The Effect of Electric Fields on Cathodoluminescence from Phosphors

by C. H. Seager

Sandia National Laboratories

Albuquerque, NM 87185

ABSTRACT

When external electric fields are applied to phosphors the cathodoluminescence (CL) at low beam energies is strongly affected. This experiment has been carried out on a variety of common phosphors used in cathode ray tube applications, and the electron beam energy, beam current, and electric field dependences of the CL are thoroughly characterized. It is found that the general features of these effects, particularly the strong polarity and beam energy dependence, are consistent with a model which assumes that the main effect of the electric fields is to alter the populations of electrons and holes at the phosphor surface. This in turn, modulates the non-radiative energy losses that strongly affect the low-beam-energy CL efficiency. Because the external fields are applied without any direct contact to the phosphor material, the large changes seen in the CL decay rapidly as the beam-created electrons and holes polarize, shielding the externally applied bias. These results have important implications for designing phosphors which might be efficient at low electron energies.

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. Introduction

With the maturing of field emission tip arrays for the production of energetic electrons under cold cathode conditions[1], the use of these arrays for flat panel displays has received increasing attention. Ideally, these displays would be used to excite phosphors at low electron energies. However, essentially all phosphors now used for conventional cathode ray tubes (CRT) become increasingly inefficient[2] as electron energies are reduced below 5 keV. It is thought that these lower electron energies allow excited electron-hole pairs to access surface or near-surface defects, resulting in non-radiative de-excitation losses. In a recent letter[3] it has been demonstrated that externally applied electric fields can drastically alter cathodoluminescence efficiency, apparently by controlling the magnitude of these losses. In this paper a thorough study of the field dependence of the cathodoluminescence (CL) has been carried out on eight common cathode ray tube phosphors and a model for this effect is presented. While this model is in accord with much of the data, a number of important features remain unexplained.

II. Experimental Methods

Conventional phosphors used in cathode ray tube applications were purchased[4] and sedimented onto brass plates using a solution of $MgNO_3.(6H_2O)$ and isopropanol. Some properties of these phosphors are listed in Table 1. Finding a method of applying an electrostatic potential difference across such thin (25-30μm)

powder layers without restricting the arrival of low energy electrons is challenging. Any deposited metal layer applied to thicknesses guaranteeing electrical continuity across a surface of aggregated particles would completely attenuate electrons in the 0.5- 2 keV range. The solution to this problem was to press a metal mesh[5] against the exposed side of the phosphor screen (here "screen" refers to the phosphor layer/back plate sandwich). Figure 1 illustrates the method. The (square) openings in this mesh were 7.5 µm wide and the areal coverage fraction of these openings was 0.36. A simple electrostatic simulation of a similar problem (the problem was calculated for circular holes since the Laplacian for axial symmetry is more tractable) showed that for a 25 µm thick phosphor layer the average potential on the phosphor surface in the mesh openings was 0.04 V_a , where V_a is the electrostatic potential applied to the screen backside, and the mesh, itself, is held at V=0. So with this experimental arrangement it is possible to apply an electric field which is largely internal to the phosphor layer. This is important, since large changes in the potential at the (front) phosphor surface would lead to CL changes caused by electric fields in the vacuum space outside the phosphor, which are of no interest here. The screen back potentials were applied with a square wave generator amplified by a high voltage amplifier. Cathodoluminesence was collected with a fiber optic cable (1 mm diameter), sensed by a Hamamatsu photomultiplier tube and amplified by a operational amplifier current-to-voltage converter. The time evolution of the CL was recorded with a digital oscilloscope. All measurements were done in a high vacuum chamber operating at ~6 x 10^{-7} Pa. For CL studies, the phosphors were excited with a Varian electron gun operating at beam energies from 0.3 to 3 keV and typical currents of 10-100nA. Some photoluminescence experiments were also carried out; in this case the excitation was provided by a

Deuterium lamp/single pass UV monochromator combination operated at a slit width of 4 mm and focussed using quartz lens optics.

III. Experimental Results

A. Typical data

Two types of experiments were carried out in this study. In the first, a bias was applied to the screen back (the front mesh was grounded) and the electron beam was pulsed on for a certain length of time by sweeping the electron gun deflection bias. Because of gun circuitry considerations, the beam turn-on time was fairly slow, approximately 20 msec. For this reason, most of the data were obtained with a second protocol where the beam was left on the sample and the screen bias was altered as a function of time. Both experiments gave similar results. Figure 2 shows an example of the first type of experiment on Y_2SiO_5:Tb; it clearly illustrates some of the important aspects of these measurements. The three lower curves illustrate the response of the pulsed CL to +,0, and – screen back biases. The positive bias enhances the CL while the negative bias suppresses it, but the effect decays with a 0.050-0.10 second time constant, and by the end of the electron beam pulse the CL is close to its value at zero screen bias. A memory effect is another important feature of this data;while the lower three traces were taken immediately after a gun pulse with zero screen bias, the upper trace is the data obtained after a pulse with –250V screen back bias. The CL enhancement in this case is approximately double that seen after the pulse at zero bias.

Figure 3 gives more information about this memory effect. Here we present data taken with constant electron beam irradiation, but time varying screen back bias. For

the upper trace (referred to the left hand scale) a square +/- 160V square wave at ~ 0.5 Hz has been applied continuously to the screen back. The lower trace (referred to the right hand scale) shows data obtained with a +320V/0V square wave of the same frequency. The offset between the left and right vertical axes makes it possible to distinguish the fact that two separate sets of data are being plotted; in fact, these two sets of results are within +/- 1% of each other. This demonstrates two features of this type of data:

a. After the CL decay, the CL is almost independent of bias. A trivial conclusion from this is that little of the screen back bias appears on the phosphor surface; otherwise the arrival energy of the electrons, E_a, would be significantly altered (in this regime, CL at fixed current is approximately proportional to E_a^2, so even small alterations of E_a result in noticable changes in brightness[6]).

b. The response of the CL seems to depend only on the voltage difference between the two halves of the square wave.

Both observations are consistent with the response of a photoconductor to a field applied externally through blocking contacts. In this case the photocarriers are created by the electron beam; the dark conductivity in these materials is vanishingly small, and the lack of physical contact to the phosphor in the open areas of the mesh means that current flow inside the phosphor caused by the screen back bias cannot be supplied continuously from our external circuit. In this case the carrier distribution in the phosphor is expect to polarize (the Maxwell-Wagner effect) until the internal electric field is zero[7]. This polarization provides a memory of the last field applied, and makes the CL depend only on the change in screen back bias. A simple theory for this effect will be reviewed in section IV.

If the polarization hypothesis is the correct description for these observations, we can use the details of the time dependence of the CL to gain information about the density of mobile charge carriers created by the beam as well as other phosphor parameters. We can also use the value of the CL immediately after a bias change to investigate the mechanism for the field induced change in brightness. In the sections which follow, these "time zero" values of CL will be used to characterize the origins of the field effect. It will be important to remember, however, that the internal phosphor field is always the external field plus the contribution from any polarization built in during the previous field exposure.

B. The Beam Energy Dependence of CL

Figure 4 shows the relative CL efficiency as a function of beam energy at three different screen back biases - +300V, 0V, and –300V for two phosphors, $SrGa_2S_4$:Eu and YAG:Tb. These data essentially span the range of behavior seen for all eight

phosphors and illustrate several noteworthy features. First, the fractional brightness change is a strong function of electron beam energy; as would be expected for a surface-related phenomena, the field has the strongest effect at low energies where the electron range is the smallest. Secondly, brighter, more efficient phosphors show a somewhat stronger dependence of the efficiency on beam energy with no external field applied. This is an expected feature of the surface recombination model if the decrease in efficiency is due to poor bulk properties, like carrier lifetime[8]. Thirdly, the magnitude of the field effect is much smaller for the less efficient phosphor.

Figures 5-7 show the beam energy dependence of CL for all eight phosphors at +300V, 0V, and –300V screen back biases respectively. For all phosphors, the effect of the negative screen bias is to markedly enhance the beam energy dependence, while for the positive bias the opposite effect is seen. The average of the least squares log-log slopes of these plots is 0.39 for the positive bias and 1.62 for the negative bias; so, the CL under negative bias has more than four times the power law slope as that measured during the positive bias cycle. This represents a very large change in the beam energy dependence. As we shall see, the data presented in the next section implies that fields not much larger than those produced by +300V bias would be expected to completely remove the variation of CL efficiency with beam energy for several of these materials.

C. The Dependence of the CL on Screen Back Bias at Fixed Beam Energy

Figure 8 shows the dependence of the CL on screen back bias for all 8 phosphors. In this case the electron beam energy was 0.6 keV and the CL values are the maximum or minimum values measured just after the sign of the screen bias has changed. All

phosphors measured show the same sign of the effect. Except for the anomalously steep dependence of the CL for Y_2O_2S:Eu, there is a strong tendency for the brightest phosphors to have the largest variation of CL with bias. In addition, the slope of the CL with bias is continuous on this plot as the sign of the bias is changed, implying that the fundamental mechanism for both the enhancement and the suppression is the same.

D. The Time dependence of the CL

In this section we explore how the time dependence of the CL after a change in screen bias depends on various experimental variables. Typical plots of the time dependence of the CL after a change in screen back bias do not show a single exponential decay. This is illustrated by the Figure 9, where the time dependent part of the decay from the − to + bias sign transition is plotted on a log-linear plot. Here we have multiplied the time axis by the beam current, I, for three different I values. The close similarity of the slopes of all three curves illustrates that the time for decay is inversely proportional to the electron beam current. In order to quantify this decay process, we define the time constant for the CL decay, τ_+, (or τ_- for the rise, in the case of the + to - bias transition) to be the time it takes the time dependent fraction of the CL to reach 40% of its initial value. This time constant is not observed to be the same for both signs of the bias transition. This is illustrated in Figure 10 for CL data obtained on Y_2O_3:Eu at different screen back biases. The dependence on bias is definitely weaker for τ_+, (for the − to + transition), than for τ_-. This asymmetry of the two decay plots is more pronounced for other phosphors. An example is shown in Figure 11 for Y_2SiO_5:Tb, where τ_-/τ_+ is ~2 at large screen biases. As we shall discuss

below, this asymmetry for the two bias directions is a result predictable from dielectric polarization theory.

We have also studied the effect of beam energy on the CL time dependence. Figure 12 shows a plot of τ_- and τ_+ as a function of beam energy at a fixed screen back bias for Y_2O_3:Eu. There is only a slight dependence of τ_+ on beam energy, while τ_- goes through a weak minimum at ~1 keV. Data from other phosphors shows similar behavior. In general, over most of the beam energy range investigated, the CL decay processes are not strong functions of this parameter.

E. The effect of Screen Back Bias on Photoluminescence

In the case where photoluminescence (PL) excitation arises from direct excitation of activator sites, we might expect that applied electric fields would influence the PL process by affecting the activator excited state lifetime. Except for ZnS:Ag, all of the phosphors measured in this study have luminescence process involving the excitation of inner shell D or F electrons at rare earth or transition metal activators[2]. These electrons are strongly shielded by outer shell electrons, and the influence of external electric fields of the magnitude applied here is expected to be minimal[9]. This was found to be the case experimentally as will be detailed below. On the other hand, excitation of PL by creation of host electron-hole pairs brings the issues of field induced carrier drift and surface recombination into the equation for efficiency, and one might expect electric fields would have a large effect on the PL in this case. Unfortunately most of the materials studied here have energy bandgaps above 5 eV. This means that observation of host-excited PL requires a light source with a strong spectral output at wavelengths less than 240 nm. Our PL excitation power at wavelengths below 240 nm was only on the order of ~10^{-7} watts/cm^2 and essentially zero below 200nm, which made

observation of host-excited PL marginal for a few phosphors like $SrGa_2S_4$:Eu and impossible for the wide gap materials like yttria and the silicates.

Figure 13 shows results of applying back screen biases to $SrGa_2S_4$:Eu at three different wavelengths. These data illustrate some of the features seen in the PL data during the application of electric fields. At 320 nm where all the PL is due to direct activator excitation, there is no effect of the applied bias. At 240 nm, where some host excitation is occuring, the PL shows a slight enhancement at positive biases and a depression at negative biases. At 220 nm, where the UV is absorbed closer to the sample surface, these effects, which are very much like those seen for CL, are obviously larger. Table 1 summarizes the PL effects for all the phosphors measured. In general it is found that, at the shortest wavelengths in the lowest bandgap phosphors, the asymmetry of response to +/- biases is seen, and the time decay of the response is similar to that observed in CL. In several cases we also verified that, as in the case of the CL , the time constant for decay was inversely proportional to the excitation strength (in this case the UV power density). A stronger source of UV in the 160-220nm region would be helpful to further investigate these effects.

IV. Discussion

We start by presenting an extremely simplified model for polarization of the beam-created electron hole population that predicts some, but not all of the observed experimental data. A realistic model of the response of both electrons and holes involves the solution of the coupled differential equations for electron and hole creation, diffusion, drift, and recombination (both bulk and surface). These equations are "stiff" in the

mathematical sense that the time scales for drift and diffusion over the key dimensions of the problem (the electron range, for instance) are much shorter (picoseconds) than those characterizing the buildup of polarization (milliseconds). A full treatment of this two carrier problem has not been achieved, and in many cases the relevant transport and trapping parameters which would be needed to evaluate solutions of these equations have not been measured for these materials. We have constructed a computational code which treats carrier drift, diffusion, and trapping in an approximate way, using accurate electron hole generation functions. A full discussion of the polarization modeling results from this code is beyond the scope of this paper; however most of the results of the simple analytic calculation discussed below are replicated by this more complete model.

For our simple model we hypothesize that:

1. All of the e-h pairs are created by the beam at a single depth d, and this depth is << the phosphor layer thickness.

2. Electrons are free to drift in the applied field, while the holes are immobile.

3. The characteristic time for an electron to be trapped, t_T, is less than the time for transit to the surface. That is $t_T < d/(\mu_e E(t))$ where μ_e is the electron mobility, and $E(t)$ is the time dependent internal electric field in the region where the carriers are drifting. The case where electrons can actually reach the surface before becoming trapped actually yields identical results, however.

4. No recombination of e-h pairs is allowed after trapping. Relaxation of this assumption will also be discussed.

Now depending on the sign of E_{ext}, the applied external field, a sheet of negative charge will grow at $x = d +/- \mu_e \cdot E(t) \cdot t_T$, exactly balanced in magnitude by a sheet of holes at $x=d$. The total density of negative charge accumulated at time t is:

$$q = e \cdot g \cdot t \qquad , \quad (1)$$

where g is the areal density of e-h pairs created by the beam per unit time, and e is the charge on an electron. The sheet of holes and the distribution of trapped electrons create a field which opposes the externally applied field, giving a net internal field (near x=d) of:

$$E(t)= E_{ext} - e \cdot g \cdot t/\varepsilon \qquad , \quad (2)$$

where ε is the total dielectric constant of the material[10]. Note that this equation only holds until E(t)=0, at which point the drift of electrons stops. Equation 2 predicts that the net internal electric field relaxes to 0.4 of its original value in a characteristic time:

$$\tau = 0.6 \cdot E_{ext} \cdot \varepsilon/(e \cdot g) \qquad ,(3)$$

so the relaxation is expected to be slower at higher external electric fields. Since g is proportional to the product of beam current and energy, larger values of each should shorten the relaxation time. If the drifting carriers (electrons in this case) reach a surface before they are trapped in the bulk, it is easy to show that equation 3 will also hold. The assumption that only one sign of carrier can move is not crucial either; if holes can drift in the field and become trapped, the displacement of the charge centroid will be different, but equations (2) and (3) will still hold. However, the issue of what region of the phosphor has trapped polarization charge after beam exposure at a particular field polarity is crucially dependent on the response of both holes and electrons. For this simple picture where charge is created by the beam in a thin sheet and only one sign of charge is mobile, the polarized regions for both field polarities obviously do not overlap. So, data like that in Figure 3, where the sample "remembers" the previous reverse polarity pulse, is not consistent with this simple calculation. However, if the charge creation is spread over a finite depth and/or both carriers are mobile, the regions of

polarization for both polarities overlap, and many of the apparent features of the data are reproduced.

We now summarize how this oversimplified picture predicts the features of the data described in section III. In all cases we will assume that the presence of an internal electric field changes the CL efficiency of the phosphor, and that this effect is monotonically dependent on the internal electric field vector component along the axis perpendicular to the phosphor surface. We will address the possible causes for this dependence in some detail below after first concentrating solely on the polarization phenomenon.

1. The lack of dependence of CL on screen back bias at long times. This is clearly consistent with the model in that the internal electric field is predicted to go to zero at long times. We can make a rough estimate of the time constant for decay. Using equation (3) with a relative dielectric constant of 6, an applied electric field of 2.4×10^5 V/cm, and a beam current of 2.5×10^{-7} A/cm^2 we get $\tau = 0.01$ sec. In making this calculation we have assumed a beam energy of 600eV and that each incident electron creates ~30 e-h pairs, consistent with a bandgap of 6 eV. Experimentally measured decay times for these parameters are 0.1- 0.15 sec. This is not far from the model prediction, especially considering the level of theoretical simplification. Reducing g by allowing e-h recombination before trapping would obviously bring the theoretical estimate closer to the observed values of τ.

2. The memory effect. In experiments like those shown in Fig. 3, we observe that the CL depends only on the **change** in screen back bias. The polarization model predicts this in a straightforward fashion. If the applied electric field before the screen back bias transition is E_1, then the internal polarization at the end of that field cycle produces an

internal field of $-E_1$. Then, if the external field goes from E_1 to E_2, the net internal becomes E_2-E_1 immediately after the change in screen bias, and the equivalence of the two data traces seems to be explained. Note however, that this explanation ignores the issue of what happens to charge trapped during the polarization process. Repeated reversals of the applied field could lead to large amounts of electrons and holes trapped in the same spatial region, or recombination of free charge with trapped charge might be occuring. In either case, we have assumed by the way we wrote equation (1) that the kinetics of the polarization process are rate limited by the electron-hole creation process, not by transport. Thus, the model predicts that the **entire time evolution** of the CL should be dependent on only the difference in screen biases as long as the previously trapped polarization charge either:

a. Remains trapped during the second part of the cycle.

b. Or, recombines with opposite sign charge moving during the cycle.

If the charge trapped during previous cycles was emitted from traps during the next field cycle, more complicated behavior might be expected.

3. The electron beam current dependence of the CL decay times. Equation 3 clearly predicts the inverse dependence of the decay times on electron current seen in Figure 9. This is a strong indication that polarization buildup is rate limited by the density of beam-created carriers.

5.   The dependence of CL decay times on the applied electric field. Equation 3 predicts a simple linear relationship between τ and E_{ext}. Although the behavior of $(\tau_+ + \tau_-)/2$ is close to linear, the data in Figures 10 and 11 demonstrate somewhat more complicated behavior than this prediction. The decay times for positive bias are generally smaller than for negative bias, and this asymmetry is a function of phosphor

type. The universal trend for τ_+ to be smaller than τ_- seems to be explicable in the simple model if carrier recombination is put back in the model in a rather ad-hoc fashion. Below we discuss that the actual CL brightness changes seem to be consistent with field induced changes in the e-h recombination rate at the phosphor surface. If we hypothesize that these same changes in e-h recombination (and hence, in the steady state populations of electrons and holes) are dependent on the sign of the electric field, the data of Figures 10 and 11 seem easier to understand. In the positive bias direction e-h recombination is suppressed and more carriers are available to establish the internal polarization field than in the negative direction. This is equivalent to saying that g, in equation 3, should be effectively higher for positive fields. This hypothesis generates two simple predictions:

a. The difference between τ_+ and τ_- should grow larger at larger applied electric fields.

b. The asymmetry between τ_+ and τ_- should be larger for phosphors which show larger changes in CL brightness at a given applied electric field (assuming that less recombination can be equated with brighter CL).

Both effects are certainly demonstrated by the data. While this simple argument seems to be in accord with experiment, it is clearly not equivalent to demonstrating how surface recombination might be added to the simple polarization model in a quantitative fashion.

6. The beam energy dependence of the CL relaxation times. In this case our simple polarization model seems to be inadequate to fully explain the data. It predicts that τ should decrease at high beam energies because the carrier generation rate is proportional to the beam energy; however, as Fig. 12 illustrates, τ_+ is only a weak function of the beam energy. The behavior of τ_- is more complex, displaying a minimum at around 1 keV. This behavior is exaggerated (not shown) for phosphors which exhibit a larger field

asymmetry of the CL decay. Adding in the effects of decreased surface recombination art higher beam energies by creating an "effective" g only makes the agreement worse since this would be expected to make g rise more sharply as the beam energy is increased.

We have argued that most of the time dependence of the CL can be ascribed to the decay of the internal electric field as electrons and holes separate and polarize. This argument, of course, starts by assuming that there is a dependence of CL on the local electric field. Why should this dependence exist? One simple postulate, reinforced by the sign of the effect, is to suppose that the primary electrons gain or lose kinetic energy directly from the internal field; this energy gain or loss would then appear as a larger or smaller activator excitation rate. However the magnitude of the observed effect (immediately after the electric field is applied) seems much too large to be explained by this mechanism. Fig. 8 shows that an applied screen back voltage of +300 V typically enhances the CL brightness by a factor of 3 at a beam energy of 600V. If all of the incident primary electrons gained 300eV of extra energy, the most one would expect from the known beam energy dependence of CL for these materials is a brightness enhancement factor of $(300eV+600eV)^2/(600)^2$, which is a factor of 2.25. This would require all of the applied bias to be dropped over the electron range, which is a tiny fraction of the entire phosphor layer thickness. Based on this simple argument this mechanism seems unlikely to apply. Note however, that these arguments do not explicitly address the issue of energy gain or loss by the secondary electron population.

It is clear that fields of the order of 10^5 V/cm should strongly influence carrier flow. For a mobility of 100 cm^2/V·sec, typical for electrons in insulators, this field produces a drift velocity comparable to a thermal velocity. This means that the

surface concentrations of electrons and holes should be strongly influenced, and hence

the rates of surface recombination will be altered as well. For a simple localized trapping

state having density N_t which can (sequentially) capture holes with a probability K_p and

electrons with probability K_n, the well known Schockley-Read-Hall recombination rate[11]

is given by:

$$U = N_T \cdot K_p \cdot K_n \cdot p \cdot n / (K_p \cdot p + K_n \cdot n) \qquad , \quad (4)$$

where n and p are the electron and hole concentrations at the trapping site. If the first

term dominates the denominator, the recombination process is rate limited by electron

capture; if the second dominates, the capture of holes is the rate limiting step. The

general behavior of U as a function of electron and hole concentration is shown in Figure

14. In this plot we have assumed that local electric fields, depending on their sign, will

enhance the concentration of either species at the phosphor surface. Two cases are

shown, one appropriate for rapid electron capture, the other for rapid hole capture.

Capture rate differences can be caused by variations in carrier mobilty or trap capture

cross sections. For instance, trap capture cross sections for neutral versus Coulombic

capture processes can differ by orders of magnitude[12]. Figure 14 shows that a variety of

behavior might be expected for the CL behavior in the case where the principal non-

radiative pathways are surface-related. In particular, it might happen that U reaches a

maximum at some particular applied field, implying that the experimentally observed

dependence of CL on electric field might not be monotonic.

The experimental data in Figure 8 all display monotonic behavior; furthermore

the sign of the effect is the same for all eight phosphors, and it indicates that surface

recombination is rate limited by electron capture. Not only is the universality of the

effect unexpected, but the sign seems contrary to expectations. Electrons are usually

17

more mobile than holes in most insulators, and this factor alone should tend to make hole capture the rate limiting step. What circumstances might force phosphor surfaces to be behave this way? While U is calculated for the actual values of n and p plotted in Figure 14, the relationship between the carrier densities and the electric field values shown in this plot is completely arbitrary. In addition, we only have direct experimental information about the **externally applied field**. It is possible that internal fields caused by the presence of space charge from the incident electron beam produce a p/n ratio that is far from unity in the absence of externally applied fields. Evidence for these internal fields has recently been presented[13], based on the observed dependence of phosphor surface potentials when internal fields are impressed on the phosphor. Steady state fields must always exist because the electron beam deposits excess negative charge near the end of range, and the flow of secondaries outwards from the surface must somehow be internally balanced to equal the incoming beam minus the (elastically) backscattered electrons. The mechanism for this balance must be the establishment of near-surface fields which accelerate or retard secondary emission. In most conducting materials it has been determined[14] that the secondary emission coefficient exceeds unity in the beam energy region between 200-300 eV and 2-3 keV. If this situation holds in these insulating phosphors, the establishment of steady state charge balance in this beam energy regime would require the establishment of an internal electric field which pushes secondary electrons away from the surface (back into the phosphor). This field would cause the p/n ratio to be large at **zero applied external field.** This would then shift the zero of the external field scale to the far left hand side of Figure 14. Under these circumstances U will decrease (brighter CL) when external fields are applied which reduce n/p at the surface, even if K_p/K_n is <1. It is clear that more information about the

details of charge balance in electron irradiated insulators must be gathered before the validity of this conjecture can be assessed.

The variation of the slopes with screen bias field seen in Figure 8 are in general accord with the surface recombination model. Phosphors with low brightness show less effect of external electric fields. This can be understood if the less efficient materials have bulk recombination losses which contribute to their poor CL performance; the effect of electric fields will obviously be less in this case. The beam energy dependence of our data shown in Figures 4-7 is also in accord with a surface loss mechanism. Recent calculations[8] of surface recombination in phosphors using a simplified, single minority carrier lifetime approach show that alterations in the surface recombination velocity should have almost no effect on CL brightness if the beam energy exceeds 3-4 keV.

V. Conclusions

The effect of externally applied electric fields on luminescence has been examined for eight phosphors. All of these materials exhibit field effects which show strong time variations of the CL in the 0.05- 0.3 sec regime. The sign of the effect, its dependence on beam energy, beam current, and electric field magnitude are quantitatively similar for all the materials. A simple picture which ascribes the time variation of the CL to polarization of the beam-created electron hole population successfully describes most, but not all of the observed data. The basic mechanism for the field induced enhancement or suppression of the CL is argued to be alterations of the

surface non-radiative recombination rate of electrons and holes. Evidence for this effect is also seen in the short wavelength PL response of several of the phosphors.

The existence of this electric field effect suggests several routes for achieving good phosphor performance at low beam energies. It is possible that direct implementation of this effect could be used to enhance the performance of traditional CRT phosphors in a practical display. In an FED environment, field enhanced CL might be possible if two conditions were satisfied. First, a method of efficiently applying an internal phosphor field must be integrated into the display. A mesh structure like that use here would be workable if the openings were aligned with the cathode emitter tips, so that efficient excitation was achieved. Secondly, internal polarization buildup would have to be periodically removed, presumably with excitation pulses applied with reverse field polarity. We suspect that neither of these design constraints is likely to generate much enthusiasm among device engineers.

However, the lessons learned from understanding these results could help in suggesting ways of tailoring new phosphors for enhanced low voltage performance. Fields might be built in to phosphors by doping techniques that allow fixed space charge and curvature of the electrostatic potential, or by coating phosphors with a thin layer of a material with a different electron affinity or band gap. The former situation actually exists in zinc rich ZnO, where strong depletion layer electric fields force electrons away from the phosphor surface[15]. These fields are possible because of negatively charged surface states, and more importantly, the presence of 10^{18}-10^{19} cm^{-3} positively charged donors which allow the conduction band to curve upwards towards all external phosphor surfaces. In fact, this phosphor is one of the few materials that can be prepared with a CL efficiency which is almost independent of electron beam energy[6] from $0.3 - 4.0$ keV. As

such, it may represent a material where the electric field effect on the CL has been fully optimized.

Acknowledgements

References

1. J. E. Jaskie, MRS Bulletin. **21**, 59 (1996).

2. L. Ozawa, in *Cathodoluminescence* (Kodansha, Tokyo, 1990).

3. C. H. Seager, Appl. Phys. Lett. **73**, (1998).

4. Nichia America Co., 3775 Hempland Rd., Mountville, Pa. 17554.

5. A commercially available transmission electron microscope grid fabricated from coper was used.

6. C. H. Seager, unpublished data.

7. Numerous treatments of conductors with blocking contacts have been given; see for example: C. Kittel, Introduction to Solid State Physics (John Wiley and Sons, NY, 1956) p. 180. It is important to note that the detailed assumptions about how the photoconductor responds to an electric field determine the exact form for the final expression for the polarization time constant.

8. Sen Yang, PhD. Thesis, Georgia Institute of Technology, 1998.

9. See for example Ligand Field Theory, by C. J. Ballhausen (McGraw Hill, New York, 1962). p4.

10. This formula can be derived from parallel plate capacitor arguments. Each succeeding increment of trapped charge produces the same contribution to the polarization field although it is trapped closer to x=d as the net internal electric field shrinks to zero.

11. Semiconductor Surfaces, by A.Many, Y. Goldstein, and N. B. Grover, (North Holland, Amsterdam, 1965), p. 79.

12. See for instance – Semiconducting Materials and Related Technologies, ed. by S. Mahajan, and L. C. Kimerling (Pergamon Press, Oxford, 1992), p. 263.

13. C.H. Seager, W.L. Warren, and D.R. Tallant, J. Appl. Phys. **81**, 7994 (1997).

14. D. C. Joy, Scanning Electron Microscopy **17**, 270 (1995).

15. K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, Appl. Phys. Lett. 68, 403 (1996).

Table 1. Selected parameters and data from the phosphors measured in this study. Peak wavelengths are accurate to within +/- 5 nm. The last three columns show the photoluminescence (PL) response at one or more wavelength values during the application of screen back bias waveforms alternating between + and $-$ 320V. The PL changes are rounded off to the nearest 0.5%. IST signifies inner shell electronic transition. DAT is donor-acceptor transition. NM – not measured.

Phosphor	Excitation Mechanism	Peak Wavelength	Band gap (eV)	PL λ (nm)	% change at +320V	% change at -320V
Y_2O_2S:Eu	IST of Eu^{3+} F electron	610 nm	4.6	320 230	-15 -2	-15 -4
Y_2SiO_5:Tb	IST of Tb^{3+} F electron	540 nm	>5	250	0	0
Y_2SiO_5:Ce	IST of Ce^{2+} D electron	410 nm	>5	300 240	0 0	0 0
ZnS:Ag,Cl	DAT	450 nm	3.7	320 220	-15 +3	-15 -2.5
$SrGa_2S_4$:Eu	IST of Eu^{2+} D electron	540 nm	3.68	320 220	0 +35	0 -2.5
Y_2O_3:Eu	IST of Eu^{3+} F electron	610 nm	5.6	280 220	-1 +0.5	-0.5 -1
Zn_2SiO_4:Mn	IST of Mn^{2+} D electron	520 nm	5.5	230	0	0
$Y_3Al_5O_{12}$:Tb	IST of Tb^{3+} F electron	540 nm	6.3		NM	NM

Figure captions.

Fig. 1 The apparatus for applying internal fields to phosphor layers during electron beam irradiation. The mesh covering the phosphor screen has openings which are roughly ¼ the phosphor layer thickness.

Fig. 2 The time dependence of CL from Y_2SiO_5:Tb during the application of a 0.4 sec e-beam pulse at 0.5keV. Three of the pulses were preceded by pulses with no back screen bias, while the CL response which shows the largest enhancement was preceded by a pulse at –250V back screen bias. This enhanced response illustrates the influence of polarization fields that buildup in response to the externally applied bias.

Fig. 3 CL measured during constant e-beam irradiation for Y_2O_3:Eu as the screen back bias is repetitively cycled between + and – 160V (upper trace, LHS) and +320 and 0V (lower trace, RHS). The electron beam energy is 0.6 keV. The near equality of the CL response in both cases illustrates that the CL only depends on the change in screen back bias, not the absolute values.

Fig. 4 The beam energy dependence of the initial CL efficiency for two phosphors at three different screen back biases. $SrGa_2S_4$:Eu - ▲, +300 V; ●, 0 V; ▼, -300 V. $Y_3Al_5O_{12}$:Tb - ■, +300 V; ♦, 0 V; ✦, -300 V. The more efficient phosphor shows a much stronger dependence on screen back bias.

Fig. 5 The beam energy dependence of the initial CL efficiency for eight phosphors at +300V screen back bias. The dependence of CL on beam energy is much weaker than with no bias applied. Y_2O_2S:Eu - ▲, Y_2SiO_5:Tb - ●, Y_2SiO_5:Ce - ▼, ZnS:Ag,Cl - ■, $SrGa_2S_4$:Eu - ♦, Y_2O_3:Eu - ▽, Zn_2SiO_4:Mn - ◊, $Y_3Al_5O_{12}$:Tb - ▢.

Fig. 6 The beam energy dependence of the initial CL efficiency for eight phosphors with no screen back bias applied. Y_2O_2S:Eu - ▲, Y_2SiO_5:Tb - ●, Y_2SiO_5:Ce - ▼, ZnS:Ag,Cl - ■, $SrGa_2S_4$:Eu - ♦, Y_2O_3:Eu - ∇, Zn_2SiO_4:Mn - ◊, $Y_3Al_5O_{12}$:Tb -◻.

Fig. 7 The beam energy dependence of the initial CL efficiency for eight phosphors at - 300V screen back bias. The dependence of CL on beam energy is much stronger than with no bias applied. Y_2O_2S:Eu - ▲, Y_2SiO_5:Tb - ●, Y_2SiO_5:Ce - ▼, ZnS:Ag,Cl - ■, $SrGa_2S_4$:Eu - ♦, Y_2O_3:Eu - ∇, Zn_2SiO_4:Mn - ◊, $Y_3Al_5O_{12}$:Tb -◻.

Fig. 8. The initial CL efficiency at 0.6 keV beam energy as a function of screen back bias for eight phosphors. Y_2O_2S:Eu - ▲, Y_2SiO_5:Tb - ●, Y_2SiO_5:Ce - ▼, ZnS:Ag,Cl - ■, $SrGa_2S_4$:Eu - ♦, Y_2O_3:Eu - ∇, Zn_2SiO_4:Mn - ◊, $Y_3Al_5O_{12}$:Tb -◻.

Fig. 9 The CL observed from Y_2O_3:Eu during the positive going half of the screen bias cycle for three different beam current densities at a beam energy of 0.5 keV. The flat, time independent value of the luminescence has been subtracted from the CL data and the time coordinate has been multiplied by the beam current value to illustrate that the CL decay scales as the inverse of the beam current. This relationship is expected if the decay is caused by an internal polarization of the electron-hole plasma which shields the active region of the phosphor from the externally applied electric field.

Fig. 10 The time constants for the decay (positive screen biases) or growth (negative screen biases) of the time dependent part of the CL for Y_2O_3:Eu measured at an electron beam energy of 0.6 keV. τ_- - ●; τ_+ - ▲. The least-squares fit log slopes for τ_+ and τ_- are 0.80 and 1.00, respectively.

Fig. 11 The time constants for the decay (positive screen biases) or growth (negative screen biases) of the time dependent part of the CL for Y_2SiO_5:Tb measured at an

electron beam energy of 0.6 keV. τ_- - ●; τ_+ - ▲. The least-squares fit log slopes for τ_+ and τ_- are 0.66 and 1.11, respectively.

Fig. 12 The time constants for the decay (positive screen biases) or growth (negative screen biases) of the time dependent part of the CL for Y_2O_3:Eu measured at different electron beam energies. τ_- - ●; τ_+ - ▲. The screen back bias was applied as a +/- 300 V square waveform.

Fig. 13 The time dependence of the photoluminescence for $SrGa_2S_4$:Eu measured during the application of a square +/- 320 V screen back bias waveform at three different excitation wavelengths. The CL has been normalized to unity for each excitation wavelength. The shorter wavelengths demonstrate time and polarity dependences like that seen for the CL, but noticeably smaller than was observed at low electron beam energies for this phosphor.

Fig. 14 A plot of electron-hole recombination rate (solid lines) and the surface electron and hole densities (dashed lines). The curve which peaks on the right hand side is for a capture process which is rate limited by electron capture, while the one peaking on the left hand side illustrates the opposite case. While the abscissa is suggestive of the way externally applied electric fields would alter the surface electron and hole densities, the actual values of n and p at zero applied field are not known.

MESH

PHOSPHOR
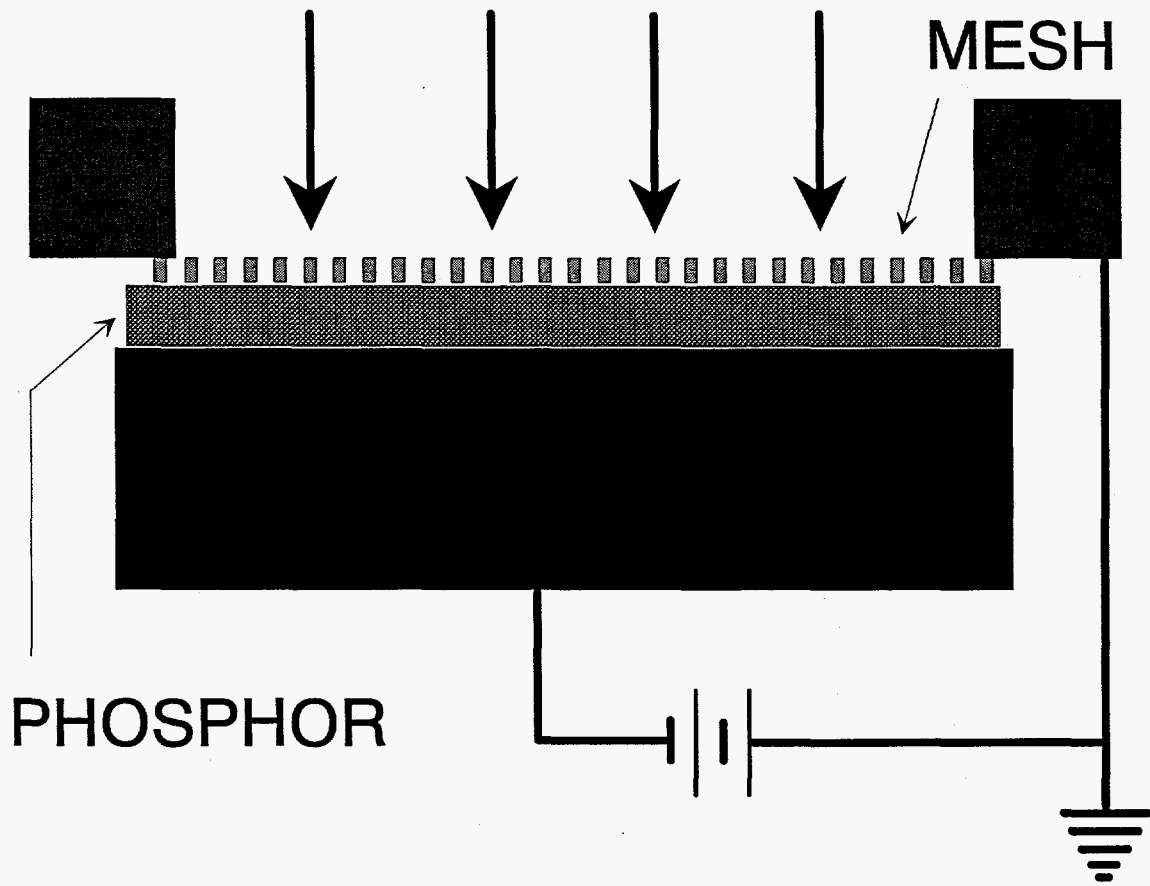
Fig. 1
seagu et al

Fig. 2 Seager et al

Y₂O₃:Eu

fig. 3 Seager et al

SrGa$_2$S$_4$:Eu

YAG:Tb

BEAM ENERGY (keV)

CL EFFICIENCY (ARB. UNITS)

Fig. 4 Seager

Y-axis: CL EFFICIENCY (ARB. UNITS)

5.0
4.0
3.0
2.0
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1

+300V BACK BIAS

X-axis: BEAM ENERGY (keV)

0.2   1.0   3.0

Fig.5 Seager

Fig. 6 Seager

-300V BACK BIAS

CL EFFICIENCY (ARB. UNITS)

BEAM ENERGY (keV)
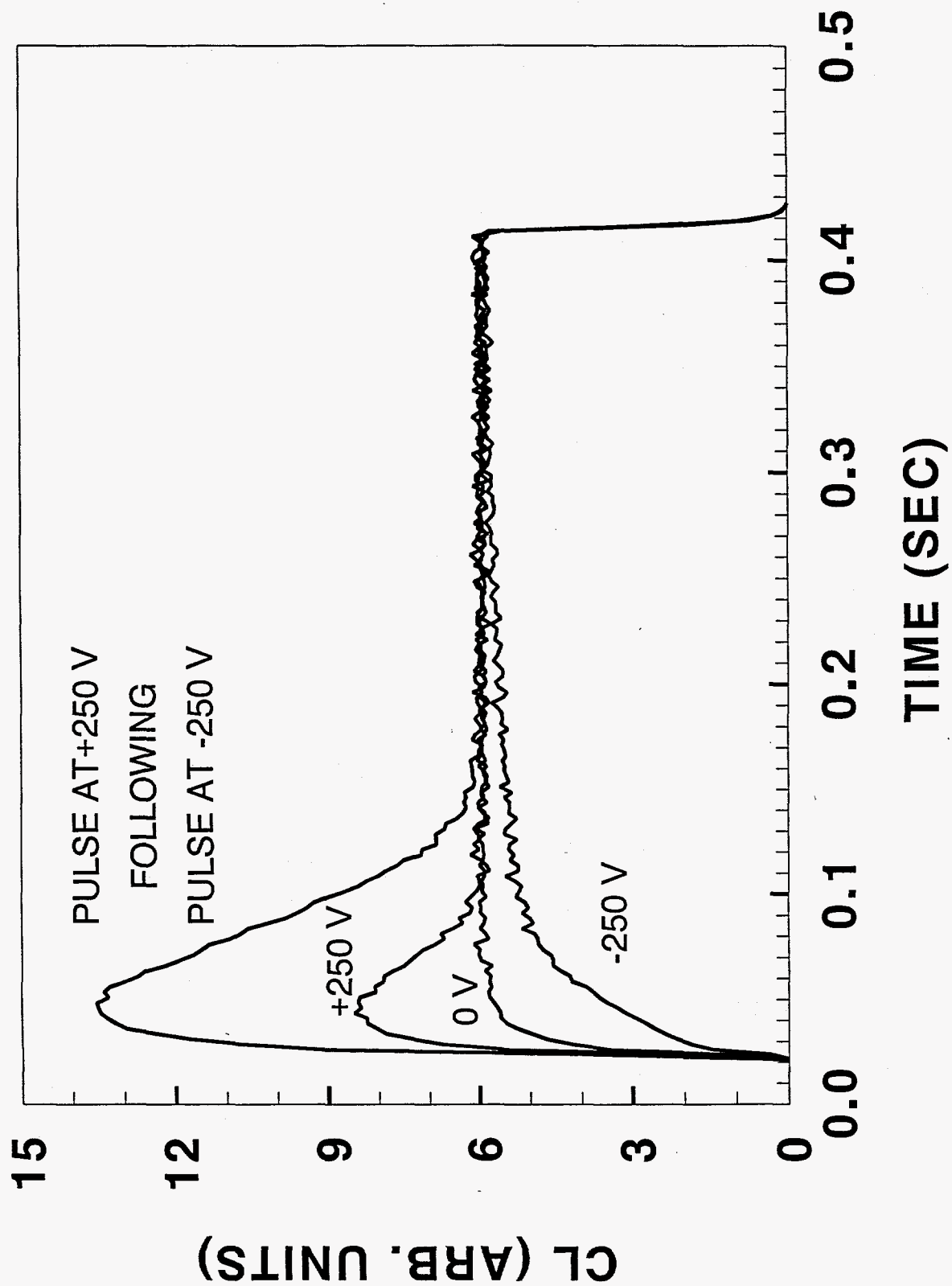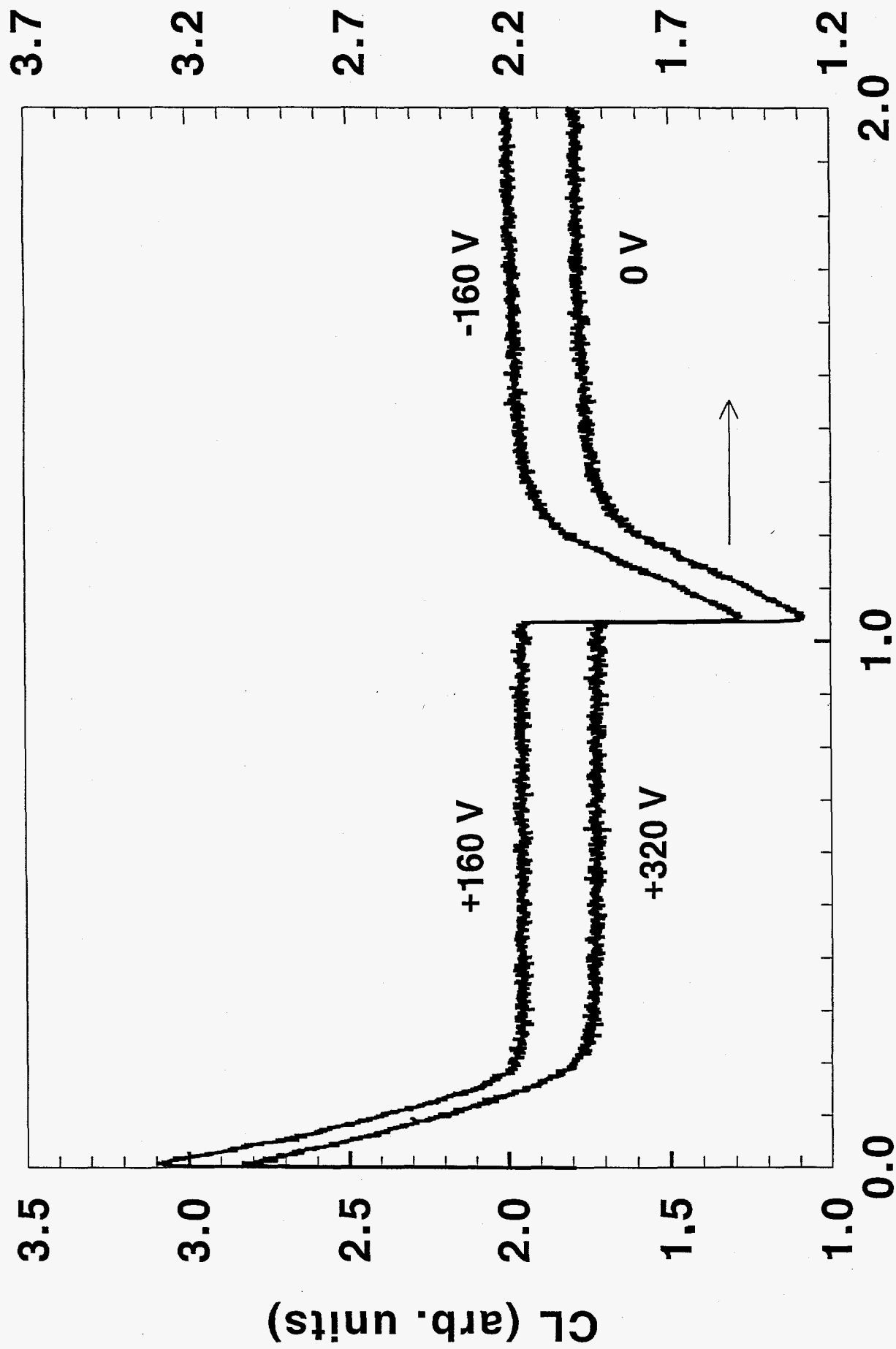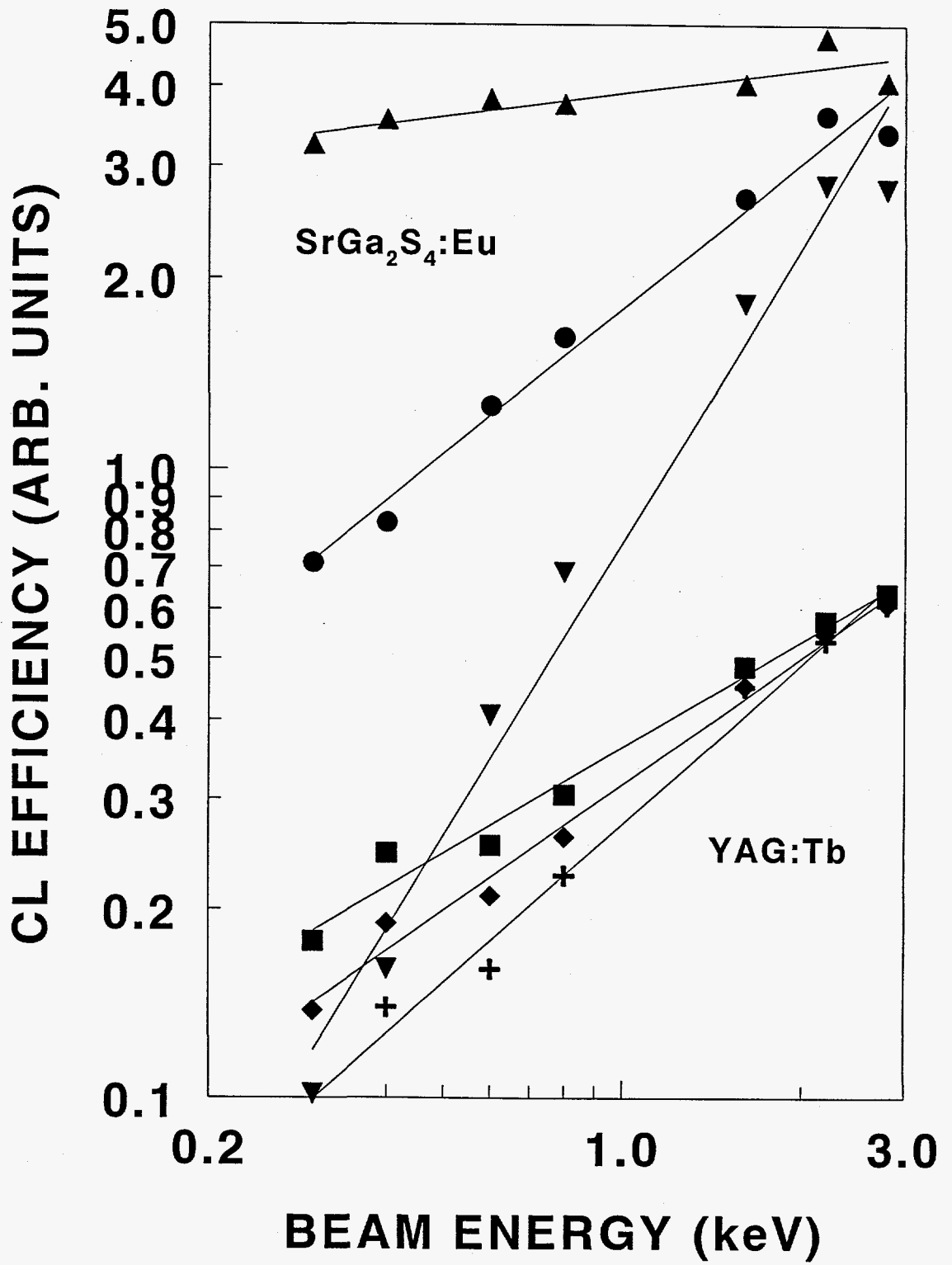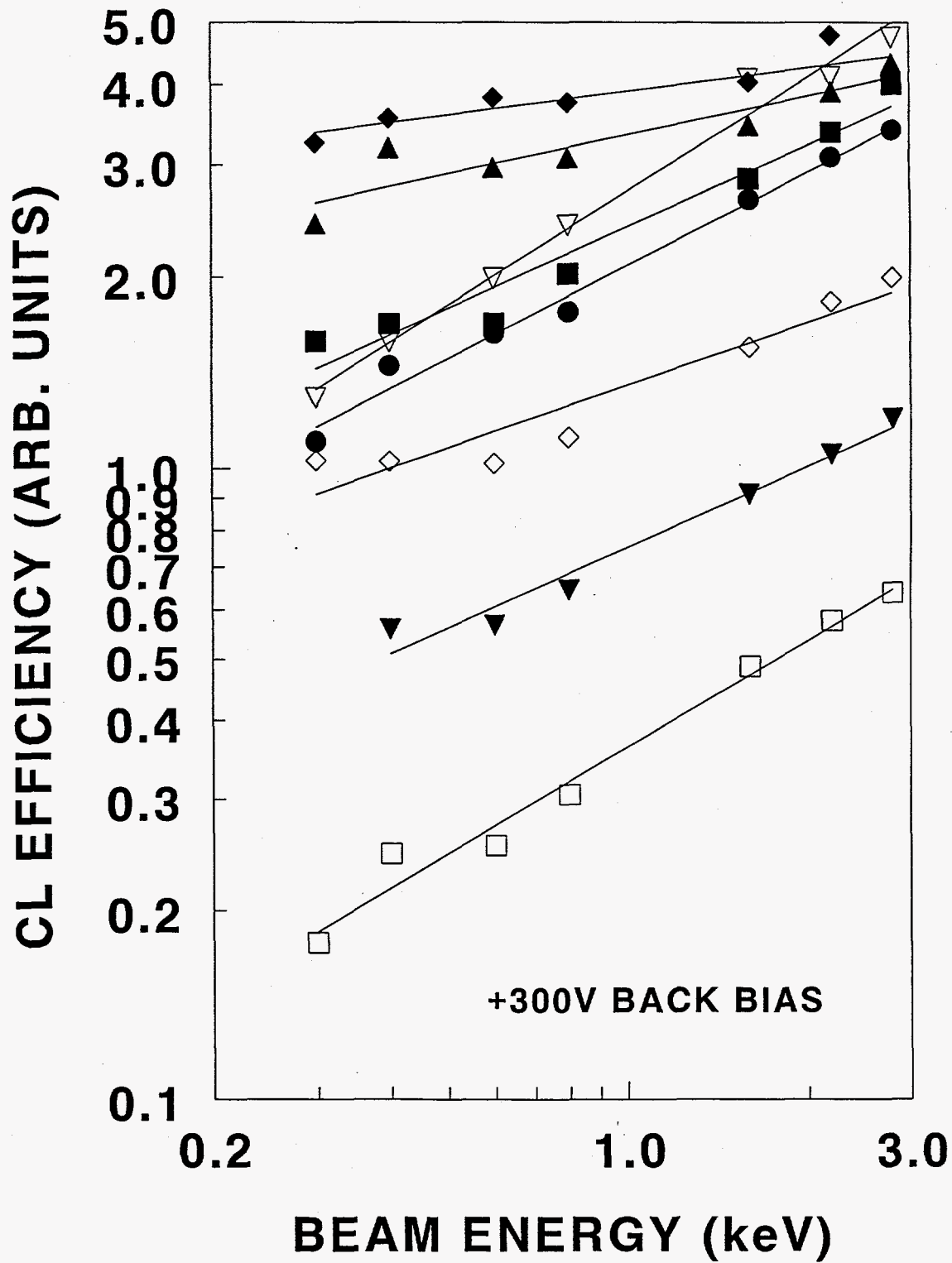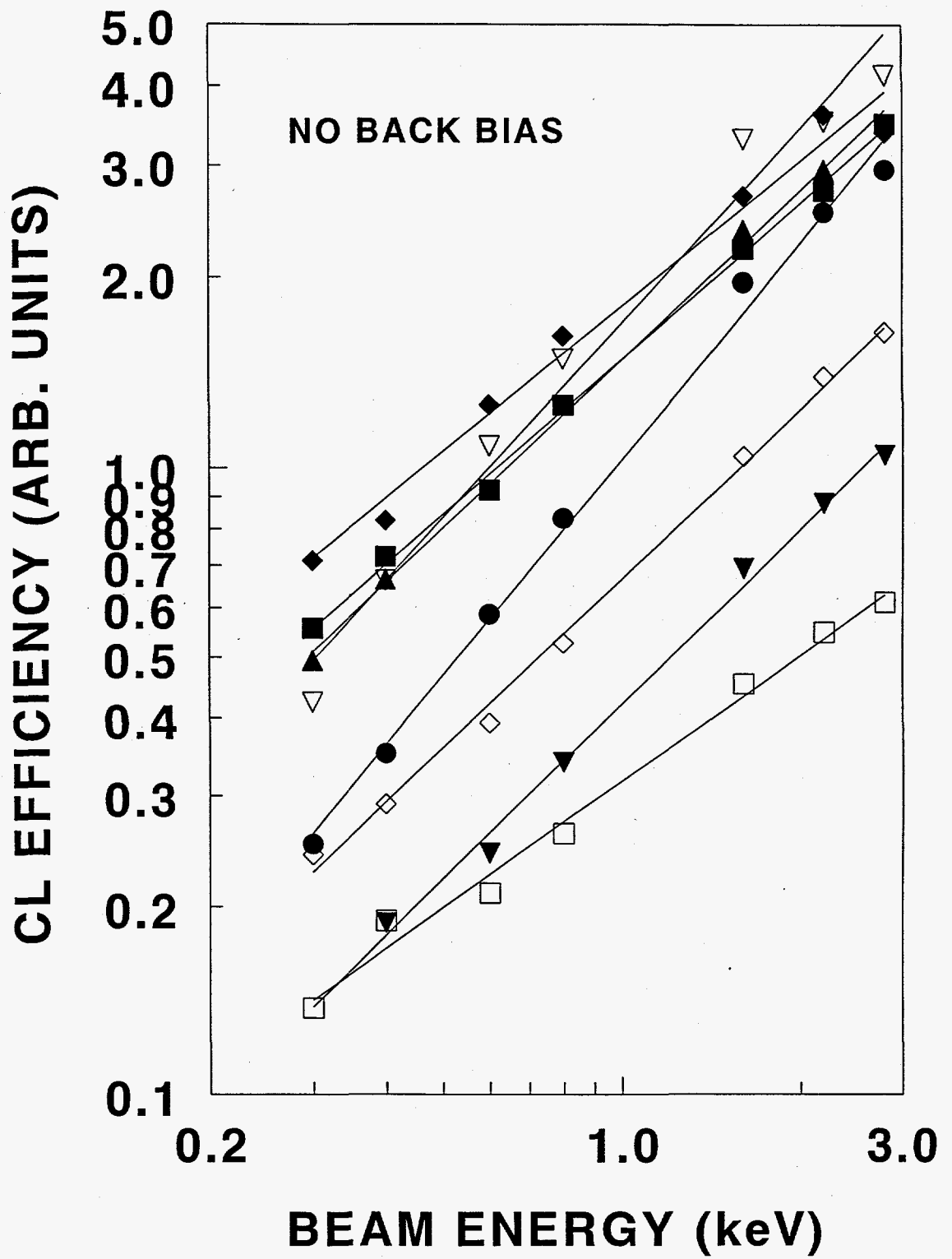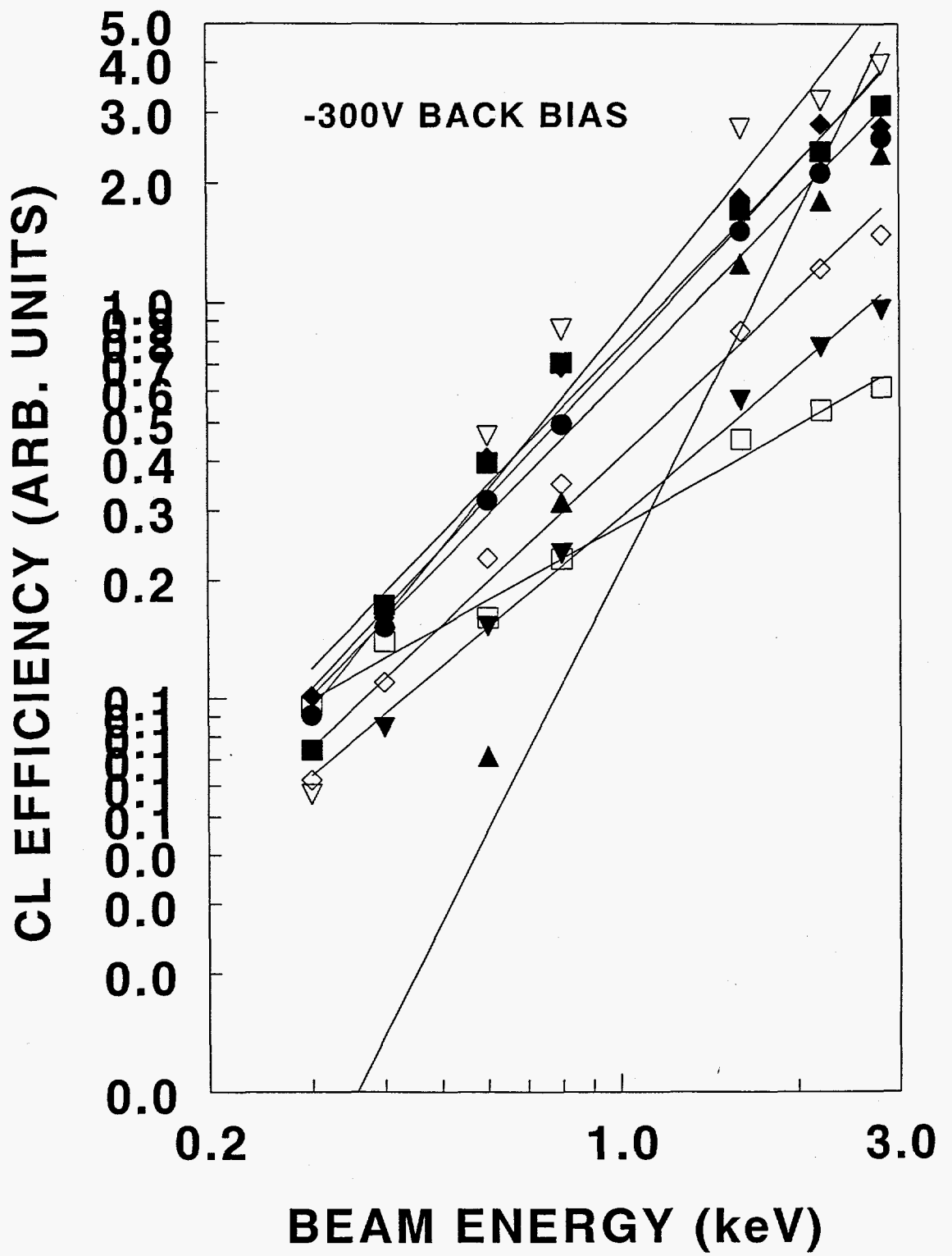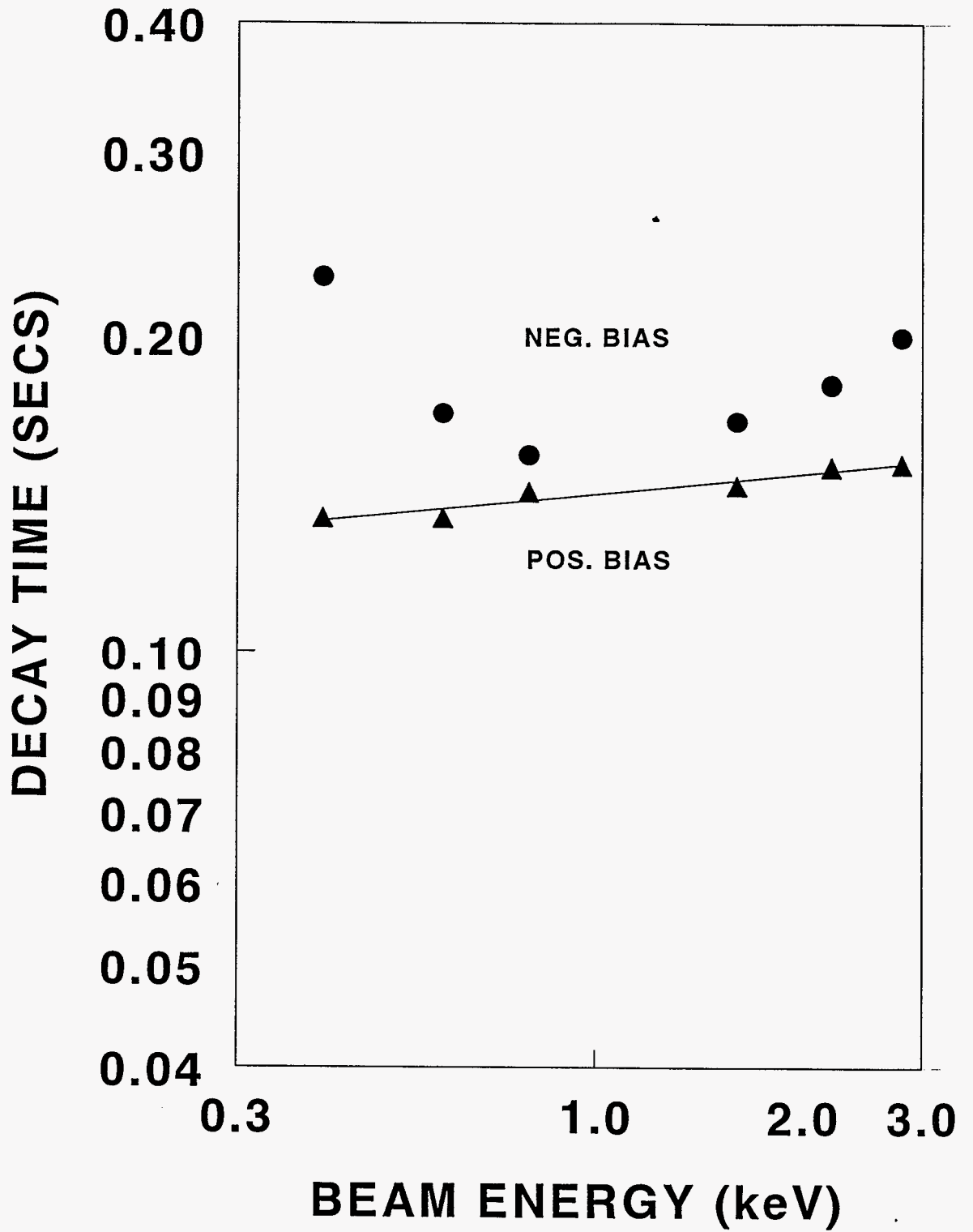
Fig. 7 Seager
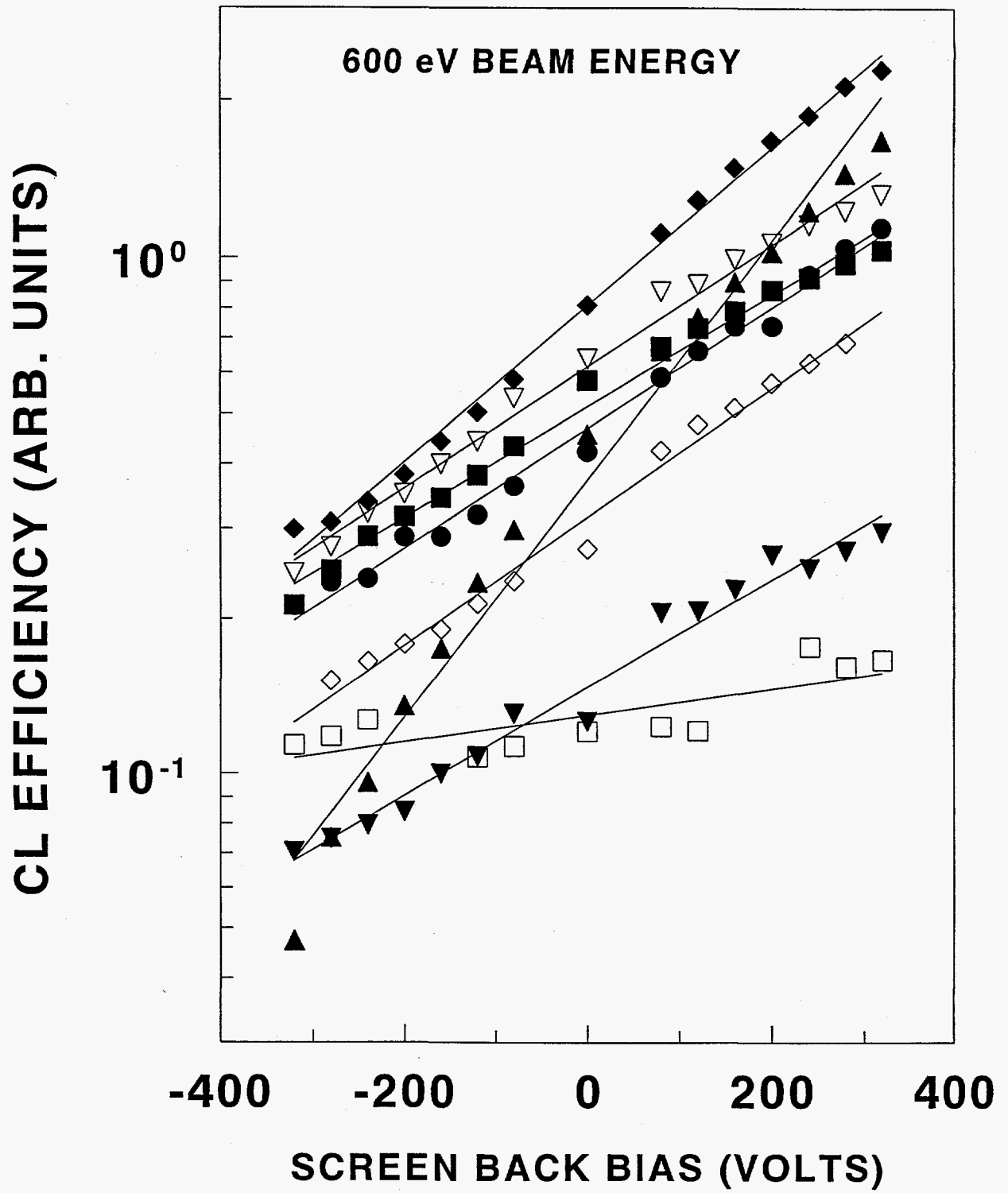
Fig. 8 Seager
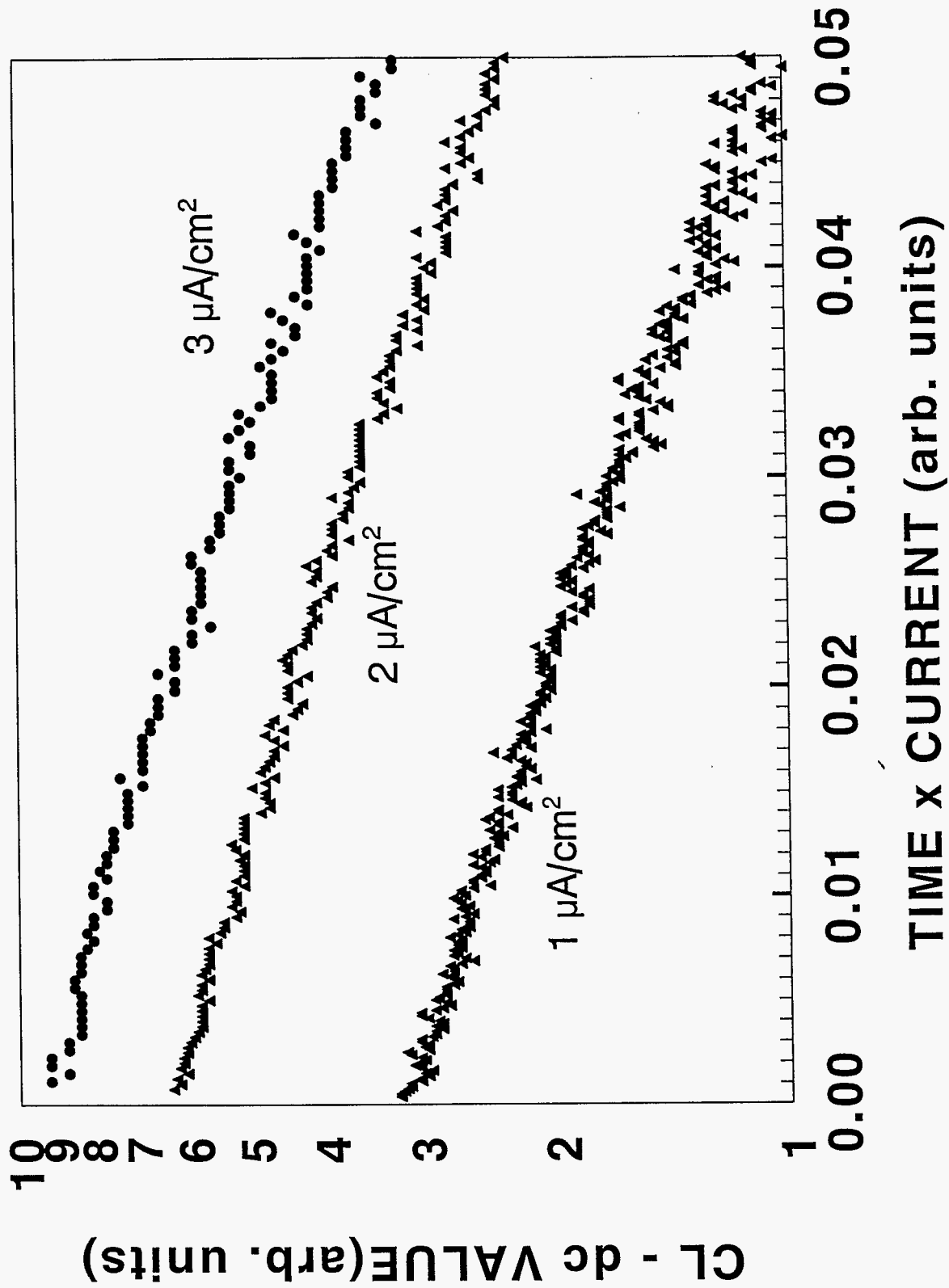
Fig. 9 Seager
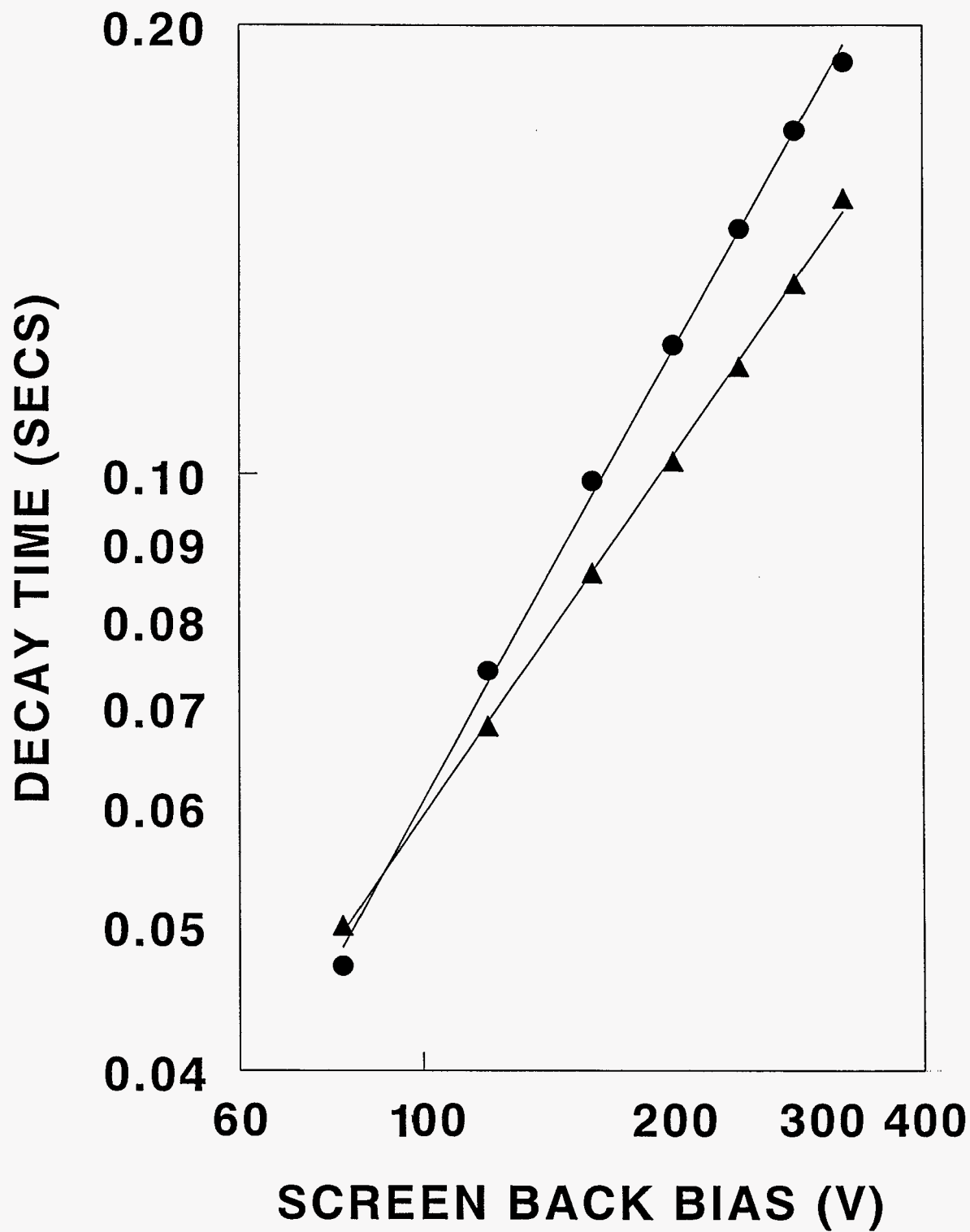
Fig. 10 Seager
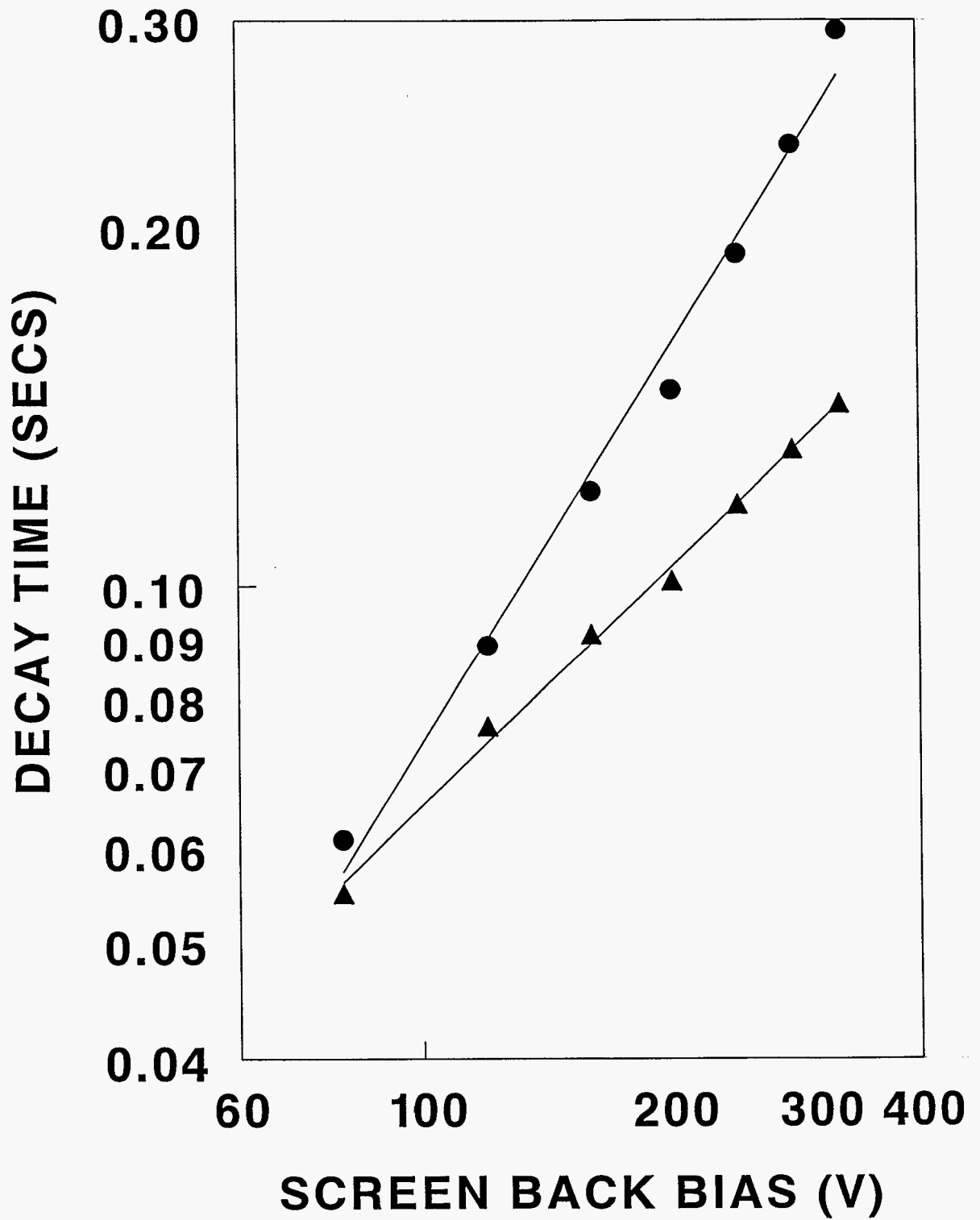
Fig. 11 Seager

Fig. 12 Seager
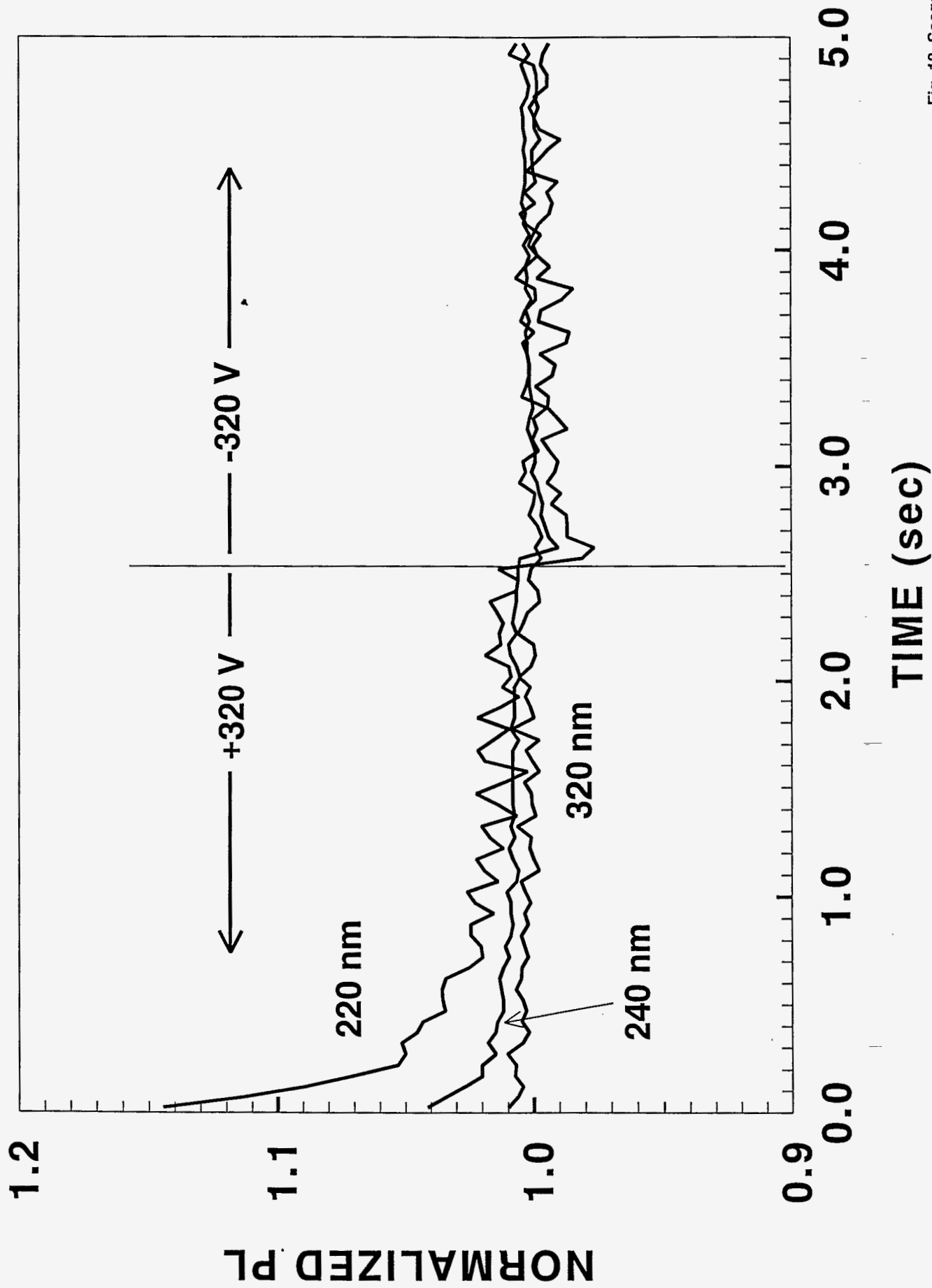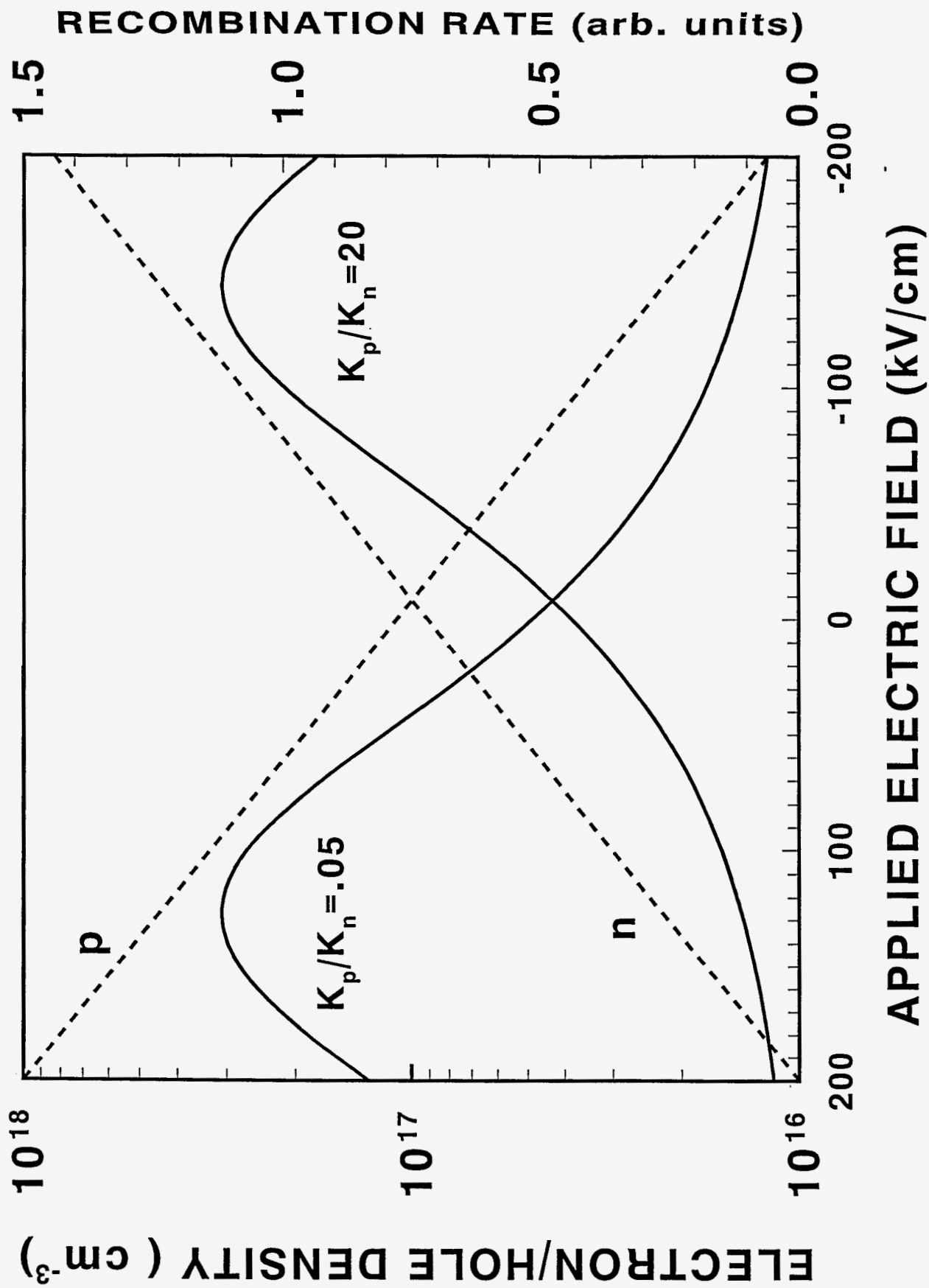
NORMALIZED PL

TIME (sec)

+320 V ←———→ -320 V

220 nm

240 nm

320 nm

Fig. 13 Seager

Fig. 14 Seager