

# Optical Switching and Limiting: New Applications for Silver Halide Technology?

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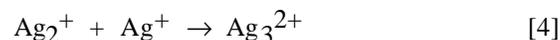
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Optical limiters are device elements which are highly transmissive at low optical fluences but become opaque when subjected to high fluences; they must furthermore be capable of rapid switching between the two states. Materials which exhibit such optical limiting function have been the subject of much research in recent years<sup>1,2</sup>. Applications include sensor and eye protection<sup>1a</sup>, optical communications<sup>3</sup>, and elements for optical information processing<sup>4</sup>. They represent a class of optically bistable materials<sup>5</sup> which have been demonstrated to be useful for optical computing, e.g. logic gating and pattern recognition<sup>4c</sup>. Recently, solutions of silver-containing metal-halide clusters have been reported<sup>1</sup> to show  $I_{1/2}$  values significantly lower than those reported for benchmark materials. These materials can be envisioned as comprising either unit cells or fragments of the unit cell of a silver halide lattice. We accordingly undertook to look for optical limiting behavior in nanosols comprising ca. 60 Å particles of silver bromide.

Detailed description of the experimental investigation has already been published<sup>6</sup>. Optical switching parameters are extracted from the results of pump-probe experiments by carrying out a *gedanken* experiment. Switching times,  $\tau$ , are consistently estimated to be in the ns regime, and values of  $I_{1/2}$ , the pulse laser exposure which elicits a 50 % decrease in transmittance of the medium, may be less than 20 mJ/cm<sup>2</sup>. Non-linearity of response,  $I_{1/2}$  and response time all increase with decreasing pAg of the nanosols. The materials can be cycled apparently indefinitely, provided they are subjected only to very short (sub-ns) laser pulses. Optical switching can be spectrally sensitized; comparable response parameters are obtained under these conditions. The non-linear character of the response is, however, very different: a true response threshold,  $I_0 = \text{ca. } 12 \text{ mJ/cm}^2$ , is observed. We suggest that these results imply a biphotonic mechanism of spectral sensitization<sup>7</sup>. Analysis of the optical

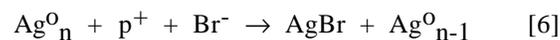
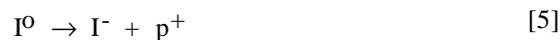
limiting mechanism suggests that iodide doping, which is adventitious in the present case, is critical to the observed photophysical behavior of the nanosols.

We propose the following reaction sequence:



with eq. 4 as a loss pathway, to account for the observed pAg dependence of  $I_{1/2}$ .

We also propose that these thermalized holes attack and oxidatively destroy the  $\text{Ag}^0_n$  color center species, reforming AgBr in the process. Thus:



where  $\text{I}^0$  designates the photohole trapped at an iodide center, and R is a positive hole sink external to the nanoparticle. Presence of such hole accepting species in the nanosol medium will lead to device fatigue, incompatible with practical optical switching utility.

Preliminary attempts to characterize the kinetics corresponding to eqs. 5-7 met with limited success. When the photolysis of the nanosol was carried out in the ns-time regime, only partial reversibility of the chemistry of eq. 1-4

was observed. We attribute this result to the possibility that eq. 7, irreversible elimination of photoholes by reaction with sacrificial donors, e.g., the PVA dispersant or alcohol solvent, can compete with the photogeneration of silver clusters, when the latter occurs on the ultra-nanosecond time scale. The result implies that the process of eq. 5 is rate determining in the above scheme. It furthermore is of photographic relevance, insofar as it provides a pathway for HIRF under conditions of nanosecond exposure, characteristic of laser recording of information and non-impact printing on photographic media, i.e, at exposure times that are short compared with ionic relaxation times in the AgX crystal.

## References

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