Absorption and luminescence of silver halide optical fibers

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Ag halide crystals are known to be transparent in the near and middle infrared, and optical fibers extruded from such crystals, in lengths of meters, have useful transmission at the CO_2 laser wavelength of 10.6 μm. It has been observed, however, that in certain cases aging and exposure to blue and ultraviolet radiation decreases the infrared transmission. These reductions can be understood in terms of recrystallization following extrusion and of photolytic darkening of the Ag halides under certain exposure conditions. The optical absorption edge of the fibers in the visible and the luminescent emission at low temperatures were measured and were found to be similar to those observed in the starting near-single-crystal preforms. The photoinduced darkening observed in fibers is characteristic of that observed in strained crystals. The large grain-boundary content and the strain present in fibers have little influence on the visible-wavelength absorption and emission characteristics but do play a role in the darkening and infrared transmission at 10.6 μm.

1. INTRODUCTION

Ag halide crystals are known to be transparent in the near- and middle-infrared spectral regions and can be formed into optical fibers by extrusion[1-3] or direct growth[4] from the melt. Thus these materials are potentially useful as waveguides in the middle infrared for applications involving high-power laser transmission, such as in laser surgery, and for applications in infrared systems. $AgCl_xBr_{1-x}$ ($0 < x < 1$) polycrystalline fibers were prepared in our laboratory by extrusion techniques and used to transmit and direct high-intensity CO_2 10.6-μm laser radiation. Transmission of several watts of cw radiation at 10.6 μm, with losses of a few decibels per meter, have been reported by us[1] and others,[2,3] and a 1983 conference report by Takahashi *et al.*[5] claims that AgBr fibers transmitting up to 50 W with losses of 0.22 dB/m have been developed. Spectral transmission in the range of 1–11 μm of AgCl fibers was recently reported.[6,7] In pure AgCl or AgBr fibers, we have observed a decrease in the infrared transmission as a function of dark storage time following extrusion. Mixed halide fibers are much more stable in this respect. Qualitatively, this can be understood in terms of recrystallization and grain growth following extrusion, which proceeds rapidly in pure halide materials but is inhibited in the mixed halide system. In most fibers, pure or mixed, room-temperature exposure to visible and near-ultraviolet radiation also generally causes a reduction in the infrared transmission and is a consequence of the well-known and quantitatively studied visible darkening of the Ag halides on exposure to band-gap excitation in the visible and near ultraviolet.[8] This darkening is understood in terms of the excitation of electrons and holes by band-gap excitation, the formation of Ag aggregates by electron trapping and Ag-ion localization, and the separate trapping of holes at specific centers or formation and release of halogen molecules. Depending on the conditions and wavelengths of exposure and the crystal purity, the darkening process occurs both in the volume of the crystal and at its surfaces,

although the mechanisms and reversibility of these two components of photolytic reduction are different. The reduction in the infrared transmission of an optical fiber on visible actinic exposure is a consequence of the absorption and scatter of infrared radiation by the volume photolytic Ag and the possible coupling out or absorption of infrared radiation by photolytic Ag formed at the cylindrical surface of the fiber. Decoration of grain boundaries by photolytic Ag[9] and a resultant enhanced-grain-boundary scattering of infrared radiation also may be involved.

At low temperatures ($T \lesssim 100$ K), AgCl and AgBr crystals show luminescent emission on ultraviolet excitation,[10-13] with no detectable darkening. The emission of AgCl near 80 K shows in all cases an emission band peaked near 495 nm with a half-width of about 0.3 eV. The emission is effectively quenched at temperatures above about 120 K. AgBr or AgBr-rich mixed crystals show only a weak red emission near 80 K, although at lower temperatures, near 4 K, an intense green emission becomes dominant. Moser and Lyu[14] have presented strong evidence that the latter emission is related to a low residual iodide-ion content in nominally pure AgBr. Although the emission in AgCl is reasonably well characterized, the radiative recombination process has not been established. It is believed to be an intrinsic process involving a self-trapped hole and electron migration to that site with subsequent radiative emission. The presence of iodide ion, which is a competing hole trap, can effectively overwhelm the intrinsic process, especially in AgBr. Kanzaki and Sakuraji[15] and Kanzaki *et al.*[16] have speculated that in AgBr-rich crystals the radiative decay involves free excitons and an exciton–phonon interaction, whereas in AgCl-rich crystals the emission occurs by radiative decay of a self-trapped exciton.

Some work was reported on the luminescence of Ag halide emulsion grains,[11,17,18] and the basic emission does not appear to be different from that observed in large single crystals. This is surprising in view of the orders-of-magnitude difference in surface-to-volume ratio in these two systems.

Studies of the luminescence in highly polycrystalline fibers, which also have high grain-boundary content as well as strain, are described in this paper.

2. EXPERIMENTAL DETAILS

In the experimental setup for measuring luminescence, the crystal or optical-fiber sample was attached to the cold finger of a vacuum optical cryostat and excited by radiation from a 200-W Osram high-pressure Hg lamp, which is dispersed by a Jarrell-Ash 0.25-m monochromator. The emitted luminescence was collected and imaged on the entrance slit of a 0.5-m Bausch & Lomb monochromator and detected by an RCA C 31034 photomultiplier. This multiplier has a nearly flat spectral response between 350 and 850 nm. The signal was recorded as a function of wavelength on an x–y recorder, thus giving a direct display of the emission spectrum. Another Hg lamp was used for exposure of the samples at room temperature when the effects of photolytic darkening on transmission and emission characteristics were investigated.

The infrared transmission of the samples at 10.6 μm was measured directly with a CO_2 laser and an energy detector by using a sample-in sample-out method. The visible spectral transmission characteristics of both fiber sections and larger crystals sections were measured by using a Cary 14 recording spectrophotometer. The transmission of fibers of lengths up to several centimeters and diameters of a millimeter or less could be measured with appropriate masking of the sample and reference beams. The Cary instrument has adequate sensitivity for even such severely masked beams.

The fiber samples studied were sections a few millimeters to several centimeters long cut from longer extruded fibers. The extrusion conditions have been described elsewhere.[1] The fiber diameter was about 0.9 mm, and the fiber end faces were either as cut using a sharp razor blade or polished by techniques suited for soft materials.

The optical quality of the end faces of the fibers prepared this way was not high and resulted in some losses at the end faces above and beyond the expected specular Fresnel reflection losses. A study of the quality of the fiber end faces is under way in our laboratory.

3. RESULTS AND DISCUSSION

A. Infrared Transmission

Figure 1 shows the initial transmission of 10.6-μm CO_2 laser radiation through a 15-cm-long $AgCl_{0.95}Br_{0.05}$ extruded fiber as well as the decrease in transmission with time when the fiber is simultaneously exposed to an unfiltered high-intensity Hg lamp placed about 5 cm from the middle and normal to the fiber. The initial transmission is independent of the laser intensity, at least up to about 10 W incident upon the 1-mm-diameter end face of the fiber.

The initial transmission of this 15-cm fiber section, with polished end faces, is about 72%, as seen in Fig. 1. To calculate an upper limit of the absorption coefficient of this fiber, we can use the expression for the normal transmission T of a plane-parallel nonscattering sample of index of refraction n, path length t cm, and absorption coefficient $\alpha(cm^{-1})$. When interference effects are neglected, T is given by[19]
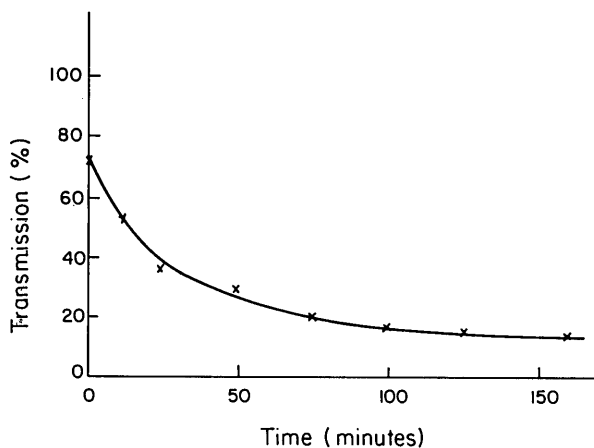

Fig. 1. Transmission of a 15-cm-long $AgCl_{0.95}Br_{0.05}$ fiber at 10.6 μm, as a function of exposure time to an unfiltered Hg lamp. The initial transmission at time zero is 72%.

$$T = (1 - r)^2 e^{-\alpha t}/(1 - r^2 e^{-2\alpha t}), \quad (1)$$

where

$$r = \frac{(n-1)^2 - k^2}{(n+1)^2 + k^2}, \quad k = \frac{\alpha\lambda}{4\pi},$$

and λ is the wavelength. r is the Fresnel reflection coefficient at the Ag halide–air interface for near-normal incidence. The index of refraction n and the absorption coefficient α are in general functions of the wavelength. The index n for this fiber is about 2.1 at 10.6 μm. Since we know that α is small, we can assume that $k \ll n - 1$, giving $r = 0.126$. For the measured $T = 0.72$ and $t = 15$ cm, Eq. (1) gives a value of 5×10^{-3} cm^{-1} for α, or about 2 dB/m. This loss coefficient may include both absorptive and scattering loss. If the fiber had no losses, Eq. (1) would reduce to $T = 2n/(n^2 + 1)$ to give a maximum transmission of 78%.

With continued exposure to the high-intensity Hg source, the infrared transmission continually decreases, falling to about 10% after 2.5 h of exposure. While the exposing and sample geometries make it difficult to analyze the darkening quantitatively, the reduced transmission is certainly a consequence of photolytic Ag formation on the end faces and cylindrical surface and in the volume of the fiber. In large crystals, the absorption spectrum of the photolytic Ag is known to depend on the strain and the state of purity of the crystal.[8] Large strained crystals show a broad and nearly spectrally flat (neutral) darkening spectrum in the visible. A measurement of the spectral character of the darkening in these fibers also showed it to be rather neutral, a result consistent with the strain and probable purity of these fibers.

Restoration of most of the initial transmission could be achieved by mild etching of the fiber in HCl, which removes surface Ag, plus thermal annealing near 300°C, which effectively bleaches most of the internal Ag by releasing trapped holes that attack the Ag aggregates.

B. Luminescence Properties of $AgCl_{0.95}Br_{0.05}$

Figure 2 shows the steady-state luminescent emission near 80 K of fiber sections of the type studied in infrared transmission ($AgCl_{0.95}Br_{0.05}$). Curve (a) shows the steady-state luminescent emission spectrum with steady ultraviolet exci-
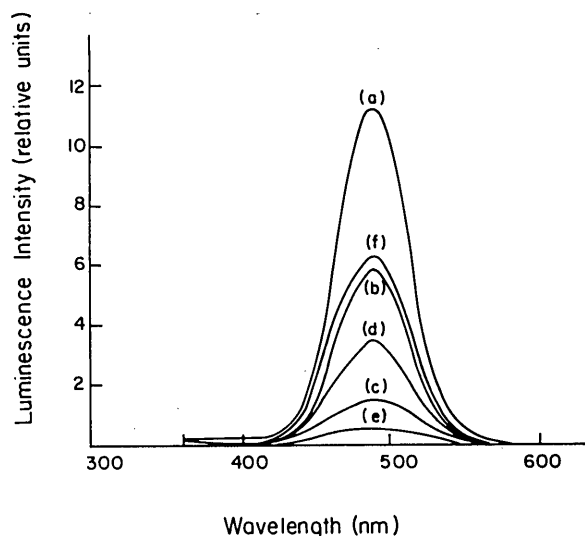
Fig. 2. Steady-state luminescent emission near 80 K of a $AgCl_{0.95}Br_{0.05}$ fiber with ultraviolet excitation [curve (a)] and following various treatments: curve (b), 1-h exposure at room temperature to an unfiltered Hg lamp; curve (c), after an additional 1-h exposure; curve (d), after annealing at 150°C for approximately 2 min; curve (e), after an additional exposure of 1.5 h; curve (f), after mild etch in HCl.

Fig. 3. Comparison of steady-state luminescent emission spectrum of $AgCl_{0.95}Br_{0.05}$ fiber [curve (a)] and large pure AgCl crystal [curve (b)] near 80 K with ultraviolet excitation.[12]

tation. The spectrum is very similar to that reported for large AgCl crystals, as illustrated in Fig. 3. The single-crystal spectrum is taken from the work of Wiegand.[12] Spectra reported by others show only small differences. This supports the conclusion that low-temperature radiative recombination in AgCl occurs at an intrinsic site and that competing recombination at grain boundaries or surfaces is small.

Returning to Fig. 2, we note that exposure of the fiber at room temperature to unfiltered radiation from a Hg lamp for periods of up to 2 h results in a marked reduction in the subsequent low-temperature luminescent emission intensity but not in the emission band shape [curves (b) and (c), Fig. 2]. Again, this reduction is believed to be a consequence of the attentuating effect of photolytic Ag on both the excitation intensity and the emission intensity. Thermal annealing at 150°C [curve (d), Fig. 2] or etching in HCl [curve (f), Fig. 2] results in partial restoration of the initial emission intensity.

A similar set of measurements, but with the Hg-lamp exposure filtered so as to transmit only the 250–400-nm spectral region, gave similar results, as illustrated in Fig. 4. The difference from the results illustrated in Fig. 2 is that the sample darkens much more rapidly. This may be understood in terms of the bleaching of photolytic Ag by longer-wavelength radiation. The darkening, the spectral character of the darkening, and the effective efficiency are the net effect of darkening by ultraviolet and blue light and simultaneous bleaching by longer wavelengths.

C. Luminescence: $AgCl_{0.05}Br_{0.95}$
Some luminescence measurements at 80 K have also been made on Br-rich fibers, namely, $AgCl_{0.05}Br_{0.95}$. The results are shown in Fig. 5. Excitation in this case was done with 365-nm radiation. As noted in the Section 1, it is known
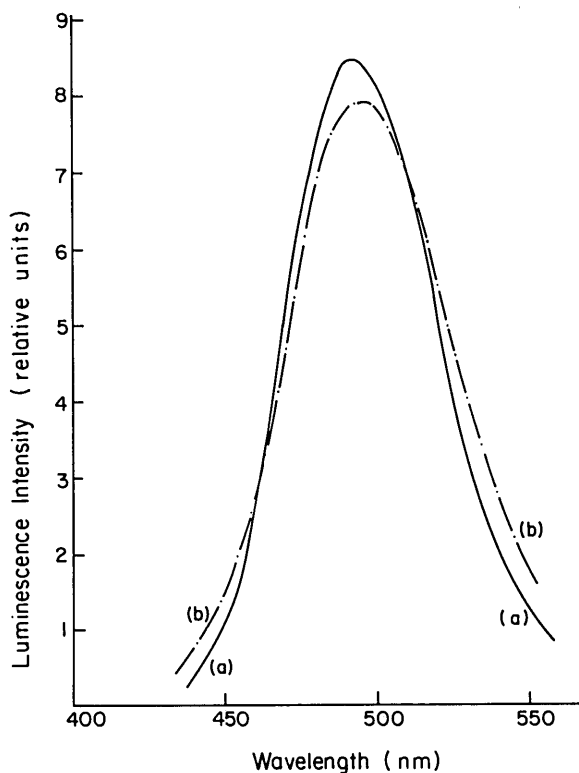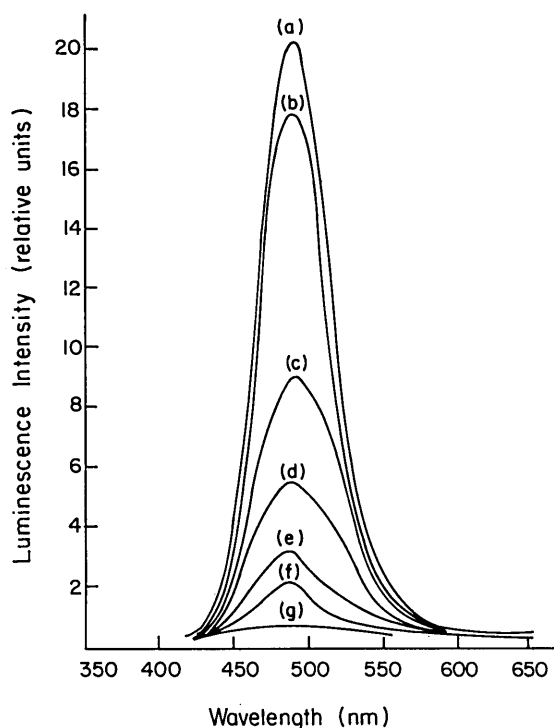

Fig. 4. Steady-state luminescent emission near 80 K of $AgCl_{0.95}Br_{0.05}$ fiber with ultraviolet excitation [curve (a)] and after various treatments: curve (b), after 10-sec exposure at room temperature to a Hg lamp filtered to transmit only the 200–400-nm spectral region; curves (c), (d), (e), (f), and (g), after total exposure times of 50, 70, 130, 300, and 1000 sec, respectively, to the filtered Hg lamp at room temperature.
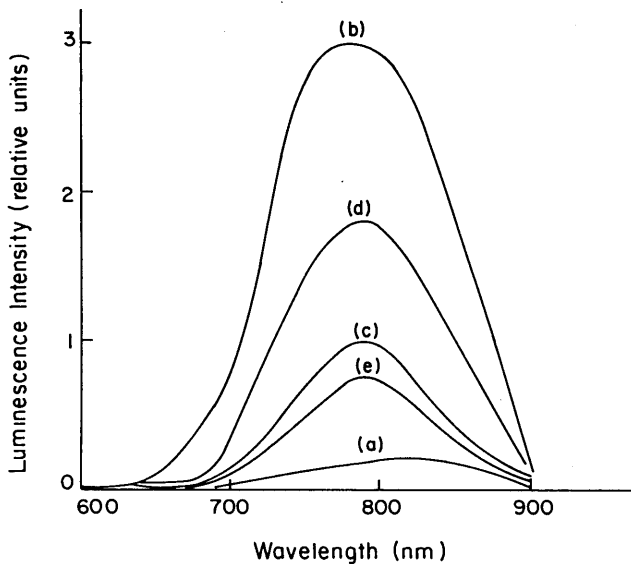
Fig. 5. Steady-state luminescent emission at 77 K of $AgCl_{0.05}Br_{0.95}$ fiber excited by 365-nm radiation [curve (a)] and following various treatments: curve (b), after 5-min anneal at 200°C; curve (c), after exposure to filtered (200–400-nm) ultraviolet radiation for 5 min at room temperature; curve (d), after second anneal for 5 min at 200°C; curve (e), second exposure to filtered ultraviolet light for 5 min.
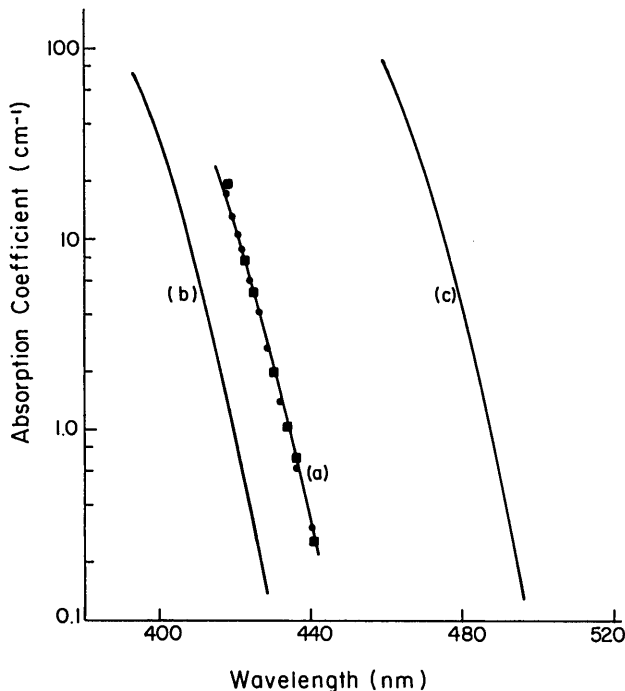

Fig. 6. Curve (a) shows the absorption edge of both the $AgCl_{0.95}Br_{0.05}$ crystal preform (filled circles) and the fiber section extruded from this preform (filled squares). Curves (b) and (c) are the optical edges of large AgCl and AgBr crystals, respectively.[13] Measurements were made near 20°C.

that AgBr luminescence is weak at 80 K. Curve (a) of Fig. 5 shows the initial luminescence observed in our fibers. After a brief anneal at 200°C, however, there is a marked increase in the subsequent low-temperature luminescence intensity, with a strong band appearing centered at about 780 nm.

This is shown as curve (b) of the figure. Riesenfeld[20] has reported a similar phenomenon in large AgBr crystals and suggested that this is related to an increased Ag-ion vacancy concentration, resulting from the thermal dispersal of aggregated cationic impurities by the 200°C treatment or a reduction of interstitial Ag ions, which could act as nonradiative recombination · centers. Exposure to ultraviolet light (200–400 nm) at room temperature for 5 min reduces the luminescence intensity [curve (c)], and a second annealing at 200°C again leads to an increase in the luminescence [curve (d)]. A second exposure to the ultraviolet light at room temperature further reduces the luminescence [curve (e)].

4. OPTICAL ABSORPTION EDGE IN THE VISIBLE

The optical absorption edge in the visible of an $AgCl_{0.95}Br_{0.05}$ fiber was measured and compared with the optical absorption of the crystal preform before extrusion and with some published data on the absorption edge of Ag halide crystals.[13] The results are presented in Fig. 6 and show that large single crystals and polycrystalline fibers have a virtually identical visible optical absorption edge.

5. CONCLUSIONS

The similarity of the optical absorption edge in the visible and the low-temperature luminescent emission in polycrystalline Ag halide fibers and large melt-grown single crystals means that grain boundaries and strain fields do not play an important role in defining these properties. The visible optical absorption edge is determined by the band structure of this solid, and the luminescence by an intrinsic radiative recombination center, particularly in the AgCl-rich system.

The reduction of the luminescence intensity and of the 10.6-μm infrared transmission with ultraviolet or blue exposure can be understood in terms of the well-known photolytic darkening of the Ag halides. The photolytic Ag attenuates the exciting and emitted light in the case of luminescence and also absorbs the 10.6-μm infrared radiation. The geometry of fibers makes it difficult to expose them in a manner amenable to quantitative analysis of the resultant optical darkening. The general behavior is similar to that observed in large single crystals.[8] Bleaching (destruction) or dispersal of the photolytic Ag by chemical or thermal means can partially restore the initial optical transmission of the fibers. The location and form of the photolytic Ag can limit the degree of reversal achieved by these methods. Chemical etching with HCl can remove only surface Ag and leaves the surface somewhat changed optically. Thermal reversal can involve electron and hole release and recombination or can be just a dispersal of larger Ag aggregates. In any case, it is most effective for internal Ag and requires temperatures above 300°C for complete reversal. Optical bleaching can be affected by longer wavelengths ($\gtrsim 500$ nm) either simultaneous with the exposing radiation or by subsequent exposure. The former case is illustrated by the results of optically filtered and unfiltered exposures, as discussed in Subsection 3.B. Optical bleaching may involve either genuine reversal or dispersal of larger Ag aggregates.

ACKNOWLEDGMENTS

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