Dynamics recording of holographic gratings in a photochromic crystal of calcium fluoride

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Abstract. Dynamics of diffraction efficiency was monitored during recording a holographic grating in additively coloured CaF$_2$ photochromic crystal at 180-200°C. Reciprocity failure revealed in the study was attributed to diffusion playing the crucial role in grating formation: recording at larger laser power goes faster but requires more energy. The efficiency of a recorded hologram is found to depend on the temperature; maximum diffraction is measured at the temperature far below that of recording, supposedly because of dramatic distortions suffered by the crystal along with exposure.

1. Introduction
Photochromic crystals of additively coloured calcium fluoride (fluorite) demonstrate extreme stability and spectral/spatial selectivity of holograms, but they are hard to manufacture and require extreme temperature and exposure time/energy for recording. That is why fluorite-based light-sensitive materials have poor chances to compete with photopolymers and silver halide media in mass production of holograms but, especially keeping in mind fluorite as an excellent optical material for visible and IR range, they provide a reliable basis for high-precision applications of diffractive optical elements such as metrology (e.g. holographic prisms), spectroscopy (supernotch spectral selectors), etc.

The mechanism of hologram formation in fluorite crystals is based on photoionization, displacement and transformation of colour centres, in general similar to alkali halide crystals. The present work is aimed at understanding the processes involved in holograms evolution in the course of exposure, and revealing the changes of their properties.

2. Experimental
Transmission-type holographic gratings with spatial periods 5 and 15 µm were recorded at different temperatures from 180 to 200°C using the second harmonic emission of a CW DPSS Nd:YAG laser (532 nm) in the bulk of a 1.2×10×20 mm plate cut from a CaF$_2$ crystal additively coloured in sodium vapour. During the experiments, the plate remained in a quartz-windowed metal frame whose temperature was stabilized within ±0.1°C. To monitor the diffraction efficiency in the course of
exposure, one of the two recording beams was blocked with an electro-mechanical shutter, and the intensity of the second beam diffracted in the direction of the first one was measured. The experiments could last for several hours and even days, therefore perfect stability of the interference pattern was checked using video recording of its microscopic image that did not reveal even a tiny shift.

![Interference pattern and grating](image)

**Figure 1.** Microscopic images of the interference pattern (a) and the grating it produced when applied to the crystal (b); their spatial profiles (c and d, respectively).

### 3. Results and discussion

Although the shape of interference pattern was found expectedly almost sinusoidal, once imprinted into the crystal, it turned into a distorted distribution of colour centres with dark strips (enriched with the centres, supposedly corresponding to bright stripes of the fringe) notably narrower than those with lower concentration of the centres (figure 1). Such an intrinsically non-sinusoidal grating shape is attributed to the specific diffusion-drift mechanism of gratings formation, though nonlinear recording itself resulting from concentration saturation can be found in different materials. Another difference between the light pattern and its material record in the crystal is a sort of grainy structure of dark stripes that was recently discovered and discussed in terms of self-organization.

An exemplary plot of diffraction efficiency as a function of time / exposure is shown in figure 2. The diffraction efficiency may exceed 25%, however at the cost of very long-lasting and energy-inefficient recording.

In many experiments more complex nonmonotonous recording kinetics were observed, partially being a payment for the simple scheme of the experiment with the same wavelength used for recording and measurements. In this case, holograms are inevitably neither purely phase nor amplitude, providing most complex dynamics and selectivity properties.
3.1. Reciprocity failure
Brighter laser light makes holographic gratings develop faster, however the rate does not scale with laser power; in other words, reciprocity (Bunsen-Roscoe) law is not obeyed. In figure 3, the recording dynamics is presented as diffracted intensity vs. time (a) and exposure energy (b). The latter plot shows relatively more efficient, though requiring more time, growth of diffraction efficiency at lower power, in agreement with the idea of crucial role of diffusion – with finite speed – in grating formation. The rate of diffusive process involved could be evaluated by comparison of recording dynamics at different spatial periods; in this work, the diffusion coefficient of colour centres at 190°C was estimated as 200±50 nm²s⁻¹ that is one or two decades below that reported for KBr at 200°C.

Figure 2. Illustrative long-lasting recording dynamics: diffraction efficiency at the recording wavelength 532 nm as a function of time / energy.

Figure 3. Check of photochemical reciprocity: recording dynamics at different power density values (0.7, 16, and 38 mW/mm²) represented as intensity of diffracted light (proportional to diffraction efficiency) vs. time (a) and total energy of laser light passed through the crystal (b). Though at large power recording goes faster, it requires more energy.
3.2. Impact of temperature: crystal swelling?
Once recorded in a fluorite crystal, holograms survive long-lasting exposure to severe heat and intense light, though they do not necessarily remain unchanged, due to various photothermal transformations of colour centres constituting them. The diffraction efficiency changes with temperature in a reversible manner because of thermal expansion/shrinkage and corresponding variations of refractive index leading to Bragg detuning. One could expect the recovery of most efficient diffraction at the temperature equal to that of recording; however this is not the case. Thus, in the example presented in figure 4, the grating recorded at 180°C exhibits maximum diffraction at about 140°C. The modulation of intensity especially apparent at the temperatures above 130-140°C results from the interference of laser beams reflected from the front and back surfaces of the crystal; its period is compatible with known thermal coefficients.

The phenomenon that looks native rather for polymeric than for crystalline media, can be explained through "swelling" of the crystal caused by spatial redistribution of colour centres along with formation of a hologram – so dramatic swelling (about 10^{-3}) that cooling down by as much as 40°C is needed to compensate it. In practice, this means both desirable thermostating of volume holographic optical elements and a convenient approach to fine tuning them.

![Figure 4](image)

**Figure 4.** Original data: the temperature and the corresponding diffracted intensity as functions of time (a); the intensity of diffracted light plotted as a function of temperature (b). The solid line in (b) results from averaging the data (dots) over 20 adjacent points. The modulation is because of interference; the temperature of maximum diffraction (140°C) is found by Lorentz approximation of the data (dashed line).

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