mechanism than the first-stage coloration,[4] it was thought necessary to make a comparison of the two crystals when irradiated without a filter. Accordingly, the two specimens used in this investigation were given a further irradiation without a filter for a period of 3 hours. At the end of this irradiation the large and small crystals showed nonuniform coloration and optical densities, $\log_{10}(I_0/I)$, of 0.650 and 0.653, respectively. These values are again in agreement to within the experimental error.

In summary, the present investigation has been unable to verify the result reported by Lin that the *F*-center concentration in the alkali halides varies directly with the percentage of cross-sectional area of the crystal irradiated. On the contrary, it is shown that the *F*-center concentration is independent of the fraction of the crystal irradiated.

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[4] R. B. Gordon and A. S. Nowick, Phys. Rev. **101**, 977 (1956); A. S. Nowick, Phys. Rev. **111**, 16 (1958), preceding paper.

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Electroluminescence from the Surface Layer of $BaTiO_3$, $SrTiO_3$, and Associated Materials

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Electroluminescence resulting from high-frequency excitation ($\gtrsim$500 kc/sec), has been observed in $BaTiO_3$, $SrTiO_3$, and associated materials. It is shown that the light emission is the result of a high rf field across a thin surface barrier. The efficiency of this emission is very low, and a tentative value of $10^{-6}\%$ was obtained. A model involving field emission from the metal electrode into the crystal surface layer is proposed to explain the observed phenomena. The characteristics of this surface layer are relatively insensitive to temperature, from at least $-40°C$ to 300°C. The ratio of permittivity to thickness, ϵ/L, was found to have a value of $\leq 1.4\times10^5$ cm^{-1} for the $BaTiO_3$ surface layer.

INTRODUCTION

THERE have been many studies of electroluminescence (EL) reported in the literature.[1] The majority of these have been concerned with ZnS or materials considered to have similar excitation and emission mechanisms. However, "recombination" radiation has been observed when semiconductors are biased in the forward direction.[2,3] More recently Newman[4] reported visible light emitted from a reverse-biased silicon *p-n* junction and proposed that it might result from avalanche breakdown. This was confirmed and extended by Chynoweth and McKay[5] who later found a somewhat different effect which resulted from high-field emission in silicon *p-n* junctions.[6] Recently the author reported electroluminescence in $BaTiO_3$.[7]

The surface layer on $BaTiO_3$ has been studied by a number of investigators.[8–12] Reported values of the thickness and dielectric constant of the surface layer have varied widely depending on the method of measurement.

It is the purpose of this paper (1) to present experimental data on electroluminescence from $BaTiO_3$ and $SrTiO_3$, (2) to establish the most probable mechanism of this light emission, and (3) to use these data to determine the ratio of the permittivity to thickness of the surface layer. The experimental apparatus has been described elsewhere.[13] Therefore, only recent modifications will be included in this paper.

EXPERIMENTAL RESULTS

(a) General Observations

EL has been observed from barium titanate, strontium titanate, and associated materials, when they were excited with rf voltages. The optimum output was achieved when the electrodes were applied in a concentric configuration as previously described.[13] This arrangement produced a high field around the small center electrode. All of the light was observed to originate from this region, apparently coming from the electrode-crystal interface. Most of the light was emitted with uniform intensity around the perimeter, or at times over the entire area of the small electrode. However, there were generally a few tiny spots that were more intense than the surrounding emission.

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[1] For a summary of this work see, for instance, G. Destriau and H. F. Ivey, Proc. Inst. Radio Engrs. **43**, 1911 (1955).

[2] K. Lehovec *et al.*, Phys. Rev. **83**, 603 (1951).

[3] J. R. Haynes and H. B. Briggs, Phys. Rev. **86**, 647 (1952).

[4] R. Newman, Phys. Rev. **100**, 700 (1955).

[5] A. G. Chynoweth and K. G. McKay, Phys. Rev. **102**, 369 (1956).

[6] A. G. Chynoweth and K. G. McKay, Phys. Rev. **106**, 418 (1957).

[7] G. G. Harman, Bull. Am. Phys. Soc. Ser. II, **1**, 112 (1956).

[8] M. Anliker *et al.*, Helv. Phys. Acta **27**, 99 (1954).

[9] W. Kanzig, Phys. Rev. **98**, 549 (1955).

[10] P. H. Fang, Bull. Am. Phys. Soc. Ser. II, **1**, 38 (1956).

[11] A. G. Chynoweth, Phys. Rev. **102**, 705 (1956).

[12] W. J. Merz, J. Appl. Phys. **27**, 938 (1956).

[13] G. G. Harman, Rev. Sci. Instr. **28**, 127 (1957).

The light intensity is low and the brightest emission thus far obtained is visible only in a darkened room. The intensity associated with most of the following measurements could be seen only after dark-accommodating the eyes and was studied with the aid of a low-noise photomultiplier.

The EL is dependent on the electrode material and to some extent on the method of application. Fired-on silver (750°C) gives extremely poor results, probably because it diffuses into the crystal surface layer. Air-drying silver paint, however, is reasonably good. The EL resulting from this electrode is somewhat erratic due to the crudeness and irregularity of its contact with the crystal surface. The optimum electrode consists of indium-gallium[14] which is rubbed on the acid-cleaned and alcohol-dried crystal surface. This electrode results in stable light emission and has been used over the range of -40°C to 300°C. Another satisfactory electrode consists of evaporated silver, soldered with indium. In general, evaporated metals are useful only when they have been soldered with indium or similar materials. The reason for this is not apparent, particularly since the EL characteristics are primarily those of the evaporated film. The electrodes that produce the best EL results also appear to be reasonably ohmic when used on conductive $BaTiO_3$.[15] The problem of contacts could well become an investigation unto itself, the EL being used as a convenient means of determining the electrode characteristics.

The present EL measurements have been made with high-frequency excitation ($\gtrsim$500 kc/sec) and low average field strengths ($<$1000 v/cm). There is another EL effect at low frequencies ($\lesssim$50 kc/sec) and high fields ($>$1000 v/cm). This effect, which almost disappears at the Curie point, is most pronounced with symmetrical electrodes and is a function of the switching-current spikes. It will be reported later.[16]

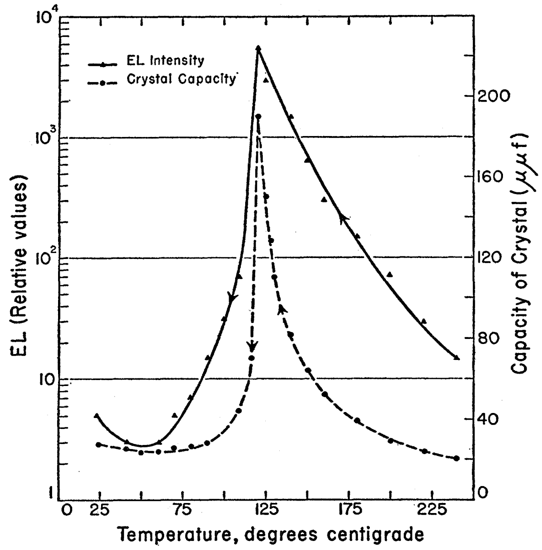

FIG. 1. Integrated light emission from $BaTiO_3$ at constant voltage *vs* temperature in the vicinity of the Curie point, frequency $=10$ Mc/sec. Heating due to dielectric loss causes some error near the Curie point.

(b) Temperature Characteristics

Figure 1 shows the change in capacitance and in light emission intensity (as recorded by a photomultiplier) *vs* temperature at constant rf voltage, for a single-crystal of $BaTiO_3$. Figure 2 gives the voltage required to produce the threshold of EL[17] at the 0°C and 120°C transitions. The EL persists far above the Curie point, to at least 300°C, and thus is not a direct manifestation of ferroelectricity in the bulk crystal.

The dramatic rise in EL at the Curie point can be explained by assuming that the light is emitted from a surface layer with a low permittivity which remains approximately constant in this temperature range. When the bulk dielectric constant increases, more of the total rf voltage appears across the surface layer and the EL increases according to Eq. (1). The equivalent circuit for the system consists of three capacitors in series as discussed by Chynoweth.[11] The rf impedances are low, so that the dc shunt resistances of the barrier zones and the body may be neglected. Calculations based on this simple model are in good agreement with the increase in the EL at the Curie point, shown in Fig. 1.

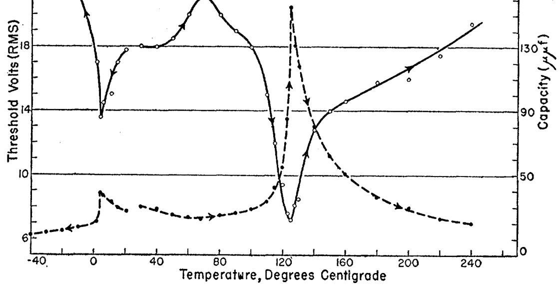

FIG. 2. The capacity and the EL threshold voltage *vs* temperature, for a $BaTiO_3$ crystal, frequency $=10$ Mc/sec.

Strontium titanate has no crystallographic transition in the temperature region shown in Fig. 3 and thus displayed a continual decrease of EL with increasing temperature, corresponding to the decrease in bulk permittivity. At 300°C the dc resistance of the sample

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[14] S. S. Flashen and L. G. Van Uitert, J. Appl. Phys. **27**, 190 (1956).

[15] G. G. Harman, Phys. Rev. **106**, 1358 (1957).

[16] G. G. Harman and R. L. Raybold (to be published).

[17] The voltage threshold of electroluminescence is here defined as the applied crystal voltage, at a given frequency, that results in the minimum reproducible current output from a selected 1P21 photomultiplier. This current is in the order of 10^{-8} to 10^{-9} amp and is held constant during a given experiment.

had decreased to a few hundred thousand ohms. EL was observed upon application of a reverse dc bias.[18] The light was emitted primarily from tiny spots distributed uniformly over the area of the small electrode. At this temperature there was a front to back resistance ratio of about 15 to 1 and the EL threshold was 20 volts. A long time-constant was associated with this rectification and the barrier required 20 or 30 seconds to build up. There was no EL at the moment of application of the reverse bias. Subsequently the EL increased and reached a peak slightly before the current stabilized at its minimum value. Only a negligible amount of EL was observed when voltage was applied in the forward direction. These observations are indicative of the avalanche breakdown mechanism as described by Chynoweth and McKay.[5] Similar dc tests were performed on $BaTiO_3$ with similar results. Unfortunately the high-temperature dc-induced EL was never intense enough for a spectral emission test, so this characteristic could not be compared with the rf induced emission. No dc-induced EL has been observed at room temperature, even with very high voltages.

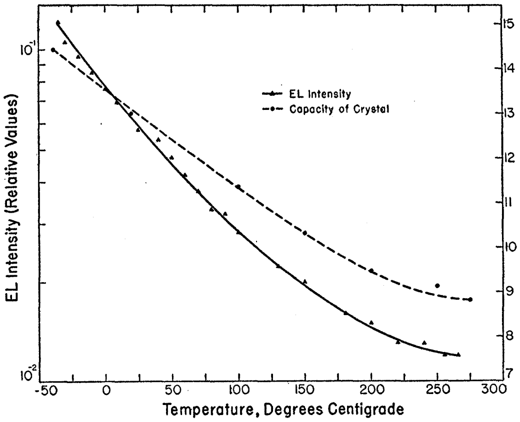

FIG. 3. Integrated light emission at constant voltage *vs* temperature, for a single crystal of $SrTiO_3$, frequency = 30 Mc/sec.

(c) Frequency and Voltage Characteristics

Measurements of the permittivity as a function of frequency, on single crystals of $BaTiO_3$, show peaks when various piezoelectric modes are excited. Light emission from these crystals, as a function of frequency, also displays such resonances (Fig. 4). Measurements of Q indicate increased capacitance and loss at the major peaks. Thus the EL increases at these resonances for the same reason that it does at the Curie point. Strontium titanate does not show any EL peaks as the frequency is increased, but instead shows a continuous rise. This is primarily due to the increase in the value of b in Eq. (1) below.

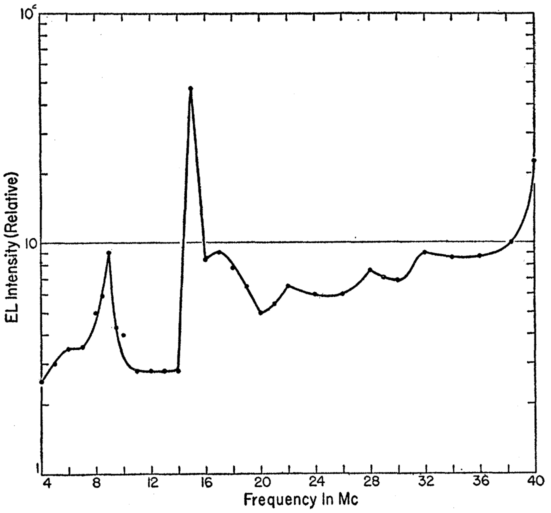

FIG. 4. Integrated light emission at constant voltage *vs* frequency, for a $BaTiO_3$ single crystal at room temperature.

The voltage dependence of EL intensity was measured at various frequencies. Neither the usual exponential-type EL equations[1] nor the similar Fowler-Nordheim equation "rectified" these data. Except for the very-low-intensity region, the best approximation is obtained with the following relation:

$$I = aV^b, \tag{1}$$

where I is the EL intensity, a and b are constants, and V is the peak applied voltage. Values of b range from about four to six. There appear to be many complicating factors in the voltage characteristics. For example both a and b are dependent on the electrode material. Data, shown on a log-log plot, are given for $BaTiO_3$ and $SrTiO_3$ in Fig. 5. Curves A and B demonstrate the effect of changing the bulk dielectric constant. The measured threshold voltage is definitely lowered as more of the total voltage is applied across the surface barrier. Some heating effects are apparent at higher voltages in Curve A, but the exponent is the same as that for Curve B. Curves C and D show that the exponent, b, changes with frequency. In general, all measurements were made at very low intensity in order to best isolate a particular variable. For instance, the EL threshold voltage changes very slowly with frequency but the frequency dependence is greatly magnified when the measurement is made at high intensities.

(d) X-Ray and Other Irradiation Tests

Most electroluminescent materials can be excited with energetic electrons, x-rays, and appropriate ultra-

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[18] As described in reference 13, the electrodes are placed concentrically on the sample so that the large outside contact has an area about 10 times that of the small center contact. If the electrodes are rectifying with respect to the semiconductor or insulator to which they are applied, it is well known that an asymmetrical geometry will result in a forward and a reverse direction to dc, whose polarity is determined by the sign of the carriers in the same manner as for a point-contact diode.

violet radiation. In order to determine the present mechanism of EL, the latter two tests were performed.

High-intensity x-rays (500 r at 50 kv max) were used on several specimens each of $SrTiO_3$, $BaTiO_3$, TiO_2, and $KNbO_3$. No luminescence was observed above the background created by x-rays scattered into the photomultiplier (in contrast, the luminescent intensity from a ZnS crystal was several orders of magnitude above this background). Barium titanate and $SrTiO_3$ were intensely irradiated with various wavelengths of ultraviolet and visible light, but no luminescence was observed. This irradiation did not result in any interaction with the EL. The above experiments eliminate the probability of an impact-type mechanism, such as that of ZnS.

(e) Emission Spectra and Efficiency

The EL emission spectra have been recorded for most materials studied. Measurements were made with a modified Bausch and Lomb 250-mm, *f*/4.4, grating monochromator. A specially selected low-noise 1P21 photomultiplier was employed so that in general no cooling was necessary to detect the weak light emission. It became evident that significantly different spectral emissions resulted from different electrode materials. This spectral dependence was strikingly demonstrated by one experiment in which the light was observed with the dark-accommodated eye. The small electrode on a $SrTiO_3$ single crystal was made of evaporated silver soldered with indium. The light that was emitted around the perimeter of this electrode was yellow, except in one spot where it appeared greenish. Later, a microscopic examination of the electrode revealed that indium had flowed over the edge of the silver in this spot.

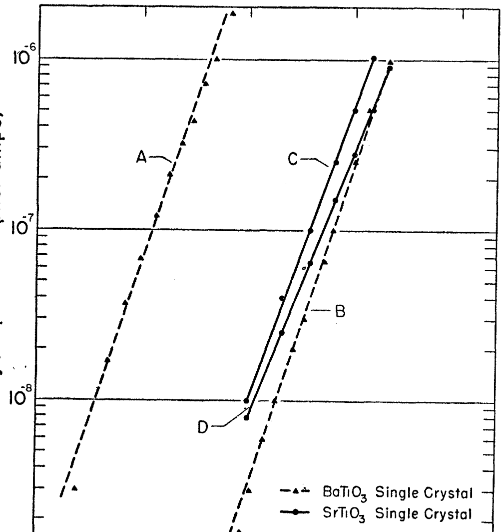

FIG. 5. Integrated light output *vs* voltage for a $BaTiO_3$ and a $SrTiO_3$ single crystal, In-Ga electrodes. Curve *A*, $BaTiO_3$ at the Curie point, frequency = 10 Mc/sec; *B*, same as *A* except taken at room temperature; *C*, $SrTiO_3$ at 30 Mc/sec, room temperature; *D*, same as *C*, except taken at 15 Mc/sec.

A comparison of the spectral emission from a pure $BaTiO_3$ ceramic sample,[19] taken with two different electrodes, is given in Fig. 6. The emission was measured from a special mount that collected the light which "leaked out" around the edges of the small electrode. The optical absorption edge of the crystal is about 4000 A (3.1 ev). At longer wavelengths internal reflections contributed somewhat to the total light collected, but on the short-wavelength side the only contribution was from the light that directly "leaked out." Photon emission, with the In-Ga electrode, was observed continuously to 3000 A (4.1 ev) which was the limit of the photomultiplier. This is considerably beyond the optical absorption edge of the crystal! Curve *A* of Fig. 6 is a typical emission spectrum for SrTiO with In-Ga electrodes. The spectral emission from $KNbO_3$ and TiO_2 resembles that of $BaTiO_3$. The spectra are identical for ceramics and single crystals.

The differences in spectral emission with different electrodes can hardly be ascribed to "doping" of the surface layer since silver, as air drying paint, can be removed with solvent and replaced with In-Ga. The spectrum then changes as shown in Fig. 6, Curves *B* and *C*. No heat was applied during the process and there were no residual effects of the removed electrode, as Diemer found for ZnS.[20]

The measured voltage threshold of EL was generally related to the work function of the electrode. This voltage was twice as high for platinum as for indium. The threshold voltages for intermediate work function materials, such as silver, nickel, etc., were within those voltage limits but were not as nicely distributed. The important thing is that different metals gave reproducibly different thresholds.

The efficiency of the EL was measured in the megacycle frequency region. Power input was calculated, using the voltage measured at the crystal holder and the *Q* of the crystal. The light emission power was measured with the calibrated monochromator-photomultiplier combination. Unfortunately this combination could not be used for measurements of wavelengths longer than about 6500 A, so the total efficiency is probably higher than reported below, depending on the amount of red and infrared actually emitted. A value of efficiency for $BaTiO_3$ of 10^{-7} to $10^{-6}\%$ was obtained. This value is somewhat increased above the Curie temperature of $BaTiO_3$ and also for $SrTiO_3$ at room temperature, because of the reduced dielectric loss. These values are similar to those obtained for avalanche breakdown in silicon.[5]

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[19] W. S. Clabaugh *et al.*, J. Research Natl. Bur. Standards **56**, 289 (1956).

[20] G. Diemer, Philips Research Repts. **10**, 194 (1955).

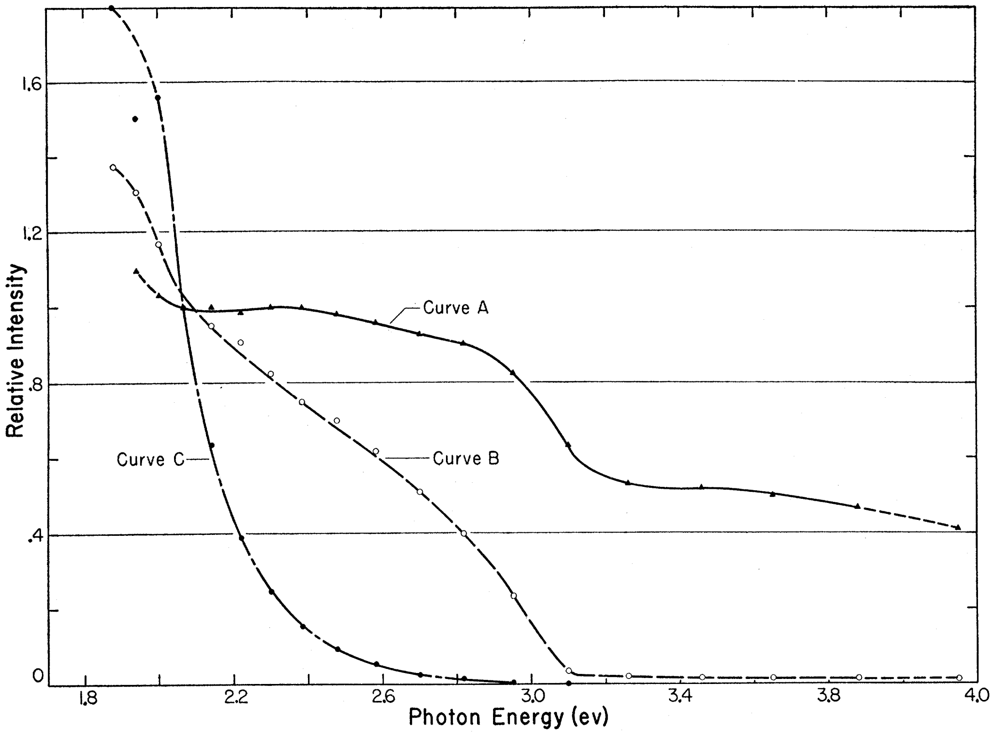

FIG. 6. Spectral emission characteristics. (*A*) $SrTiO_3$ single crystal, In-Ga electrodes; (*B*) $BaTiO_3$ ceramic, In-Ga electrodes; (*C*) same ceramic sample as in (*B*), silver electrodes. The dotted lines indicate uncertainty due to the large correction factor for the photomultiplier, monochromator combination. The curves are normalized at 2.07 ev.

(f) Influence of the Ambient Atmosphere on the EL

The EL from $BaTiO_3$ was found to be similar in a vacuum to that found in dry air at atmospheric pressure. This ruled out the possibility of a gas discharge producing some or all of the light.

In order to establish definitely that the light emission was a surface-state phenomenon, as indicated by the previously mentioned observations, the EL was studied under various ambient atmospheres. A nickel pressure-contact was employed in order to allow gas diffusion under the electrode. The techniques were similar to those used by Anderson.[21] Both dry oxygen and helium were similar to dry air and produced no change in EL. The EL threshold voltage for $SrTiO_3$ was raised from 25 v rms at 30 Mc/sec in dry oxygen to 50 v rms in water vapor saturated oxygen. This effect was completely reversible. Dry ammonia was tested and resulted in an even greater threshold increase. However, this was not reversible. These results indicate that the EL is primarily a surface phenomenon since the gases could not diffuse into the body of the crystal at room temperature during a one-hour exposure. In addition, volume EL in an insulator should be dependent on the field strength and not on a slight change in the electrode or crystal surface. For instance, ZnS type materials emit light in strong ac fields without contacting the electrode at all, and this has never been observed in the titanates.

(g) EL of Some Associated Compounds

Many compounds, in addition to those described above, were tested for high-frequency induced EL. A list of these is shown in Table I, where the EL threshold voltages are qualitatively presented relative to the threshold voltage of $SrTiO_3$. The voltage required

TABLE I. Various materials tested for high-frequency induced electroluminescence (relative to $SrTiO_3$).

Material	Single crystal (s.c.) or ceramic	Voltage necessary to produce EL threshold at 30 Mc/sec, relative to $SrTiO_3$	Comments
$BaTiO_3$	s.c. and cer.	Lower	
$KNbO_3$	s.c.	Somewhat higher	Weak room temp. dc EL noted (similar to 300°C EL in $SrTiO_3$)
$CaTiO_3$	cer.	About the same	
$PBZrO_3$	cer.	About the same	
TiO_2	s.c. and cer.	Much higher	
ZnS	s.c.	Higher at this frequency	
Rochelle salts	s.c.	...	No EL observed at highest voltage available (~100 v rms at 30 Mc/sec)
KDP	s.c.		
ADP	s.c.		
GASH	s.c.		
KCl:Tl	s.c.		
Si	s.c.		Dc avalanche breakdown was measured with an unformed metal point-contact (20 v)

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[21] J. R. Anderson *et al.*, J. Appl. Phys. **26**, 1387 (1955).

to produce the threshold of EL in $SrTiO_3$ is about 20 v–30 v at 30 Mc/sec and varies somewhat with contact configuration and the type of electrode employed. It can be assumed that other high permittivity compounds, particularly in the ABO_3 class, will electroluminesce similarly under high-frequency rf excitation.

Impurities that did not significantly influence the conductivity of $BaTiO_3$, such as small percentages of iron or silver, did not affect the EL emission spectrum or intensity. No differences have been observed for crystals made in different laboratories. However, trivalent and other elements that decreased the resistivity to a few hundred ohm-cm[22] changed the nature of the EL, apparently resulting in weak "recombination radiation," generally in the red or yellow spectral region. No fine structure was observed, as has been reported for cathodoluminescent emission in samarium-doped $BaTiO_3$.[23]

DISCUSSION

(a) Proposed Mechanism of Light Emission

The failure of high-intensity x-rays and ultraviolet light to excite luminescence, and of the latter to influence the EL intensity in these materials, rules out the possibility of an activator system of the ZnS type. There is no typical "recombination radiation"[3] emission pattern around the optical absorption edge; in fact the emission generally shows a decrease in that region.

The EL processes that can best account for the continuous radiation observed at energies considerably above the optical absorption edge are the avalanche breakdown[5] or the field emission[6] mechanisms; visual observations indicate a mixture of these. Both of these require a thin barrier region in which a high electric field must exist. In the case of an insulator excited by rf, the barrier must be dielectric in nature (i.e., permittivity of the barrier$\ll$permittivity of the bulk). Evidence for this was shown by the measurements at the Curie point.

The dependence of the EL threshold voltage on the type of metallic electrode can be explained by assuming field emission from the electrode into the crystal surface layer. The origin of the EL in the surface layer was further demonstrated by the significant influence of the ambient atmosphere on the EL threshold voltage.

The following model is proposed to account for the observed phenomena. Barium titanate contains a small number of oxygen vacancies. These centers should serve as electron traps and would be ionized by the high rf fields that exist in the electrode-crystal interface region. The resulting free electrons would then be accelerated sufficiently to produce energetic electron-hole pairs by collision. The remaining ionized centers would be isolated point charges. When located within a few atomic diameters of the surface, these charges would produce field emission from the electrode, as proposed by Geller.[24] These additional electrons would continue the "pair" production process. Intraband and interband radiative transitions would produce the observed light in the manner described by Chynoweth and McKay.[5,6] Some of the initial electrons, then, would be supplied by the electrode (on the negative cycle) and other electrons would come from the material itself, depending upon the concentration of oxygen vacancies in the surface layer. The lifetime of the free electrons is perturbed by the rapid polarity change of the rf field. It is possible, considering the extremely low efficiency of EL, that some of the light results from electrons that receive additional energy from the field on successive cycles, or are at least left in the conduction band and can be accelerated over the next entire half cycle. This effect should become more apparent as the frequency is increased and explains why the threshold voltage decreases somewhat with increasing frequency. Another factor would be introduced by the magnitude and direction of the space-charge potential in the surface layer. Since $BaTiO_3$ is an insulator, the field-emitted electrons would have to return to the electrode in order to maintain electrical neutrality of the material. On the average, this should occur during the second half of the ac cycle in which they were emitted.

The point charges near the crystal surface and the surface properties of the electrode would be influenced by the ambient atmosphere, this would account for the effect of the atmosphere on the EL, as observed. Electrodes with lower effective work functions should result in lower observable EL voltage thresholds. It is not obvious why the spectral emission should depend on the electrodes. However, the contact potential would change with the electrodes and this could influence the band structure within the thin surface layer.

(b) Surface Layer Characteristics

Isolated (nonoverlapping) point charges, as required for the above model, are not probable in a medium of high permittivity such as $\epsilon\sim200$, suggested by Kanzig[9] for the $BaTiO_3$ surface layer. Merz,[12] however, assumed a dielectric constant of ~5 for the surface layer and this value would meet the requirements of the proposed model.

In order to determine the characteristics of the barrier layer, a $BaTiO_3$ single crystal (0.04 cm thick) was cut into a cylindrical geometry with an S. S. White Industrial Airbrasive Unit. The outside diameter was 0.5 cm and the diameter of the hole through the center was 0.075 cm. Both the inside and outside surfaces were coated with In-Ga as the electrodes. The measured capacity was $20\,\mu\mu$f, thus the bulk permittivity $\epsilon_2\sim2000$. The observed threshold voltage was 18 v peak at 30 Mc/sec. The following assumptions were made in order to analyze this data: (1) C_2 is the body (or bulk)

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[22] P. W. Haaijman *et al.*, German patent No. 929 350.

[23] Keichi Oshima *et al.*, J. Chem. Phys. **24**, 903 (1956).

[24] M. Geller, Phys. Rev. **101**, 1685 (1956).

capacity and it is computed as that of a cylindrical capacitor (fringing may be neglected due to the extremely high permittivity of $BaTiO_3$). The capacity of the inner barrier C_1 and that of the outer, C_3, are computed as flat plate capacitors with $C_3=RC_1$, from the geometry. (2) Assuming that the threshold for electron-hole "pair production," E_p, is slightly under twice the energy gap[25] or 5 ev, it is evident that this is about the minimum amount of the total voltage that can be applied across the barrier in order to produce enough light for a practical measurement. The following definitions will be used: ϵ_1 = permittivity of the barrier; R = ratio C_3/C_1; L = thickness of the barrier; a = diameter of small electrode; E_T = measured threshold voltage.

For the impedances we have, according to these assumptions:

$$X_{C3}=(1/R)X_{C1}, \tag{2}$$

$$X_{C1}\geq\frac{E_p}{E_T-E_p}(X_{C2}+X_{C3}). \tag{3}$$

Substituting and solving for ϵ_1/L, we obtain

$$\frac{\epsilon_1}{L}\leq\frac{(E_T-E_p)R-E_p}{E_pR}\left(\frac{2\epsilon_2}{a\ln R}\right)\approx\frac{(E_T-E_p)}{E_p}\,\frac{2\epsilon_2}{a\ln R}, \tag{4}$$

and $\epsilon_1/L\leq 7.4\times10^4$ cm^{-1} for $BaTiO_3$. Since a permittivity of 5 is about the lowest reasonable value (equal to the optical dielectric constant), the barrier thickness is $\sim10^{-4}$ cm or larger.

This thickness would be decreased if E_p were significantly lower (not very probable) or if the space charge potential of the surface layer is about 1 or 2 v. Then E_p in the equations would be replaced by E_p minus the space charge, assuming that they are additive on one-half of the cycle. Considering the large change in characteristics from the bulk to the surface layer, a space charge potential of 2 v is reasonable. Computed on this basis $\epsilon_1/L\leq1.4\times10^5$ cm^{-1}; with the permittivity of the barrier layer taken to be 5. A barrier thickness of 3.5×10^{-5} cm is obtained which is in agreement with Chynoweth.[11] Using the value $\epsilon_1=5$ rather than, for instance, $\epsilon_1=200$ is justified since the latter results in $L\geq1.4\times10^{-3}$ cm. However, work on crystals of about this thickness (see Merz[12] or Chynoweth,[11] for example) does not indicate surface layer domination of the characteristics.

The treatment has also been applied to $SrTiO_3$. Using the above conditions, with $\epsilon_2=300$, $E_T=30$ v peak, $a=0.095$ cm, $R=6.1$; $\epsilon_1/L\leq3.3\times10^4$ cm^{-1} for a single-crystal cylindrical specimen. This implies that the surface layer is about 4 times as wide as that region for $BaTiO_3$.

Measurements made on several $BaTiO_3$ and $SrTiO_3$ crystals have resulted in a factor of 2 spread in the ϵ_1/L ratio of each material. It is not known whether this spread is due to an actual difference in surface properties or inaccuracies in the measurements. The latter is most probable since the measured threshold voltage is slightly dependent on the crystal thickness, which does not appear in Eq. (4). The low value for the dielectric constant of the surface layer appears reasonable when one considers that to obtain a significant fraction of the applied voltage across a very thin dielectric barrier, its permittivity must be considerably less than that of the bulk material.

As indicated in Table I, no EL has been observed from the O—H bond type ferroelectrics at room temperature. This could be for one or more of the following reasons: (1) they possess no significant surface layer; (2) any surface layer that they do possess has a dielectric constant very near that of the base material; (3) light could be emitted in spectral regions not detectable with available equipment; (4) the band structure of these materials is such as to reduce the already low probability for a radiative transition. There is some experimental evidence on KH_2PO_4 to support the first.[26]

ACKNOWLEDGMENTS

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[25] P. A. Wolff, Phys. Rev. **95**, 1415 (1954). This threshold, E_p, is difficult to ascertain in any material, and no known measurements of this type have been made on the surface layer of $BaTiO_3$. However, the simplest momentum considerations would indicate a value of at least 1.5 times the gap width and the present material is surely more complex than that. In the absence of any information on the band structure of the surface layer we assume the value $E_p=5$ ev, which is consistent with work done on other materials.

[26] C. Jaccard *et al.*, Helv. Phys. Acta **26**, 521 (1953).