OPTICAL AND LUMINESCENT PROPERTIES OF CaF₂ CRYSTALS IRRADIATED WITH 14 MeV ENERGY

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The paper studies color centers in synthetic calcium fluoride crystals, which arise from irradiation with 14 MeV electrons at room temperature. The irradiated samples also measured the kinetics of phosphorescence decay and thermoluminescence. The concentration of the formed color centers was calculated using the Smakula-Dexter ratio. It was found that the phosphorescence of the irradiated calcium fluoride crystal lasts up to ~7 days. The thermoluminescence curves show four peaks.

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INTRODUCTION

Single crystals of calcium fluoride (CaF₂) are a widely used material, which has led to the study of its properties for many years. It occurs naturally as a mineral called fluorite. It is used industrially in metallurgy, for producing hydrofluoric acid, and in optics, for producing optical components such as windows and lenses in spectroscopy, telescopes, and lasers. It is transparent in a wide range from the ultraviolet (UV) to the infrared (IR). In addition, under certain conditions, calcium fluoride can produce luminescence, which corresponds to the name of its natural crystal, fluorite. Irradiated synthetic calcium fluoride, like natural fluorite, exhibits thermoluminescence, which is used in thermoluminescent dosimeters.

Natural calcium fluoride can appear as a colorless crystal or have different colors, which is related to the type of dopants or structural defects (vacancies, mainly anion vacancies). Undoped synthetic CaF₂ is colorless.

The study of color centers and the nature of their formation in CaF_2 is of great interest. Color centers play an essential role in their luminescent properties, particularly in phosphorescence and thermoluminescence. In addition, other methods for studying color centers have been described in the literature, including Raman scattering, EPR, and photoconductivity [1-4].

It is generally accepted that the color centers in CaF_2 , as in alkaline-halide crystals, are an anionic vacancy that has captured a free electron. One method for forming coloring centers in CaF_2 is irradiation with high-energy particles, X-rays, gamma quanta, and electrons [5, 6]. The following leading absorption bands have been identified at 320, 385, 520 and 670 nm in CaF_2 . Irradiation for the formation of color centers is most expedient by electrons, which has several advantages over other types of irradiation. At an electron energy of more than 1 MeV, the formation of color centers is carried out uniformly throughout the depth of the sample, and both anionic vacancies can be formed due to elastic scattering on the fluorine atom and the creation of nonequilibrium charge carriers.

The present work studied the formation of color centers in a synthetic lithium fluoride crystal without dopants irradiated with 14 MeV electrons at room temperature.

EXPERIMENT

In this work, undoped lithium fluoride samples of 1×1 cm and 1 mm thickness were studied. The irradiation of the samples was carried out on the metrological stand of the M-30 microtron of the Department of Photonuclear Processes of the Institute of Electron Physics of the NAS of Ukraine. The irradiation was carried out at room temperature; the temperature was monitored remotely with a copperconstantanum thermocouple. Because the beam size at the output of the M-30 microtron is 5×15 mm, the output beam was scattered on a thin tantalum target with a thickness of 50 µm using a shaping collimator to form the required irradiation field, which improved the uniformity of the electron beam at the sample installation site. The magnitude and inhomogeneity of the generated field were measured by a Faraday cylinder with a calibrated inlet and did not exceed 0.5% at the sample location. The Faraday cylinder calibrated a translucent secondary emission monitor connected to a current integrator, determining the set electron fluence. The electron irradiation was accompanied by inherent braking gamma radiation due to the interaction of accelerated electrons with the accelerator's structural elements and the scattering foil. It was shown in [7, 8] that the contribution of braking gamma radiation did not exceed 10%.



Fig. 1. M-30 microtron for radiation experiments

After the irradiation and the technological interval (~80 s), phosphorescence was measured in the samples. A photoelectron multiplier FEU-106 in the photon counting mode measured the phosphorescence decay kinetics. The temperature of the samples under study was kept stable using the software. A spectrophotometer SF-46 measured the optical absorbance of the samples. The optical absorbance of the samples was measured immediately after the phosphorescence decay, and the samples were also measured 24 and 48 h after irradiation to check the stability of the leading absorption bands. After the crystals' phosphorescence decav and optical absorption measurements, thermoluminescence was measured in the 25...300°C temperature range, with a linear heating rate of $1^{\circ}C/s$.

MAIN RESULTS

The change in the optical absorption of calcium fluoride CaF_2 is shown in Fig. As can be seen from the data, when irradiated by electrons with an energy of 14 MeV, the studied samples form well-known absorption bands at 320, 385, and 560 nm.



Fig. 2. Changes in optical absorption of calcium fluoride CaF_2 samples with irradiation dose

The concentration of the formed color centers was calculated using the known Smakula-Dexter ratio:

$$N = 0.87 \cdot 10^{17} \frac{n_0}{(n_0^2 + 2)^2} \cdot \frac{\Delta H \cdot \alpha}{f}$$

where *N* is the concentration of absorbing centers, cm⁻³, n_0 is the refractive index (n_0 = 1.41), *f* is the oscillator strength (for alkaline-halide crystals, f = 0.7...0.8), ΔH is the peak half-width, α is the absorption coefficient, cm⁻¹.

As can be seen from Fig. 2, the concentration of color centers in the samples under study increases with the irradiation fluence. The concentration of color centers in the studied crystals after ~ 24 h of irradiation practically does not change.

The typical kinetics of the phosphorescence decay of the investigated crystal irradiated with a fluence of $5 \cdot 10^{12}$ el. cm⁻² is shown in Fig. 3.



Fig. 3. Phosphorescence decay kinetics of the investigated crystal irradiated with a fluence of $5 \cdot 10^{12}$ el·cm⁻²

Fig. 4 shows the thermoluminescence curve of the investigated crystal irradiated with a fluence $5 \cdot 10^{12}$ el. cm⁻².



Fig. 4. Thermoluminescence curve of the investigated crystal irradiated with a fluence of $5 \cdot 10^{12}$ el. cm⁻²

It was found that the phosphorescence of the irradiated calcium fluoride crystal, unlike lithium fluoride, has a much more extended decay period, up to ~7 days. As shown in Fig. 4, 4 peaks were detected on the thermoluminescence curve, the position of which coincides with those found in [9].

REFERENCES

1. D. Papadimitriou, A.G. Nassiopoulou, F. Bassani, F. Arnaud d'Avitaya. Low temperature Raman and photoluminescence study of Si / CaF₂ multiquantum wells // *Materials Science and Engineering:* B. 2000, v. 69-70, p. 546-548. https://doi.org/10.1016/S0921-5107(99)00321-9.

2. Stephan Logunov, Sergey Kuchinsky. Experimental and theoretical study of bulk light scattering in CaF_2 monocrystals // *J. Appl. Phys.* 2005, 98, 053501. https://doi.org/10.1063/1.2034085.

3. Xinyue Zhang, Luo Li, Yingxin Yu, Qingchun Zhang, Ningyu Sun, Zhu Mao, and Dongzhou Zhang. High Pressure–Temperature Study of MgF₂, CaF₂, and BaF₂ by Raman Spectroscopy: Phase Transitions and Vibrational Properties of AF₂ Difluorides // ACS Omega. 2024, 9 (22), 23675-23687. DOI: 10.1021/acsomega.4c01347.

4. F. Beuneu, C. Florea, and P. Vajda. EPR-study of electron-radiation induced Ca colloids in CaF₂ crystals // *Radiation Effects and Defects in Solids*. 1995, 136 (1–4), 175–179.

https://doi.org/10.1080/10420159508218816

5. H. Shi, L. Chang, R. Jia and R. Eglitis. Ab Initio Calculations of the Transfer and Aggregation of F Centers in CaF₂ // *The Journal of Physical Chemistry*. 2012, v. 116, p. 4832-4839.

DOI:10.1021/jp208845w.

6. L.B. Su, J. Xu, W.Q. Yang et al. Effect of gamma irradiation on undoped and uranium doped calcium fluoride crystals // *Solid State Commun.* 2004, 132, 757–760. https://doi.org/10.1016/j.ssc.2004.09.038.

7. V.T. Maslyuk, I.G. Megela, B. Obryk, and T.O. Vieru-Vasilitsa. Luminescent properties of LiF:Mg,Cu,P detectors irradiated by the 10-MeV electrons, Radiation Effects and Defects in Solids 172 (9–10) (2017) 782–789.

https://doi.org/10.1080/10420150.2017.1393425.

8. M.I. Romanyuk, J.J. Hainysh, Y. Plakosh, V. Kovtun, O.M. Turhovsky, G.F. Pitchenko, I.G. Megela, M.V. Goshovsky, O.O. Parlag, V.T. Maslyuk, N.I. Svatiuk. Microtron M-30 for radiation experiments: formation and control of irradiation fields // *Problems of atomic science and Technology (PAST)*. 2022, 3(139), 137-143. https://doi.org/10.46813/2022-139-137.

9. В.Т. Маслюк, І.Г. Мегела, Т.О. Вієру-Васіліца, І.Ю. Роман. Дослідження впливу радіаційних дефектів на оптичні та люмінесцентні властивості кристалів CaF₂ // Ядерна фізика та енергетика. 2016, т. 17, № 1, с. 53-58.

http://jnas.nbuv.gov.ua/article/UJRN-0000525157.