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Investigation of Optical Characteristics of Photochromic Materials

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Abstract

This work is devoted to the optical properties of sodalite crystal $Na_8A\ell_6Si_6O_{24}[C\ell_2]$. Research results show that the color of crystals changes under the influence of both ultraviolet and gamma rays, and maximum absorption occurs at a wavelength of λ=530 nm. In addition, the diffraction efficiencies of the samples in terms of thickness, photosensitivity and transmittance after staining and bleaching were obtained.

Keywords: absorption spectra, sodalite, coloring and discoloration photochromic materials.

1. INTRODUCTION

The recording of holograms on photochromic materials is based on their ability to change color when irradiated with light, which is explained by the transition of an optically excited electron from one color center to another with a corresponding change in the absorbing properties of both centers and changes in the absorption spectrum of these materials. Thus, exposure of a photochromic recording medium to an information light flow provides a change in the color of the material that corresponds to the information structure of the flow. These changes can be either reversible or irreversible. To return the medium to its original state, irradiation with light of a different wavelength is necessary. The main advantage of photochromic materials is their virtually unlimited intrinsic resolution, since absorption occurs within the region occupied by an atom or molecule. Disadvantages include a narrow sensitivity range, the need to use two wavelengths for recording and erasing, and the inability to selectively erase. It should be noted that photochromic materials implement amplitude-phase recording. In works [1-4], the main holographic characteristics of photochromic materials are compared and studied.

In [5], the possibility of holographic recording on sodalite crystals colored by Co^{60} γ-radiation was reported. The optical density of the colored crystals at the absorption maximum was ~1.5. Stable holograms were obtained with a diffraction efficiency of DE η=0.14% at room temperature. The recording was made using radiation with λ=488 nm, which is close to the maximum of the absorption spectrum of the sodalite crystal. According to work [6], the measured diffraction efficiency of holograms recorded on the surface of pre-colored alkali halide crystals did not exceed 0.1%.

2. MATERIALS AND METHODS

For the study, we prepared sodalite samples of various thicknesses and, after appropriate processing, they were irradiated with γ-radiation with a dose of 10^7 R. After γ-irradiation, the samples had a crimson color. The holographic characteristics of the photochromic sodalite crystal $Na_8A\ell_6Si_6O_{24}[C\ell_2]$ as a recording medium were studied. As a result of the study, photosensitivity, exposure characteristics, recording cycles and erase energies were determined. The crystals were obtained using the hydrothermal method. According to the crystal chemical classification, the selected sodalite belongs to the group of aluminosilicates. The crystal structure of sodalite is an aluminum-silicon-oxygen framework, the cavities of which are occupied by sodium and chlorine ions [7]. The framework consists of $A\ell O_4$ and SiO_4 tetrahedra present in equal quantities. The connection between them is carried out through oxygen atoms located at the vertices of the tetrahedra (each oxygen atom is common to two tetrahedra).

Fig. 1 shows a diagram of a sensitometric installation, where, using photo shutter 3 and 10, the crystal was alternately colored and bleached. A helium-neon laser with a radiation wavelength of 632.8 nm was used for bleaching.

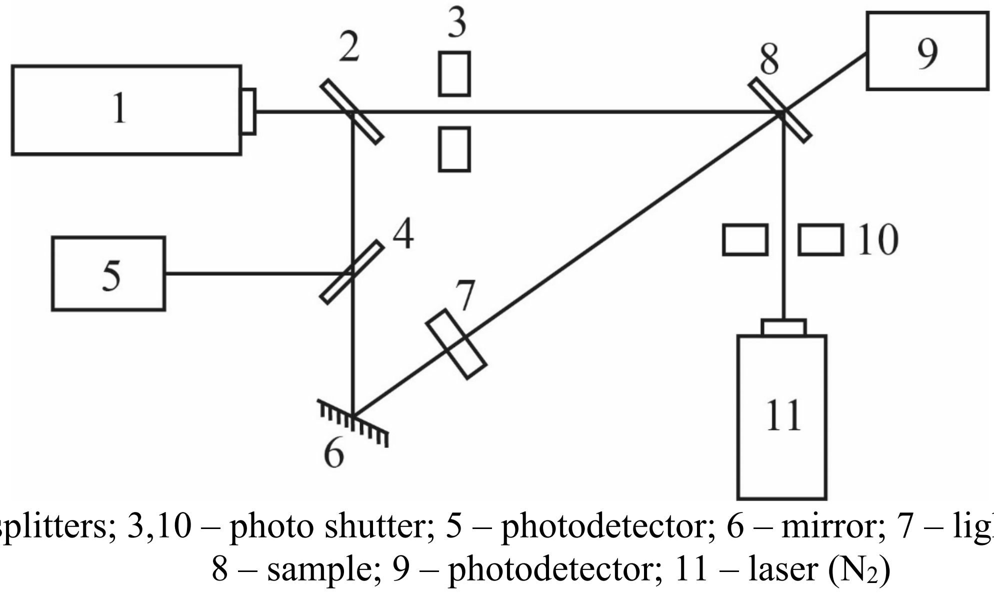


Fig. 1. Scheme of the sensitometric installation: 1– laser (He-Ne); 2,4 – beam splitters; 3,10 – photo shutter; 5 – photodetector; 6 – mirror; 7 – light filter; 8 – sample; 9 – photodetector; 11 – laser (N_2)

Staining was performed with a pulsed nitrogen laser with a wavelength of 337 nm. Pulse repetition frequency 100 Hz. The change in the amplitude transmittance coefficient was controlled by a probing beam, the intensity of which was selected so (using light filters 7) that it did not affect the coloring process of the crystal. Fluctuations in the intensity of the laser beam were controlled using a control beam output to photodetector 5.

To measure the diffraction efficiency of a sodalite crystal, a setup was used, the diagram of which is shown in Fig. 2.

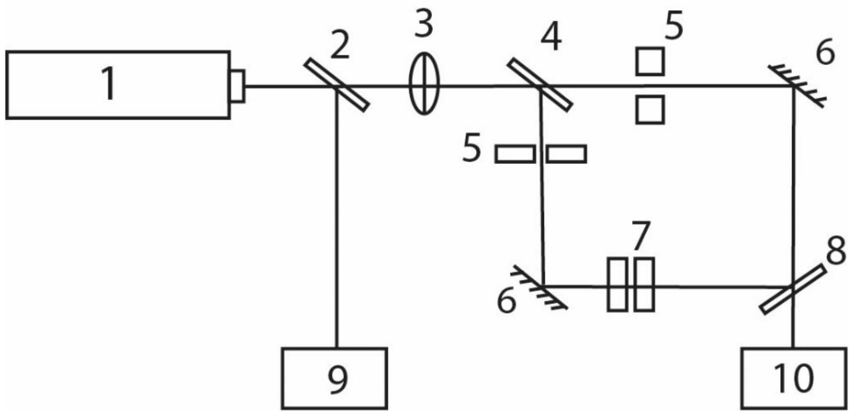


Fig. 2. Scheme of the installation for measuring diffraction efficiency: 1– laser; 2,4 – beam splitters; 3 – lens; 5 – photo shutter; 6 – mirror; 7 – light filter; 8 – sample; 9,10 – photodetector

Part of the helium-neon laser beam is separated using beam splitter - 1 to control fluctuations in the intensity of laser radiation. The rest of the beam is divided into two identical parts using beam splitter - 2, which are aligned on the test sample using reflective mirrors at an angle of 12°. To increase the radiation density, a long-focal lens is placed in front of the beam splitter - 3. To reduce the influence of the reading beam on erasing information, when reading, the intensity of the reconstruction beam is reduced using light filters - 7. The brightness of the image restored from the hologram is recorded by the photodetector 10 after blocking one of the beams with a photo shutter - 5. The absorption spectra were studied using a Shimadzu UV 3600 spectrometer.

3. RESULTS AND DISCUSSION

The mechanism of the photochromic effect can be explained as follows. The color center in sodalite is classified as an F-center (sodalite cell), which plays a large role in the coloring process. However, the properties of coloring and discoloration are also significantly influenced by the presence of impurities, the size and shape of the crystals.

When sodalite is irradiated with ultraviolet light, electrons transition from U-centers (donor levels) to the conduction band and the subsequent capture of these excited electrons by F-centers. The coloring of sodalite occurs due to the fact that, when illuminated with visible light, these electrons move from the lowest ground state (1s) to the excited state (2p), which corresponds to the absorption of light. To bleach the material, the material is irradiated with UV light in the absorption band, which transfers electrons back into the conduction band, allowing recombination with holes in the U-levels.

Fig. 3 shows typical absorption spectra of sodalite obtained after its excitation with ultraviolet light.

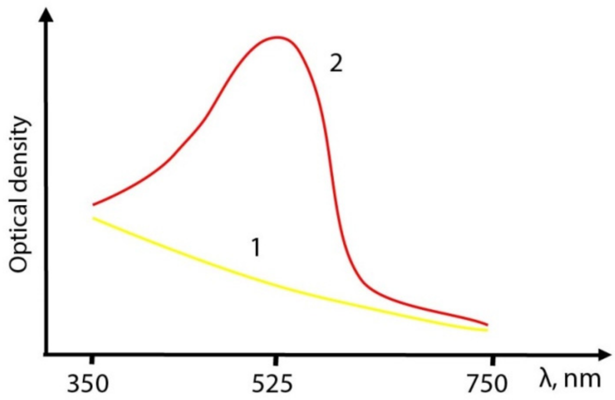


Fig. 3. Absorption spectra of sodalite: 1) unexcited 2) excited UV radiation

The shape and value of the optical density in the absorption band are very similar for all main types of sodalite (Cℓ, Br, I).

Measurements of absorption spectra showed that the wavelength corresponding to the maximum absorption of the material is linearly related to the size of the sodalite cell. For sodalite $Na_8A\ell_6Si_6O_{24}[C\ell_2]$, the band gap is 6.1 eV, the lattice constant a_0 is 8.87 Å, and the wavelength λ_{max} corresponding to the absorption maximum of F-centers is 525 nm. When sodalite is irradiated with certain doses of γ-radiation, changes in the optical absorption spectra are detected. At a dose of 10^7P, sodalite crystals acquire a noticeable blue color, characterized by a wide absorption band in the region of 450÷650 nm. As the irradiation dose increases, the blue color changes to red and a maximum at 530 nm is clearly visible in the absorption spectrum. This state is optically unstable and can be easily removed with light at a wavelength of 530 nm. However, it can be restored upon subsequent illumination with UV light λ~360 nm. These facts indicate that illumination in the 530 nm band only leads to delocalization of charge carriers, and irradiation with light with λ~360 nm causes the reverse transfer of charges into traps associated with color centers at 530 nm and close to the maximum of the absorption spectrum of sadolite.

Fig. 4 shows the maximum diffraction efficiency η = 0.2%, which was observed in a crystal with a thickness of T-1.67 mm at an energy consumption of 100 J/cm^2.

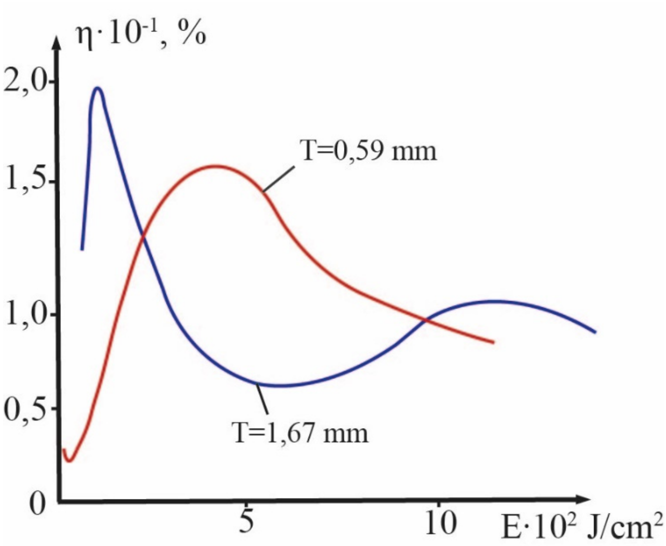
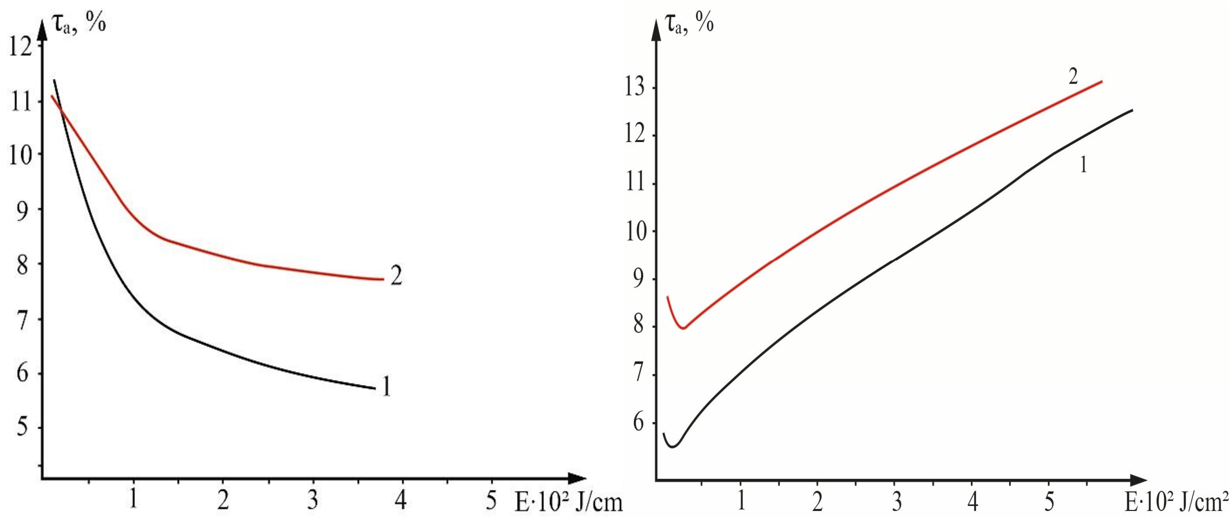


Fig. 4. Diffraction efficiency of sodalite

It should be noted that the use of more advanced sodalite single crystals will make it possible to obtain higher diffraction efficiencies and more perfect holograms.

From the study we can conclude that these crystals, under certain conditions, can be used in optical systems for processing and storing information, in particular, when recording volumetric holograms.



a **b**

Fig. 5. Dependence of sample transmittance on radiation energy: 1 – initial, 2 – after 20 cycles: a) coloring, б) discoloration

Fig. 5 shows the amplitude transmission curves τ_a depending on the exposure E during crystal bleaching. The measure of photosensitivity was the exposure required to change the initial transmittance by 50%. Thus, the sensitivity of sodalite with an admixture of sulfur, 3.90 mm thick, to radiation with a wavelength (λ-632.8 nm) E = 33 J/cm^2, and after 20 cycles of staining and bleaching, the sensitivity of the crystal decreased by 25% (curve 2 in Fig. 5a).

Fig. 5 clearly shows a slight drop in performance. This is explained by an increase in absorption due to the appearance of other unstable color centers.

Experiments have shown that the sensitivity of the crystal to UV radiation with λ=337 nm will be of the order of E=30 J/cm^2. After 20 cycles of staining and bleaching, it changes by 1.5 times (Fig. 5b).

Fig. 6 shows the dependence of photosensitivity on crystal thickness. It is clear from the curves that with increasing thickness the sensitivity of the crystal to UV and red radiation decreases.

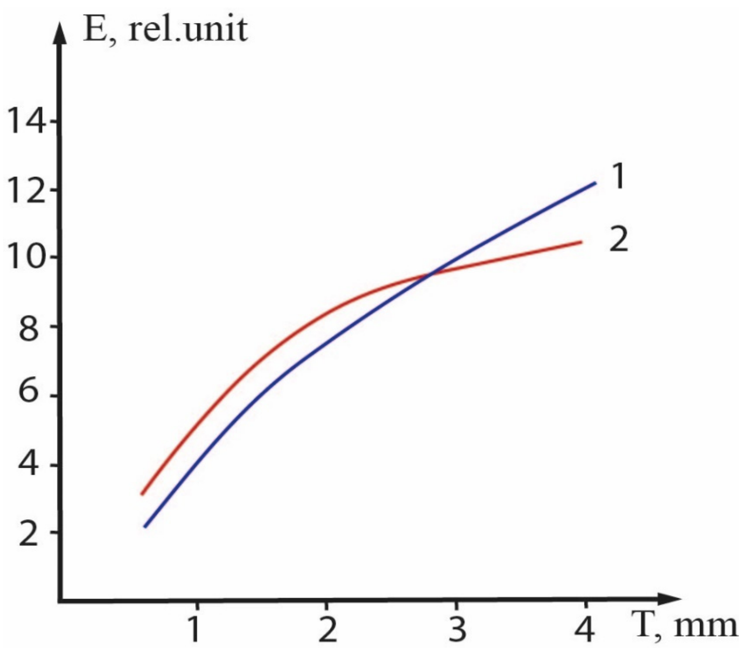


Fig. 6. Dependence of photosensitivity on crystal thickness: 1) λ=337 nm, 2) λ=632,8 nm

4. CONCLUSION

The holographic characteristics of photochromic sodalite crystals have been studied. Stable holograms with a diffraction efficiency of $\eta = 0.2\%$ at a recording energy of 100 J/cm^2 were obtained in samples of various thicknesses, irradiated with γ-rays with a dose of 10^7 R and having absorption bands in the range of 480÷540 nm. The recording was made with a laser beam λ=441.6 nm (He-Cd laser) and λ=632.8 nm (He-Ne laser). After bleaching, the optical absorption edge shifts toward shorter wavelengths. The sensitivity of crystals to blue light reaches 15 J/cm^2, and to UV radiation with a wavelength of λ=337 nm (nitrogen laser) is 30 J/cm^2. After 20 cycles of staining and bleaching, the sensitivity changes by 1.5 times.

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