Electrical Pumping of Color Center Lasers

ROBERT W. BOYD, MICHELLE S. MALCUIT, AND KENNETH J. TEEGARDEN

Abstract—This paper presents an assessment of the feasibility of using electrical pumping to achieve laser action in color centers in the alkali halides. We discuss mainly the self-trapped exciton in the alkali halides, which is a prime candidate for such a pumping scheme because it is known to produce strong electroluminescence. The theory of electrical contacts to insulating crystals is reviewed, as is the theory of space-charge-limited currents in insulators. It is shown that sufficient energy can be delivered to an alkali halide crystal by a space-charge-limited current to reach the threshold for laser action. We present experimental evidence which demonstrates that when ohmic contact is made to a KI single crystal, large space-charge-limited currents can flow. Finally, from the measured value of the electroluminescent intensity we infer the value of the population inversion achieved through electrical pumping of KI with blocking contacts.

I. INTRODUCTION

COLOR center lasers have proven to be a versatile source of tunable radiation for the near infrared spectral region [1] and there is hope that this region of coverage can be extended to both longer and shorter wavelengths. All color center lasers thus far developed have been pumped optically, often by a large and expensive gas ion laser. The usefulness of color center lasers would be greatly increased if it were possible to pump them electrically. Also, there are color centers that cannot be pumped optically because of the lack of suitable pump sources. Electrical pumping could extend the range of color center lasers into the visible and near ultraviolet. This paper presents a theoretical study of electrically pumped color center lasers, and demonstrates that it is possible to deliver enough electrical energy to a color center laser crystal to reach the threshold for laser action. Also included is a discussion of relevant experimental results.

Electrically pumped solid-state lasers already exist, of course, in the form of semiconductor diode lasers. In these lasers, current is passed through a forward biased p-n junction, and lasing occurs by electron-hole recombination radiation. Tunability is limited to the extent that the bandgap energy can be modified by some external parameter, such as temperature or pressure.

In a color center laser, tunability results from the large homogeneously broadened emission linewidth. Color center lasers are conventionally used as optically pumped lasers, using the pumping scheme shown in Fig. 1.

A potentially more efficient pumping scheme involves impact excitation by a current passing through the crystal. The phenomenon of electroluminescence [2]–[8] is well established in the alkali halides. It has been found that certain color centers can be excited by the application of a transient electric field of magnitude between $10^4$ and $10^5$ V/cm. Measurements of emission spectra show that in pure crystals an intrinsic emission due to the recombination of electrons with self-trapped holes is excited by the electric field. Heavy metal impurities such as Ag or Tl can also be excited by this method [9], [10]. These color centers luminesce in the visible and ultraviolet. No attempt has been made to observe electroluminescence from infrared emitting centers, but the general principles involving electroluminescence in the visible and the ultraviolet should also be applicable in the infrared.

The present paper deals primarily with the self-trapped exciton because in the alkali halides this center is most easily excited with an electric field. In addition, there exist centers which are closely related to the self-trapped exciton and which are also candidates for electrically pumped laser action. Heavy metal impurities in the alkali halides display electroluminescence which may be due to host-sensitized luminescence resulting from a resonant interaction between the self-trapped exciton and the impurity. It is known that such a transfer can take place when the trapped exciton is excited optically [11]. Energy transfer between trapped excitons and near infrared emitting color centers should also be possible.

Optically pumped laser action involving the self-trapped exciton in KBr has been reported by Fink [12]. The observed emission wavelength is different, however, from that of the intrinsic luminescence of KBr [13] and it thus appears likely...
that the laser action is in fact due to some impurity effect, such as a self-trapped exciton perturbed by a lattice vacancy or an impurity. In addition, electrically pumped ultraviolet laser action in NaCl has been described in a very brief report by Vorob'ev et al. [14].

II. THE PHYSICS OF SELF-TRAPPED EXCITONS

As in other materials, excitons in the alkali halides consist of bound hole-electron pairs. A mobile exciton may be thought of as an excited negative ion, and consists of an electron in an orbital around a neutral halogen atom \( X^- \) and its surrounding nearest-neighbor positive ions. The charge on these ions is unbalanced as a consequence of the excitation and provides a long-range Coulomb potential which binds the electron. The hole can be thought of as the absence of an electron in the normally closed outer shell of the negative ion. The self-trapping, or localization, of a mobile exciton has been elegantly described by Seitz [15]. A neutral halogen atom on a normal lattice site is unstable. The hole is used to form a covalent bond with a neighboring negative ion, and consequently an excited \( (X^\text{2-})^* \) molecule is formed in a position centered on a negative-ion lattice site with its axis along the \((110)\) direction in the crystal, as is shown in Fig. 2. The formation of this molecule occurs in a few picoseconds while the electron is still in its excited orbital. The accompanying lattice relaxation reduces the energy of the exciton and traps it at a single lattice site. This is the self-trapped exciton. It should be noted that since a halogen ion in its ground state \( X^- \) is isoelectronic with a rare gas atom, bonding between an excited negative ion and one in the ground state to form an \( (X^\text{2-})^* \) molecule is similar to the formation of excimers in the rare gases. Also, if a negative ion is ionized to form a neutral atom, it will form an \( X^2_- \) molecule oriented along the \((110)\) direction. This is also known as the \( V_k \) center. Thus, a self-trapped exciton can also be thought of as a \( V_k \) center that has trapped an electron.

An excited molecule returns to its ground state when the electron recombines with the hole. This can occur with the emission of a photon if the temperature is low enough to eliminate thermal decay processes. The \( X^2_- \) molecule is unstable in its ground state; when the electron and hole recombine strong Pauli repulsive and electrostatic repulsive forces return the \( X^- \) ions to their equilibrium positions in the lattice. This process is also thought to take place in a few picoseconds. Thus, the life cycle of the exciton is 1) excitation of the negative ion, 2) relaxation to the self-trapped exciton state in a few picoseconds, and with the emission of photons, 3) decay of the excited electron to give an \( X^2_- \) molecule in its ground state with perhaps the emission of a photon and, 4) relaxation of the \( X^2_- \) radical to form two separated \( X^- \) ions situated at normal lattice sites. This cycle can be represented by a configuration coordinate diagram, as is shown in Fig. 1, where the ground and excited states of the \( X^2_- \) have been plotted as a function of the separation between the negative ions.

Self-trapped excitons luminesce at sufficiently low temperature, usually below 80 K. The spectrum of the luminescence in many cases consists of two bands in the visible and near ultraviolet. The highest energy emission is usually characterized by a decay time of a few nanoseconds, while the low energy band decays in a few microseconds. The heights of the two emission bands vary for different alkali halides. The emission spectrum of the self-trapped exciton in KI is presented in Fig. 3 as an example. The decay times of the short-wavelength emission bands of KI, RbI, and CsI are given in Table I.

Detailed studies of both the polarizations and decay times of the emission bands confirm the molecular model of the self-trapped exciton presented above. On the basis of polarization studies, Kabler and Patterson [16] have assigned the high-energy emission band to the \( 1^2S^- \) state, and have suggested that the long-lived emission is due to a triplet state. This assignment is also consistent with the observed decay times.

III. ELECTRICAL PROPERTIES OF INSULATORS

Large peak electrical powers must be delivered to a crystal containing electroluminescent color centers in order to reach the threshold for laser action. Thus, this section is devoted to a discussion of the electrical properties of insulating crystals.

Contacts to Insulators

Electrical contact between a conducting metal and the insulating crystal must be established in order to pass currents through the crystal. The theory of such contacts has been reviewed by several authors [17]-[20]. A contact can be classified as either blocking or ohmic, depending upon whether or not the contact produces an asymmetric current-voltage relation. Ideally, it is possible to predict the type of contact that will be formed from the relative values of the work function \( \phi_m \) of the metal and the work function \( \phi \) of the insulator: for \( \phi_m > \phi \), the contact will be blocking for the injection of electrons while for \( \phi_m < \phi \), the contact will be ohmic. In practice, the presence of surface states prevents this rule from being universally valid.

The distinction between ohmic and blocking contacts is illustrated in Fig. 4. For the case of an ohmic contact, electrons flow from the metal into the insulator, establishing a region of negative space charge within the insulator and a corresponding surface layer of positive charge within the metal. This space charge produces a built-in electric field, raising the electronic energy levels within the insulator relative to those within the...
Fig. 3. Optical emission spectrum of the self-trapped exciton in KI at 80 K. Both the single band at 4.2 eV and the triplet band at 3.3 eV are present.

TABLE I

<table>
<thead>
<tr>
<th></th>
<th>KI (1\textsuperscript{2} \textsuperscript{2}+)</th>
<th>NaI (1\textsuperscript{2} \textsuperscript{2}+)</th>
<th>RbI (1\textsuperscript{2} \textsuperscript{2}+)</th>
<th>KCI:Li (F\textsubscript{a}())</th>
</tr>
</thead>
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<tr>
<td>(\lambda) (\textit{\AA})</td>
<td>2970</td>
<td>2980</td>
<td>3190</td>
<td>2.7 \times 10\textsuperscript{5}</td>
</tr>
<tr>
<td>(\Delta\nu) (\textit{\AA})</td>
<td>6 \times 10\textsuperscript{13}</td>
<td>6 \times 10\textsuperscript{13}</td>
<td>6 \times 10\textsuperscript{13}</td>
<td>1.5 \times 10\textsuperscript{13}</td>
</tr>
<tr>
<td>(\tau) (ns)</td>
<td>5</td>
<td>8</td>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>(\Delta N) (cm\textsuperscript{-3})</td>
<td>3.6 \times 10\textsuperscript{16}</td>
<td>4.7 \times 10\textsuperscript{16}</td>
<td>2.6 \times 10\textsuperscript{16}</td>
<td>3.5 \times 10\textsuperscript{15}</td>
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The exact form of the electric field distribution within a blocking contact can be obtained for idealized situations. A Mott-Schottky barrier is formed by a contact between a metal and an insulator containing \(N\) shallow traps per unit volume. By a shallow trap, we mean one that is thermally ionized and thus acts as an electron donor. The establishment of electrical contact causes all of the electrons within a region of thickness \(d\), known as an exhaustion layer, to move into the metal, leaving behind a space charge of immobile ionized traps of density \(\rho = eN\). If a negative bias potential of magnitude \(V_o\), with \(V_o \gg \phi_m - \phi\), is applied across the contact, the form of the field and potential within the insulator can be found by solving Poisson's equation. The width of the exhaustion region is found to be equal to (in CGS units)

\[
d = \left(\frac{eV_o}{4\pi Ne}\right)^{1/2}
\]

where \(e\) is the dielectric constant of the insulator. Within the exhaustion layer \((0 \leq x \leq d)\) the potential varies as

\[
V(x) = \frac{2\pi Ne}{e} \left(\frac{x-d}{d}\right)^2
\]

where the distance \(x\) is measured into the insulator, and the electric field varies as

\[
E(x) = E_o \left(1 - \frac{x}{d}\right)
\]

where the maximum field occurs at the boundary \(x = 0\) and is given by

\[
E_o = \left(\frac{8\pi NeV_o}{e}\right)^{1/2}
\]

A different type of barrier region, often known as a Rose-type barrier [21], is obtained if it is assumed that the traps...
are uniformly distributed in energy, and that the number density of ionized traps is proportional to the local value of the electrostatic potential, as would be the case if the traps were being ionized by the applied field. Denoting the number density of ionized traps is proportional to the local value of the electrical conductivity.

For ZnS and by Paracchini [4] for the alkali halides, and have been shown to be untenable. The hypothesis that direct excitation or direct ionization of the emitting centers by the applied potential is the cause of electroluminescence is untenable because the field strength required by this mechanism (~10^7 V/cm) is greatly in excess of that which is observed to produce electroluminescence. Excitation by the injection of minority carriers at the electrodes, which later recombine with majority carriers, is untenable because electroluminescence is observed from a given electrode on both halves of a sinusoidal applied voltage.

A model based on the impact excitation mechanism that describes many of the observed features of electroluminescence has been developed by Piper and Williams [23] and Alfrey and Taylor [24]. This model assumes that the electroluminescence is excited within a Mott-Schottky exhaustion region. The application of a strong electric field (~10^5 V/cm) field ionizes electrons trapped at deep (~0.2 eV from the conduction band edge) electron traps. These freed electrons are accelerated by the applied field, leading to the excitation of luminescence. Alfrey and Taylor show that the number of photons released per half cycle of the applied potential (which need not be sinusoidal) of peak value $V_o$ is given by

$$ Q = AV_o^2 e^{-\alpha/V_o^{1/2}} $$

where $A$ is some constant, $n$ is a parameter of order unity determined by the energy distribution of deep traps, and the parameter $\alpha$ is given by

$$ \alpha = \frac{W_e}{8nNe^2l} $$

where $W$ is the excitation energy of the luminescence, $l$ is the electron mean-free path in the material, and $N$ is the density of shallow donors, i.e., of donors that are thermally ionized even in the absence of an applied field.

Several alternative predictions of the voltage dependence of the intensity of electroluminescence have been derived by using different assumptions regarding the excitation mechanism. Alfrey and Taylor [24] have shown that if the mechanism involves the thermal excitation of trapped electrons, the luminescent yield will be given by (10) with $n = 1$. Paracchini [4] has treated the case of electroluminescence excited by injected electrons within a Rose-type barrier. He finds that the luminescent yield scales with the internal field strength $E$ as $E^{3/2} e^{-bE}$ for some constant $b$ if the average energy of a free electron is less than the threshold energy for impact ionization and varies as $E^{1/2} e^{-bE^3}$ in the opposite limit.

V. CONDITIONS FOR LASER OPERATION

This section presents a calculation of the threshold population inversion and electrical pump power required for laser oscillation in an alkali halide laser crystal.

We define $P_{in}$ to be the input electrical power and $P_{out}$ to be the output optical power due to fluorescence at the threshold of laser action. These powers are related by

$$ P_{out} = n_{el} P_{in} $$

where

$$ n_{el} = n_{exc} n_{in} $$

This section outlines the rather sketchy level of current understanding of excitation mechanisms of electroluminescence in insulators.

Impact excitation of the emitting center seems to be the most likely source of electroluminescence. Other possible mechanisms have been considered by Piper and Williams [23]...
where we have expressed the electrical efficiency $\eta_{el}$ as the product of an excitation efficiency $\eta_{exc}$ and a luminescent quantum efficiency $\eta$. These latter two quantities, respectively, the fraction of the input energy converted into the excitation of the fluorescing levels and the fraction of these levels that actually decay radiatively. The quantity $\eta$ is thus related to the observed luminescent decay time $\tau$ and to the radiative lifetime $\tau_{rad}$ of the fluorescing level by

$$\tau = \eta \tau_{rad}. \quad (13)$$

The gain coefficient per pass (at the peak of the gain curve) for radiation passing through a medium of refractive index $n$, population inversion (per unit volume) $\Delta N$, and length $L$ is given as [25]

$$\gamma = \Delta N \frac{\lambda^2 L}{4\pi n^2 \Delta \nu \tau_{rad}} \quad (14)$$

where $\lambda$ is the wavelength of the radiation and $\Delta \nu$ is the full width at half maximum of the line shape function (which is assumed to be Lorentzian). The threshold condition is that $\gamma$ be equal to the negative of the natural logarithm of the fractional loss per pass. Equation (4) was used to calculate the values of the threshold population inversion $\Delta N$ given in Table I, under the conditions $\gamma = 1, L = 1 \text{ cm}$, and the assumption $\eta = 1$.

The fluorescent output power at threshold is given by

$$P_{out} = \frac{\Delta N \hbar \nu \Omega}{\tau_{rad}} \quad (15)$$

where $\hbar \nu$ is the energy of a radiated photon, $\Omega$ is the volume of the active medium, and where we have assumed the case of an ideal four-level laser so that the upper level population is equal to the population inversion. By combining (12), (14), and (15) the input electrical power can be related to the other physical quantities by

$$P_{in} = \frac{4\pi n^2 \hbar \nu \gamma \Delta \nu}{L^2 \eta_{el}}. \quad (16)$$

The geometry of the laser that we envisage has planar electrodes of area $A = nL$, placed on the large surfaces of a thin crystal of thickness $D$. A voltage $V_o$ is applied between these electrodes, inducing a current $I$ to flow and a power $P_{in} = V_o I$ to be delivered to the crystal. The current per unit area of electrode that must flow in order for the threshold condition (16) to be met is then

$$J = \frac{4\pi n^2 \hbar \nu \gamma \Delta \nu}{L^2 \eta_{el} V_o} \quad (17)$$

A typical value of the required current density can be obtained by adopting the data listed in Table I for the KI ($I^2_4$) center, and choosing the values $D = 0.01 cm$, $L = 1 cm$, $V_o = 2000 V$, and the idealization $\eta_{el} = 1$ to obtain the result $J = 20 A \cdot cm^{-2}$. Currents of this magnitude have been observed in the insulator CdS [22].

VI. EXPERIMENTAL RESULTS

In this section we present preliminary experimental results for the electrical conductivity and electroluminescent intensity of KI with indium or silver electrodes. KI was chosen for this work because it is known to electroluminescence strongly [2]. Single crystals of KI, obtained from the Harshaw Chemical Company, were cleaved to a size of $1 \times 1 \times 0.05 cm^3$ and were then thinned in a saturated solution of KI in water to a thickness of $\sim 0.01 cm$.

The electrical properties of such crystals with In contacts were studied by measuring the current versus voltage relations for an applied ac potential in the range 0-2000 V. These measurements were performed in vacuum at a pressure of $\sim 1 \times 10^{-6}$ torr. Electrical contacts produced by freezing molten In onto the KI crystal were found to be initially blocking. However, ohmic contacts could be “formed” by applying a large pulsed voltage as has been described for ZnS by Alfrey and Cooke [26]. The results for the current density versus applied potential are shown in Fig. 5. The data shown in the lower curve were taken before the electrodes underwent the forming process. The current in this case was out of phase with the applied potential and its magnitude depended linearly upon that of the applied potential. We thus believe that this current results from the capacitance of our samples and in fact, the estimated capacitance (~1 pF) of our samples is sufficient to account for the observed current. The other curves show data taken on two different samples after ohmic contacts were formed as described above. These currents are in phase with and exhibit a nearly quadratic dependence upon the applied ac voltage. We thus believe that these currents are space-charge-limited. The magnitude of the current density obtained with ohmic contacts varied greatly from sample to sample, but always showed a nearly quadratic dependence on voltage. This variation is probably due to the lack of control over the forming process. The maximum current density obtained to date is with ohmic contacts and is $\sim 0.15 A/cm^2$; however, electroluminescence has been observed only with blocking contacts. Measurements at still higher current densities with ohmic contacts are being planned.

With In or Ag electrodes as blocking contacts, electroluminescence was observed for ac field strengths greater than $\sim 10^4 \text{ V} \cdot \text{cm}^{-1}$. The electroluminescence measurements were performed with the crystal immersed in liquid nitrogen, both to provide electrical insulation and because the decay of the self-trapped exciton is radiative at this temperature. The luminescence was excited by a voltage pulse whose magnitude was variable over the range 500-2500 V and whose length was 200 ns with a rise and fall time of $\sim 10$ ns. The luminescence from the crystal was then measured with a calibrated EM1 9558Q photomultiplier tube. The effective population inversion $\eta \Delta N$ can then be inferred, using (15), from the measured luminescent intensity as long as the centers are excited in a time short compared to their luminescent decay time. This condition is best met for the long-lived long-wavelength band, and in Fig. 6 we show $\eta \Delta N$ for this band as a function of the applied field strength $E_a = V_o A^{-1}$. Our data are in good agreement with the prediction of (10) with $n = 0$, which applies to excitation within a Mott-Schottky barrier. However, we are also able to obtain fairly good agreement when we fit our data to the functional form $\eta \Delta N \propto e^{-\Delta E_a}$, which could be encountered for a Rose-type barrier. To date, the maximum value of $\eta \Delta N$ obtained is $\sim 3 \times 10^{11} \text{ cm}^{-3}$. In an effort to improve this number we have examined the effect of different contact material. Silver conducting paint was used; this gave slightly less light output, but the slope of the In $\eta \Delta N$ versus...
Fig. 5. Current-voltage relation measured at 80 Hz for KI with In contacts.

$J \sim \frac{A}{cm^2}$

Fig. 6. Effective population inversion as a function of applied field strength for KI with In or Ag blocking contacts.

$(E_A)^{-1/2}$ line was greater. Theoretically, this slope [α given in (11)] should not depend on the contact as long as it is blocking and the applied potential is much greater than the contact potential. Further investigations are planned using evaporated contacts where surface effects will be more controlled. Also, to reach a population inversion closer to that needed for laser threshold, the field strength must be increased so that it is very close to breakdown. It can be seen from (10) that the $V^n$ factor will become increasingly dominant as the applied potential is increased. Investigations are currently being carried out in our laboratory at higher field strengths.

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REFERENCES


Robert W. Boyd was born in Buffalo, NY, on March 8, 1948. He received the B.S. degree in physics, in 1969, from the Massachusetts Institute of Technology, Cambridge, and the Ph.D. degree, also in physics, in 1977, from the University of California, Berkeley. His dissertation describes the design, construction, and utilization of an astronomical infrared imaging system, based on the nonlinear optical interaction known as upconversion.

In 1977 he was appointed Assistant Professor and in 1982 he was made Associate Professor at the Institute of Optics, University of Rochester, Rochester, NY. His research interests include...
A Comparison of the Cassegrain and Other Beam Expanders in High-Power Pulsed Dye Lasers

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Abstract—We have constructed and compared high peak power YAG-pumped dye lasers using a variety of beam expansion methods, particularly the Cassegrainian telescope, grazing-incidence, and achromatic-prism beam expander designs. We find that the Cassegrainian design offers a modest advantage over the conventional Hänisch or refractive telescope design in larger magnification and hence, narrower linewidth, while retaining several inherent drawbacks in cost, alignment difficulty, and amplified spontaneous emission (ASE) problems. New problems specific to the Cassegrainian design in high-power operation include limited wavelength range of the telescope secondary and a severe diffraction grating damage mechanism during alignment. We conclude that, on the whole, the Hänisch and Cassegrainian designs offer roughly equal performance. By comparison, the grazing-incidence design offers significant advantages in cost, ease of alignment, and linewidth without an etalon, but with reductions in efficiency, power output, and in some cases, wavelength stability. Our final judgment is that for high-power multimode operation, the four-prism achromatic beam expander is generally superior to the other designs. For single-mode operation, however, the prism design is rivaled by several ingenious grazing-incidence variations.

INTRODUCTION

RECENTLY, Beiting and Smith introduced a pulsed dye laser cavity [1] employing an on-axis reflective Cassegrain telescope in place of the refractive telescope beam expander used in the Hänisch dye laser oscillator [2] (see Fig. 1). This new design held the potential to overcome several drawbacks of the Hänisch design. First, the nearly aberration-free on-axis Cassegrain telescope allowed simple construction of a high quality achromatic beam expander at very low cost in optics, in contrast to the expensive (~$1000) multielement achromatic refractive telescope. Second, the availability of “micro-optics” [3], [4] permitted the fabrication of compact high magnification devices promising more efficient, higher resolution laser operation with less amplified spontaneous emission (ASE). Third, Beiting and Smith reported that the new design admitted a simpler alignment procedure than did the...