, vanadium, titanium, nickel, as well as cobalt and iron color corundum in a color characteristic of each impurity ([1]). For example, ruby, i.e., a corundum crystal containing chromium, has a red coloration, the density of which varies depending on the amount of chromium. At small amounts of $Cr_2O_3$ in the specimens (from 0 to 0.5%), absorption increases as the chromium content rises. With a further increase in the chromium content in ruby (up to 2% $Cr_2O_3$), no strong increase in absorption is observed. In the case of defective crystals, strong absorption is sometimes observed also in specimens containing a comparatively small amount of chromium. The appearance of green coloration with an increase in the content of chromium oxide has also been noted ([2]).

Analysis of the data available at the present time makes it possible to conclude that chromium can enter corundum in the form of a trivalent ion in sixfold coordination as an isomorphous impurity $Cr^{3+}$ ([6]), or as an impurity that disturbs the crystal lattice.

In the visible region, ruby has two absorption bands. One of them is located in the green, and the second in the blue part of the spectrum. The absorption maximum of the second band is located at the boundary between the visible and ultraviolet regions of the spectrum. There are also narrow absorption bands that do not affect the color of the crystal.

In studying the processes by which various metals are introduced into corundum, it was found that for each impurity element there is a limiting concentration, depending on the growth conditions. Exceeding this limiting concentration leads to clouding or cracking of crystals grown in an oxyhydrogen flame. For most of the metals added to corundum, the limiting concentrations are very small: hundredths, even thousandths, of a percent. Accordingly, the intensity of the

Fig. 1. Optical density $D$ of ruby for the ordinary ray (A) and for the extraordinary ray (B), recorded at various irradiation doses. 1 —unirradiated specimen; 2 —irradiated with a dose of $10^3$ r; 3 —$10 \cdot 10^3$ r; 4 —$80 \cdot 10^3$ r; 5 —$240 \cdot 10^3$ r

Figure 1: Fig. 1. Optical density $D$ of ruby for the ordinary ray (A) and for the extraordinary ray (B), recorded at various irradiation doses. 1 —unirradiated specimen; 2 —irradiated with a dose of $10^3$ r; 3 —$10 \cdot 10^3$ r; 4 —$80 \cdot 10^3$ r; 5 —$240 \cdot 10^3$ r

coloration of the crystals cannot vary over wide limits. In practice, two metals are introduced into corundum, one of which is chromium, the other usually Ti, V, Mn, Ni. In this case, it turns out that three cases of impurity entry into the crystal are possible: 1) both metals can enter the crystal isomorphously at the same time; 2) one of the metals enters isomorphously, the second in the form of an impurity that disturbs the crystal lattice of corundum; 3) both impurities form chemical compounds present in the crystal in the form of the smallest inclusions.

There is no doubt that lattice defects, introduced into the crystal in any way, can have a substantial influence on the presence and position of the light-absorption bands and, consequently, on the coloration of the specimen.

At present, one of the simple methods of creating disturbances in a crystal is the process of radiation exposure. Irradiation with X rays and $\gamma$-rays, electrons, neutrons, and other penetrating particles creates in the crystal a complex of relatively stable defects that influence the absorption of light. With respect to ruby crystals, the study of light absorption by radiation defects is especially important in connection with the fact that corundum can be used as one of the elements of opti-

physical systems operating in a zone of intense radiation. On the other hand, quantum emitters are made from ruby crystals, and their light output may depend substantially on the number and type of light-absorbing levels.

Therefore, it is of great interest to study the action of penetrating radiation on various properties of synthetic ruby (corundum). Several works are known ([3–7]) devoted to the study of these questions.

**Fig. 1.** Optical density $D$ of ruby for the ordinary ray (**A**) and for the extraordinary ray (**B**), recorded at various irradiation doses.
1 —unirradiated specimen; 2 —irradiated with a dose of $10^3$ r; 3 —$10 \cdot 10^3$ r; 4 —$80 \cdot 10^3$ r; 5 —$240 \cdot 10^3$ r.

In work ([2]) the action of X-rays on the coloration and luminescence of ruby was investigated. The authors of works ([4–5]) discovered the appearance of a number of absorption bands in $\alpha$-$Al_2O_3$ under neutron irradiation, which are completely annealed out only when the specimen is heated to 1800° in vacuum. In work

Fig. 1. Thermoluminescence of irradiated ruby. 1—$0.12 \cdot 10^6$ r; 2—$0.50 \cdot 10^6$ r

Figure 2: Fig. 1. Thermoluminescence of irradiated ruby. 1—$0.12 \cdot 10^6$ r; 2—$0.50 \cdot 10^6$ r

([6]) the effect of an electron beam, as well as of X-rays, on certain properties of $\alpha$-$Al_2O_3$ was investigated.

We investigated crystals of light-pink synthetic ruby containing about 0.2—0.4% $Cr_2O_3$. Irradiation was carried out with $\gamma$-rays from $Co^{60}$, with a dose rate of $\sim 350$ r/sec at a source temperature of 34°.

The absorption spectrum of the ordinary (Fig. 1A) and extraordinary (Fig. 1B) ray was recorded on an installation comprising a universal UM-2 monochromator, a light polarizer, and an FEU-22 photomultiplier. Figure 1 gives the optical densities of a specimen 10 mm thick, recorded at various irradiation doses. As is evident from the figure, already at a dose of $10^3$ r the absorption spectrum of ruby changes noticeably. As the dose increases, the density of ruby grows over a broad spectral region, beginning with the green and extending to the violet. In the red part of the spectrum ruby becomes more dense after a dose of $10^3$ r, and subsequently, even at comparatively large doses, this density changes hardly at all. In the region 420—530 mμ pleochroism appears, and it intensifies with increasing irradiation dose. At doses of the order of $10^6$ r a noticeable saturation of the coloration is observed. It is of interest to note that upon irradiation an effect of displacement of the spectrum toward the short-wavelength region is observed.

We also investigated the thermoluminescence of synthetic ruby caused by irradiation. Figure 2 shows thermoluminescence curves recorded at various doses. The curves were recorded at a heating rate of $4 \pm 0.3$°/min. In the temperature range from room temperature to 500° there is one broad glow maximum at 300°. Specimens subjected to such heating (annealing) almost completely lose the coloration induced by irradiation.

Heating the irradiated sample to 250° with subsequent slow cooling introduces no change into its absorption spectrum. Illumination of the irradiated sample by ultraviolet rays from a mercury lamp, however, is accompanied by more intense luminescence than that of the unirradiated sample. As a result of such illumination, the radiation-induced absorption bands are bleached and the sample loses its thermoluminescent ability.

**Fig. 1.** Thermoluminescence of irradiated ruby.
1—$0.12 \cdot 10^6$ r;
2—$0.50 \cdot 10^6$ r

We carried out qualitative studies of the paramagnetic-resonance spectrum of irradiated samples on an EPR-2 apparatus. The parallel spectrum at a frequency of 9368 MHz was studied. The investigations showed that, at doses of

the order of several hundred thousand roentgens, the number of absorption centers increases appreciably and the lines broaden at the point of maximum slope. The line due to the transition $M = 1/2 \leftrightarrow -1/2$ is relatively more sensitive to irradiation than the transitions $M = -1/2 \leftrightarrow 1/2$.

To explain the results obtained, certain assumptions may be put forward. In the ruby sample we studied, apparently, in addition to $Cr^{3+}$ ions entering isomorphously into the crystal lattice of corundum, there is also a sufficient quantity of chromium ions which, together with other impurities, occur in the form of separate inclusions.

Upon irradiation with $\gamma$-rays, electrons are localized at these defects, and bonds are also broken in the inclusions themselves; as a result, the ruby becomes colored and is enriched with centers of paramagnetic absorption.

The very fact of coloration may find practical application: changing the absorption regime and bleaching the energy of lasers, controlled coloration of corundum in the manufacture of bearings and optical instruments, etc.

Institute of High-Pressure Physics
Academy of Sciences of the USSR

Institute of Nuclear Physics
Academy of Sciences of the Uzbek SSR

Received
6 XI 1963

## REFERENCES

1. Tr. Inst. kristallogr. AN SSSR, **8**, 3 (1953).
2. E. Thilo et al., *Zs. anorg. u. allgem. Chem.*, No. 1–2, 279 (1955).
3. R. S. Krishnan, *Proc. Indian Acad. Sci.*, **A26**, No. 6, 450 (1947).
4. P. W. Levy, *Disc. Farad. Soc.*, No. 31, 118 (1961).
5. W. D. Compton et al., *Disc. Farad. Soc.*, No. 31, 130 (1961).
6. P. W. Levy, *Defects in Crystal. Solids*, London, 1959, p. 256.
7. S. T. Konobeevskii et al., *Atomic Energy*, **5**, No. 5, 572 (1958).

*Note: Figure translations are in progress. See original paper for figures.*