Indirect optical absorption and radiative recombination in silver bromoiodide

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(Received 23 September 1987)

The low-temperature (4.2 K) and room-temperature absorption spectra of several $AgBr_{1-x}I_x$ ($x = 0-0.25$) samples have been obtained. Conventional analysis of these spectra yields the band-gap energy (E_g), which decreases with iodide content. The band-gap energies at 4.2 K range from 2.684 eV for pure AgBr to 2.448 eV for $AgBr_{0.75}I_{0.25}$. The more accurate band-gap information is used to estimate the trap depth of the acceptor states observed in the low-temperature emission. Data indicate that *both* donors and acceptors are *shallow* traps in $AgBr_{1-x}I_x$ systems.

INTRODUCTION

The band-gap energy (E_g) and the individual positions of the valence- and conduction-band edges in $AgBr_{1-x}I_x$ are of fundamental as well as practical importance. The band-gap energy determines the onset wavelength of intrinsic electron-hole production by light as well as the wavelength of emission. The relative positions of the valence and conduction bands control the injection of electrons and holes by spectral sensitizers. The relative positions of the band edges also control the flow of charge carriers in heterojunction structures.

The optical emission and optically detected magnetic resonance (ODMR) spectra of $AgBr_{1-x}I_x$ ($x = 0-0.03$) have been examined at liquid-helium temperatures.[1] In that investigation the donor-acceptor nature of the recombination luminescence in $AgBr_{1-x}I_x$ ($x \geq 0.01$) was noted. Numerous investigations of the iodide-related luminescence in AgBr, usually at low concentrations, have been published.[2-7] Only a few reports of the absorption and band-gap energy in $AgBr_{1-x}I_x$ are available.[8-10]

The theory of light absorption by semiconductors can be found in texts on solid-state physics.[11,12] The essential results as outlined in Ref. 12 will be given below. The form of the absorption coefficient (α) as a function of energy ($h\nu$) for a phonon-assisted ($\Delta k \neq 0$) indirect transition between indirect valleys consists of two parts corresponding to phonon absorption and emission:

$$\alpha_a(h\nu) = \frac{A(h\nu - E_g + E_p)^2}{\exp(E_p/kT) - 1} , \qquad (1)$$

$$\alpha_e(h\nu) = \frac{A(H\nu - E_g - E_p)^2}{1 - \exp(-E_p/RT)} , \qquad (2)$$

where A is a constant and E_p is the phonon energy. Both phonon absorption and emission are possible when $h\nu > E_g + E_p$ so that the absorption coefficient is given by

$$\alpha(h\nu) = \alpha_a(h\nu) + \alpha_e(h\nu) . \qquad (3)$$

Plots of $\sqrt{\alpha}$ versus energy should have two straight-line portions, which extrapolate to $E_g + E_p$ and $E_g - E_p$. Changes in temperature will change the relative contribu-

tions of phonon absorption and emission, as well as change the value of E_g, because of changes in the lattice constant.

In heavily doped indirect-gap semiconductors, it is possible to conserve momentum by a scattering process and phonon assistance becomes unimportant.[12] The absorption coefficient becomes

$$\alpha(h\nu) = A'N(h\nu - E_g - \xi)^2 , \qquad (4)$$

where N is the concentration of scatterers and ξ is a filling term that may be zero for dopants that do not substantially change the Fermi level.

In this paper, we will examine the band-gap energy in $AgBr_{1-x}I_x$ ($x = 0-0.25$). We will also reexamine the nature of the radiative recombination and acceptor trap depths in these systems.

EXPERIMENT

The low-temperature absorption and emission spectra were obtained with a 1-m Czerny-Turner spectrometer, an RCA C31034 photomultiplier, and a lock-in amplifier. A tungsten-halogen lamp was used for absorption studies and a high-pressure xenon lamp, in conjunction with a monochromator and filters, was used to excite the sample for emission studies. The low-temperature measurements were made with the samples immersed in liquid helium in a double-glass Dewar flask. For measurements at 77 K, liquid nitrogen was used in place of the liquid helium. The absorption spectra were measured by first obtaining the lamp spectrum and then determining the 100% transmission level from an extrapolation of measurements in the region of zero absorption in the forbidden gap. Thus the need to make separate reflection corrections was eliminated. Room-temperature absorption measurements were made on a Cary 17 spectrophotometer. Values of α obtained on pure AgBr matched those in Ref. 1 within 10%.

For the luminescence-decay experiments, the sample was excited with the 337-nm line of an N_2 laser. The laser pulses had a width [full width at half maximum (FWHM)] of ~0.5 ns and energies of 3–5 μJ per pulse. The emission was collected with a lens and focused

through a uv-cutoff filter into a compact monochromator with a red-sensitive photomultiplier tube (RCA 4832). The spectral resolution was ~3 nm.

The photomultiplier response was fed into a computer-controlled Tektronix (7912 AD) programable digitizer. Termination in 1 kΩ gave a measured RC time constant of <0.5 μs and was used for measurements in the range 1–200 μs. All emission-decay curves were the average of at least 32 transient emission signals.

Two types of sample were used. Sheet crystals grown between quartz plates were provided by W. K. Lam, of these laboratories. The melt-grown sample was cut from a boule grown by conventional Bridgman techniques. A melt-grown sample was shown to be uniform in iodide content by taking cuts from around the sample used and having them analyzed by neutron-activation techniques. The sheet crystals are known to have some nonuniformity in their iodide content.[13] Usually, this is a thin layer of higher iodide on the last surface to cool.[13] The overall iodide content in each sample was determined by neutron-activation analysis and is given in Table I.

RESULTS

The absorption spectra in the region of the indirect edge are given in Fig. 1 for the series of $AgBr_{1-x}I_x$ samples. These spectra generally exhibit a parabolic shape characteristic of an indirect absorption. The exception is the sample containing 0.3 at. % iodide, which has a shoulder at ~2.7 eV. This feature has been identified as a transition allowed by momentum conservation due to the iodide.[3] A similar feature was observed at low bromide concentration in a $AgCl_{1-y}Br_y$ system and identified as a disorder-induced indirect transition.[14] It is evident from an examination of Fig. 1 that the absorption edge moves to longer wavelengths with increasing iodide content.

Plots of the square root of α versus energy are given in Fig. 2 for samples containing 0, 3, 6, 15, and 25 at. % iodide. The extrapolations of these plots to $\alpha = 0$ are also shown. The data derived from these plots and similar plots (not shown) for the 300-K spectra are given in Table II.

The steady-state emission spectra for the $AgBr_{1-x}I_x$ samples are given in Fig. 3. For donor-acceptor transitions with Coulomb interactions in the ground state, the emission shifts to lower energies as a function of time after pulsed excitation.[1] Emission spectra (not shown) were obtained with various delay times after pulsed excitation. The straight-line portion of the high-energy side
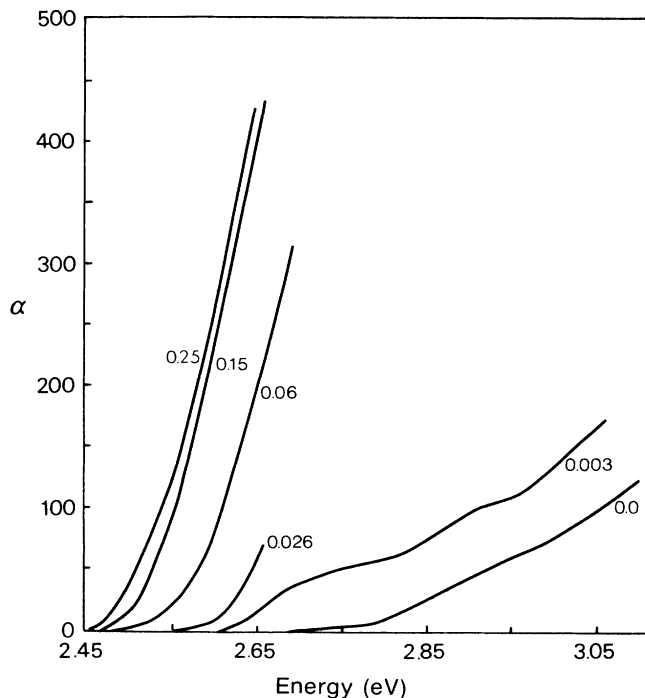

FIG. 1. The absorption spectra of $AgBr_{1-x}I_x$ ($x = 0$–0.25) at 4.2 K. The samples were 100-μm-thick sheet crystals except the 3-at. % sample, which was 840-μm.
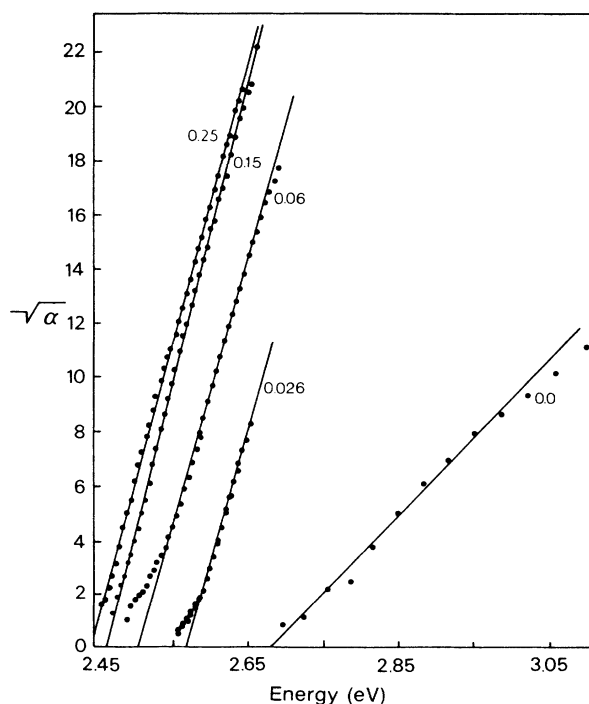

FIG. 2. Plots of the square root of α vs energy for $AgBr_{1-x}I_x$ at 4.2. The linear extrapolations to $\alpha = 0$ are shown.

TABLE I. Neutron-activation analysis of the samples.

Designation	Type of sample	Iodide fraction
AgBr	Sheet	<0.0001
$AgBr_{0.997}I_{0.003}$	Sheet	0.0035
$AgBr_{0.97}I_{0.03}$	Melt-grown	0.026
$AgBr_{0.94}I_{0.06}$	Sheet	0.061
$AgBr_{0.85}I_{0.15}$	Sheet	0.15
$AgBr_{0.75}I_{0.25}$	Sheet	0.25

TABLE II. Data derived from extrapolation of $\sqrt{\alpha}$ plots.

Sample	E_g (eV)	Temperature (K)
AgBr	2.684[a]	4.7
	2.675[a]	75
	2.571[b]	~300
$AgBr_{0.97}I_{0.03}$	2.565±0.005	4.2
	2.532±0.005	77
$AgBr_{0.94}I_{0.06}$	2.503±0.005	4.2
	2.412±0.005	~300
$AgBr_{0.85}I_{0.15}$	2.460±0.005	4.2
	2.358±0.005	~300
$AgBr_{0.75}I_{0.25}$	2.440±0.005	4.2
	2.348±0.005	~300

[a]Data taken from Refs. 11 and 14.
[b]Obtained from data given in Ref. 8.

of the emission obtained with delay times > 100 μs is extrapolated to zero to give E_{edge}. Data derived from these spectra and the absorption measurements are given in Table III.

DISCUSSION

Results obtained at 4.2 K are examined first since interpretation is simplified by the absence of absorbed-phonon components in the band-to-band transitions at very low temperature.[12]

The change in absorption band shape and E_g with iodide concentration are completely analogous to the changes observed in the chloride-rich $AgCl_{1-y}Br_y$ system.[14] In both cases, a larger anion is introduced as an impurity in the halide sublattice. Very small amounts of impurity (0.1–0.3 at. %) induce a shoulder near the band origin and a tail extending to wavelengths much longer than would be expected for a phonon-assisted transition. At concentrations exceeding a few percent, the absorption edge rises more steeply than the pure crystal and the band edge is significantly shifted to lower energy.

The shoulder is understood to arise from a phononless indirect transition assisted by impurity scattering. The tail may be due to a localized state of the iodide ion, or to the perturbing effect of the iodide ion on the valence-band edge. Analysis of the band-edge data over a range of iodide concentrations is complicated by possible iodide nonuniformities in some samples, by possible changes in
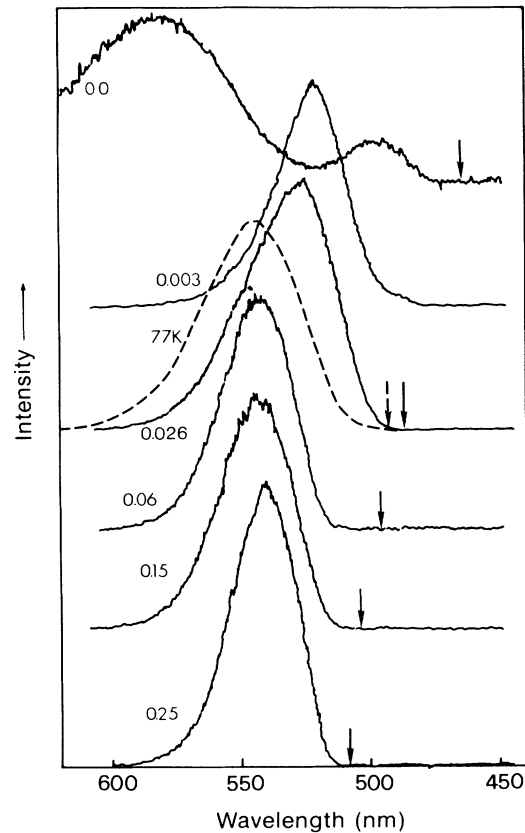

FIG. 3. The emission of the six samples listed in Table I at 4.2 K. The emission spectrum for $AgBr_{0.97}I_{0.03}$ at 77 K is also shown. The arrows indicate the values of E_g for each sample.

the absorption mechanism from photon-assisted to impurity scattering, and by disorder contributions in the regions of very weak absorption. The iodide nonuniformity has been examined in some samples.[13] It consists of a thin layer of higher iodide content (10% higher) on the side of the sample that solidified last. This layer, which is less than 1% of the sample thickness, should not make a large contribution to the absorption but may contribute to some of the tailing at long wavelengths. A large disorder contribution occurs at low iodide concentrations (0.3 at. %) (Refs. 3 and 14), and these data were not used to determine band-gap energies.

TABLE III. Data derived from the emission spectra and the absorption measurements.

Sample	λ_{max} (nm)	λ_{edge} (nm)	$E_g - E_{edge}$ (meV)	Temperature (K)
AgBr	495;580	476;530		4.2
$AgBr_{0.008}I_{0.003}$	519	495		4.2
$AgBr_{0.97}I_{0.03}$	525	498	75±20	4.2
	545	509[a]	95±20	77
$AgBr_{0.94}I_{0.06}$	540	514	90±20	4.2
$AgBr_{0.85}I_{0.15}$	543	522	85±20	4.2
$AgBr_{0.75}I_{0.25}$	541	522[a]	65±20	4.2

[a]Estimated from emission spectra in Fig. 3.

The band-gap energies (E_g) are derived from a graphical fit to the data in Fig. 2. For pure AgBr, E_p (~ 0.009 eV, Ref. 14) is subtracted from the intercept to account for the energy of the emitted phonon [see Eq. (2)]. At concentrations exceeding 1 at. % iodide, it is assumed that an impurity-scattering mechanism dominates. According to Eq. (4) and previous discussions, the intercept gives the band gap directly. From a practical point of view, uncertainty in choosing between these two mechanisms amounts to only a small correction (~ 10 meV) to the band-gap determination. Graphical analysis indicates that the intercept is determined with a standard deviation of $\sim \pm 5$ meV. The results are given in Table II and plotted in Fig. 4. There is a rapid drop in E_g with small amounts of iodide, followed by a leveling off. It might be expected that E_g decreases slowly from the value at 25 at. % iodide up to the solubility limit.[15]

At higher temperatures the curves contain contributions from phonon absorption as well as phonon emission and impurity scattering. At any level of iodide, raising the temperature causes the absorption edge to shift to longer wavelengths and the tail to become larger and broader. The shifting is attributed to a change in the lattice constant, while the tailing is presumably due to phonon absorption and increased disorder. Band gaps were determined in the same way as at 4.2 K and are presente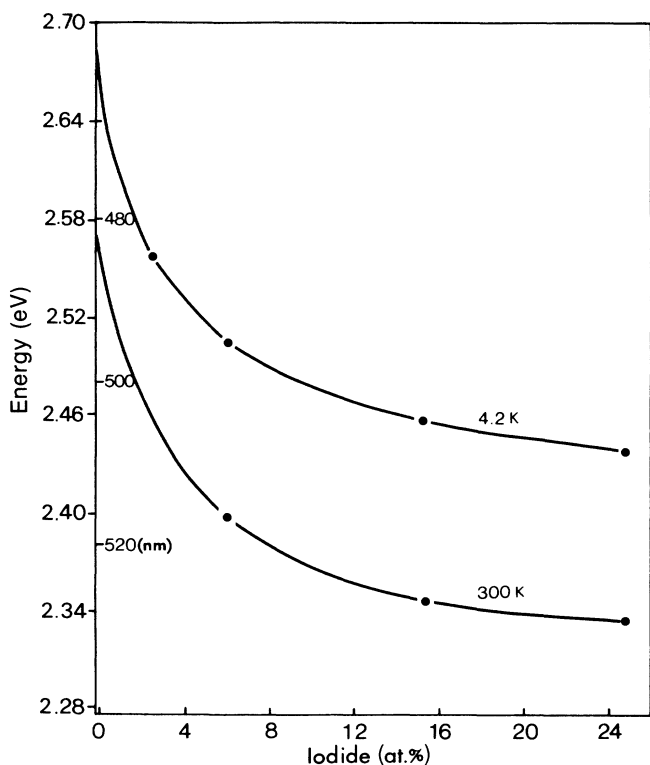d in Table II and Fig. 4. Changes in band-gap energy at room temperature with increasing iodide concentration parallel those obtained at 4.2 K.

The data given in Tables II and III allow a reexamination of the donor-acceptor model for radiative recombination in the AgBr$_{1-x}$I$_x$ system.[1] The donor-acceptor emission energy (E_{DA}) is given by

$$E_{DA} = E_g - (E_D + E_A) + \frac{e^2}{\epsilon r} , \tag{5}$$

where E_g is the band-gap energy, E_D and E_A are the donor and acceptor binding energies, respectively, and the last term is the Coulomb energy of the pair, which approaches zero for large value of the separation.[12] Experimentally, the short-wavelength leading edge of the luminescence (λ edge) is taken as the wavelength of the donor-acceptor emission. This value of $E_g - E_{edge}$ is then approximately equal to the sum of the donor and acceptor binding energies minus some average of the Coulomb energy. If the E_{edge} is determined from spectra taken with long delay times between excitation and emission, then the Coulomb term becomes negligible owing to decay of closer pairs and the sum $(E_D + E_A)$ is obtained directly.

Absorption measurements in the infrared on electrons bound to divalent cation impurities or silver-ion interstitials, which are thought to be the donors in AgBr and AgBr-I, give values of 25–35 meV for E_D.[16–19] Using an average of these values, E_a is estimated to be 50 ± 30 meV from the 4.2-K data in Table III for AgBr$_{1-x}$I$_x$ samples with iodide concentrations 1 and 25 at. %. The acceptor-trap depth inferred from this value is much smaller than that obtained in Ref. 1, which used the value of E_g for AgBr.

The nature of the acceptor species in AgBr$_{1-x}$I$_x$ ($x > 0.01$) is still not clear. In an earlier investigation, it was shown that the acceptor had a net negative charge in its ground state,[1] and ODMR data suggested the association of iodide ions with the acceptor.[1] Thus the acceptor is believed to be negatively charged, to have associated iodide ions, and to be a shallow trap (~ 50 meV).

A plausible acceptor is a silver-ion vacancy with iodides in the first shell. It has the correct charge and associated iodide ions. Since it is a shallow trap, its binding energy is estimated by

$$E_A = \frac{M^*}{\epsilon^2} R_0 , \tag{6}$$

where M^* is the effective mass of the hole, ϵ is the static dielectric constant, and R_0 is the binding energy of an electron in a hydrogen atom (13.6 eV).

For a value of E_A equal to ~ 50 meV, the ratio of (M^*/ϵ^2) is on the order of ~ 0.004. Given that the value of ϵ is 10.6 at 4.2 K for AgBr,[20] this leads to a value of ~ 0.45 for M^* of a bound hole, which is less than the values for the free hole in AgBr.[21] The values of ϵ for AgBr$_{1-x}$I$_x$ should be somewhat larger than the value for AgBr but that should not significantly change the estimate of M^*.

Estimates of the conduction-band shift for AgBr$_{1-x}$I$_x$ based on lattice parameter changes indicate only a small

FIG. 4. Plot of the band-gap energy as a function of iodide content at 4.2 and 300 K.

downward movement (10 meV for 4 at. % iodide).[10] Thus, most of the decrease in E_g must be due to an upward shift of the valence band with iodide incorporation. This conclusion was also inferred from recent studies of hole injection by spectral sensitizing dyes,[22] and was confirmed by recent x-ray photoemission spectroscopy measurements.[23]

CONCLUSIONS

The systematic decrease of the band-gap energy with increasing iodide content in silver bromide has been quantified for crystals at 4.2 and 300 K. This work has also shown that the acceptor-trap depth in the silver bromoiodide system is of the same order as the donor depth.

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