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Electroluminescence in lead titanate single crystals

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Abstract. Electroluminescence in $PbTiO_3$ single crystals is studied with variation in applied electric field, frequency (20 Hz to 5 kHz) and temperature. The EL onset depends on the rate at which the dipole switches. Extremely sharp upward rising nature of the pulses of micro second duration suggest that there is a self maintained discharge in the dielectric due to secondary γ_p mechanism. Frequency dependence of EL suggests that both the secondary mechanisms, viz. the γ_p and γ_i are active after the application of a high field and the critical field at which this occurs decreases with increase in the frequency of the applied voltage. Similarly the onset voltage decreases with increase in frequency. The temperature dependance of EL at the applied frequency of 50 Hz shows that the onset voltage is intimately connected with the coercive field of the crystal and it is minimum at the Curie point. The study suggests that EL occurs in the bulk and there is a breakdown in the dielectric due to an avalanche formation.

Keywords. $PbTiO_3$; electroluminescence; ferroelectrics.

1. Introduction

Following the discovery of electroluminescence (EL) in $BaTiO_3$ by Harman (1958) various mechanisms of its origin have been proposed. Bhide *et al* (1965) and Bhide and Gondhalekar (1966) studied a.f. and r.f. induced EL from $BaTiO_3$ crystals and put forward the view that the a.f. induced EL is associated with the polarization reversal whereas the r.f. induced EL is produced in the surface layer on the crystal and is not associated with dipole reversal or domain rearrangement. Katpatal and Deshmukh (1972) studied EL in $KNbO_3$ single crystals at low frequency and postulated the existence of complex charge layers on these crystals; space charge layers and charge layers due to domain reversal being responsible for the formation of such complex charge layers. Recently Katpatal and Deshmukh (1976) studied EL in $BaTiO_3$ crystals and proposed the existence of complex charge layers on the surface of these crystals also. It has been assumed by these workers that EL originates in surface layers as and when the field across the layer is sufficient to cause field emission. The existence of the surface layers was suggested by Kanzig (1955) to explain the effect of particle size on the dielectric constant and confirmed by several other workers, in different phenomena (Anliker *et al* 1954; Chynoweth 1956; Brezina and Fotchenkov 1964; Fatuzzo and Merz 1961; Merz 1956; Williams 1965; Callabay 1965, 66; Schoiject 1964). Electrical breakdown in single crystal of $BaTiO_3$ has been studied by Fang (1963), Kawabe *et al* (1964), and that in $SrTiO_3$ by Barrett (1964). Light emission during polarization reversal has been observed and studied by Ishibashi and Stadler (1968) and Bogatko *et al* (1969). Ueda *et al* (1964) have studied temperature dependence of breakdown field in polycrystalline $BaTiO_3$ and suggested that the breakdown is avalanche type. Most workers have used the concept of one or the other type of surface layer to explain the observed EL. Deshpande *et al* (1977) have studied EL in $BaTiO_3$ and $KNbO_3$ crystals at 50 Hz and found that the onset of EL pulses depends on the rate at which the switching of dipoles takes place and EL originates in the bulk only rather than in the surface layers. It is the object of this study to find whether or not the phenomenon of EL in other ferroelectrics is similar in characteristics to that of $BaTiO_3$ and $KNbO_3$ crystals. In this paper some of our results which elucidate the nature of the EL and its origin in $PbTiO_3$ which is similar in many respects to $BaTiO_3$ and $KNbO_3$, have been discussed.

2. Experimental

The experimental arrangement is shown in figure 1. The crystal is excited by a high sinusoidal voltage with the help of a HP audio frequency oscillator coupled to a high gain voltage amplifier capable of delivering 0 to 700 V rms in the frequency range 20 Hz to 10 kHz. This is connected to a crystal in series with a low value GR standard resistor, whose resistance is less than 1/100th of the impedance of the crystal at the applied frequency. The potential difference across the resistance is fed to Y_1 input of a double beam CRO so that the crystal current waveform is obtained on its screen. The crystal is kept in contact with a transparent conducting glass plate on one side and the metal electrode on the other. The EL is detected by RCA 931-A photomultiplier tube and two independent recorders: (i) the microammeter shown in figure 1 measures the average light output, and (ii) the pd across the resistance R between the cathode of the photomultiplier and ground fed to Y_2 beam of the double beam CRO measures the instantaneous value of the light output. The occurrence of (i) the EL current pulse on Y_1 beam, (ii) average light output in the photomultiplier (detected by the μA), and (iii) the instantaneous magnitude of the light output on Y_2 beam, can be simultaneously observed with this arrangement.

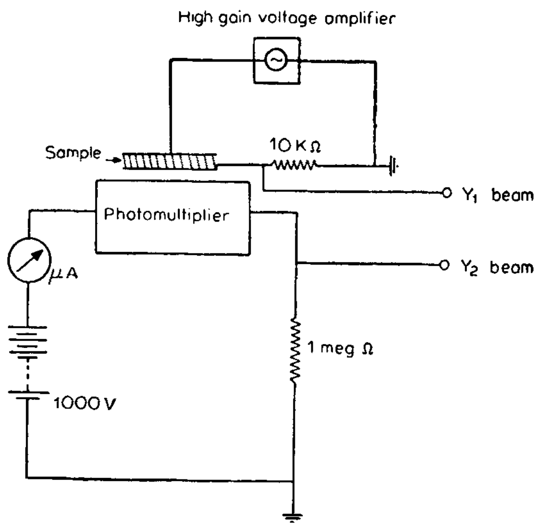

Figure 1. Schematic arrangement of EL experimental set up.

Lead titanate crystals used in this study have been grown in this laboratory. The method of crystal growth and some properties of the crystals are reported elsewhere (Kher *et al* 1978).

The experiments were repeated with different electrode pairs (copper, silver, stainless steel and tantalum-silver) and essentially similar results were obtained. The threshold voltage was also found to be independent of the nature of the electrodes.

3. Experimental observations

3.1. *EL variations with instantaneous voltage*

For studying the variation of EL current pulse in an ac cycle with the instantaneous applied voltage, the voltage developed across the series resistance (figure 1) is fed to Y_2 beam of another double beam CRO and the applied voltage is fed to its Y_1 beam. A 90° phase shift between the two waveforms showed that the current is purely displacement one. As the voltage is further increased the sinusoidal current waveform is distorted in a certain region to the right side of the current peak. No light output pulse is observed in the photomultiplier. On increasing the applied voltage further a large vertical single EL current pulse is seen on the right side of the current peak. The rms value of this voltage (read on a VTVM) is hereafter referred to as the threshold voltage. Simultaneously with this a large light output pulse is also observed in the photomultiplier. Figure 2 schematically shows the observed EL current pulses as well as light output pulses just above the threshold. Actual photograph of the EL pulses at potentials much above threshold is shown in figure 3. On increasing the applied voltage beyond the threshold the EL current pulse increases in height and shifts slightly to the left on the current waveform and a few more new pulses are created. These countable pulses develop into a cluster on further increase of voltage. As the number of current pulses increases the number of light output pulses also increases with increase in the microammeter deflection. It is observed that EL current pulse occurs exactly at the same phase instant as the light output pulse.

During the observations the trace of the current waveform at various applied voltages is noted. The height of the vertical current pulses and the microammeter reading are also noted. The x-distance of the first pulse from the zero of the sinusoidal

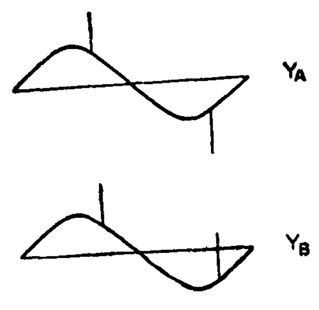

Figure 2. Sketch of the observed EL current and light pulse just beyond the switching distortion. Y_A—EL pulse on the current waveform. Y_B—EL light pulse as recorded by the photomultiplier. (observed waveform is due to 1 meg ohm resistance in the PM circuit).

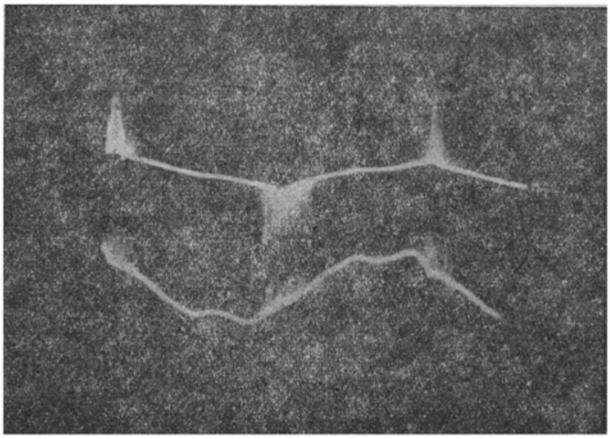

Figure 3. CRO photograph of the simultaneous current and light EL pulses.

Table 1. Variation of instantaneous EL onset voltage with peak value of the applied voltage.

Applied voltage	Peak voltage (v_p)	PM current in micro A	EL onset voltage (instantaneous) $v_t = v_p \sin \omega t$	Spread of the pulse (in milli second)
350 V	490 V	0·001 μA	469 V	Single pulse
370	518	0·005	468	1·16 ms
390	546	0·01	455	1·39
410	574	0·015	454	1·86
430	602	0·04	449	2·32
450	630	0·11	431	2·6
470	658	0·18	392	2·97
480	672	0.22	385	3·35
490	686	0·30	339	3·44
500	700	0·40	329	3·63

current trace is measured and from it the instantaneous value of the applied voltage corresponding to the onset of EL pulses was calculated. Table 1 gives representative set of observations for $PbTiO_3$ crystal from the above study.

3.2. *EL variation with applied field and frequency*

It has been observed that EL pulses are created at and certain well defined threshold applied voltage. Figure 4 shows the variation of EL light output (recorded by the microammeter) as a function of the applied voltage at several frequencies. It is observed that light output increases less rapidly at low voltages but increases more rapidly at high voltages. Dependence of EL light output on voltage may be described by the following relation

$$I = A(V - V_0)^b$$

where I is the EL light output intensity, A and b are constants, V_0 is the observed threshold voltage and V is the applied voltage. It is observed that there is a change in

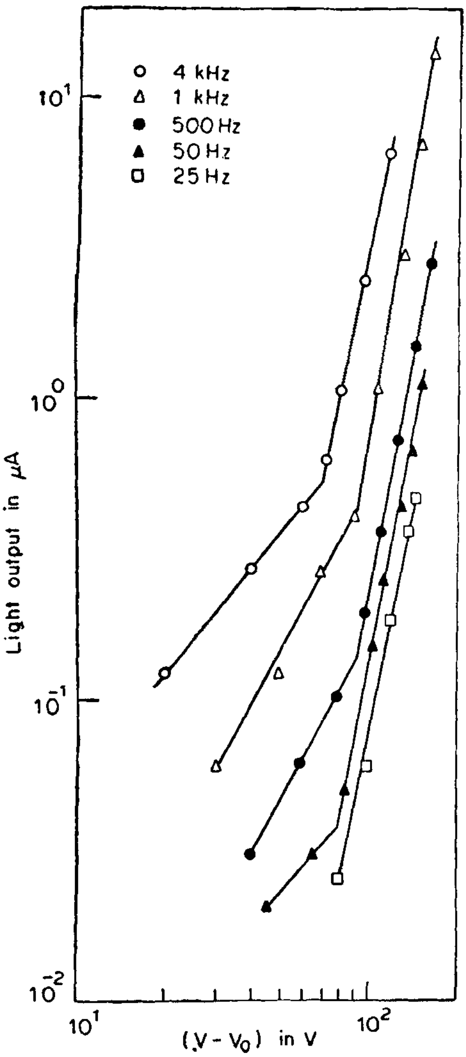

Figure 4. A plot of log $(v-v_0)$ vs log of the observed EL current intensity, I.

the value of b at higher voltages and the voltage at which this change occurs decreases with increase in the frequency of the applied voltage. It is also seen from table 2 that the threshold voltage necessary for the onset of EL decreases with increase in frequency of the applied voltage.

3.3. *EL variation with temperature*

A typical plot of EL onset voltage with temperature is shown in figure 5. It is seen that the threshold voltage at 50 Hz for EL onset decreases with increase in temperature of the crystal up to its Curie point (490°C). Further increase in temperature beyond the Curie point increases the threshold voltage. Near the Curie point the decrease in the threshold voltage is sharp.

Table 2. Variation of EL onset voltage with frequency.

Frequency	EL onset in V
25 Hz	370 V
60	350
150	345
500	330
1 kHz	325
2 kHz	320
4 kHz	310

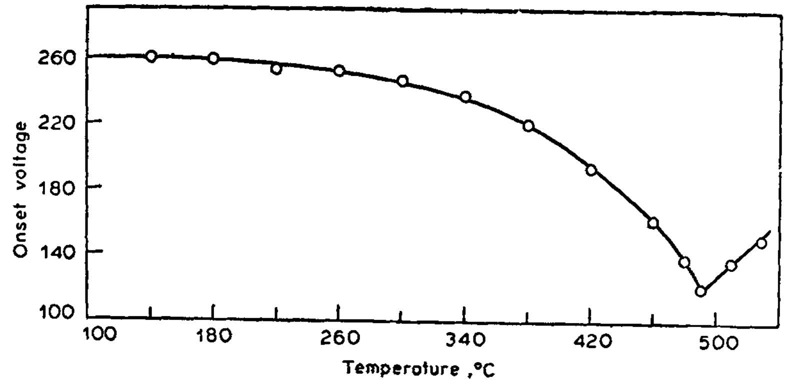

Figure 5. A plot of EL onset voltage with variation in temperature.

4. Discussion

4.1. *Amplitude dependence of EL*

From the current waveform and the readings from table 1 it is observed that the onset of EL takes place when the instantaneous voltage across the sample is 469 V and the peak value of the applied voltage is 490 V corresponding to 350 V rms. Just before the appearance of the EL pulses a small kink is seen on the distorted waveform at the same position at which a pulse appears subsequently. This clearly indicates that there is a sudden increase in current when the instantaneous applied voltage is slightly less than 469 V. It is significant to note that the EL current pulse is created when the instantaneous voltage across the crystal is 469 V while the peak value of the pd is 490 V and no EL pulses are observed when the peak applied voltage is between 469 V and 490 V corresponding to 335 V rms and 350 V rms. Thus it is clear that the onset of EL depend not only on the instantaneous value of the electric field E_i but also on the rate of change of E_i at that instant. Figure 6 schematically shows the variation of dE_i/dt at different rms voltages. It is seen from the figure that for the same instantaneous value E_i, dE_i/dt changes with change in the applied rms voltage. Hence it may be concluded that the onset of EL pulses depends on the optimum electric field E_0 and the optimum rate at which the switching of dipoles takes place which is proportional to dE_i/dt.

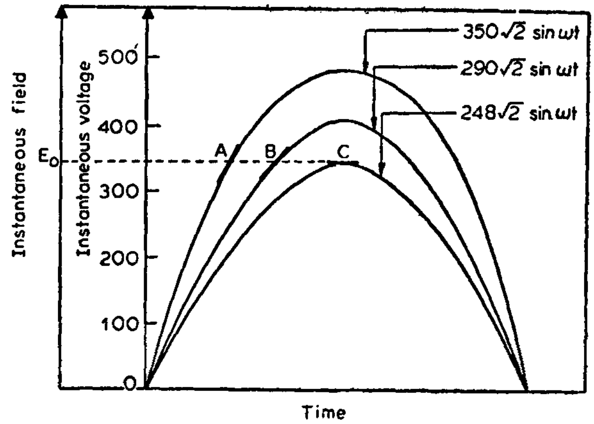

Figure 6. Schematic diagram showing variation of dE_1/dt at different applied rms voltages. Points A, B and C show change of slope at the same instant of time when the peak value of the applied voltage is varied.

It is noted that at the threshold voltage (and even above it) no EL pulses are observed when the voltage across the sample is changing from 469 V to the peak value and from the peak value (490 V) to zero. During the fall of voltage from the peak to 469 V both the conditions that $E_l > E_0$ and dE_l/dt being large are satisfied at certain points and yet no current pulses observed. This is mainly due to the fact that at the rising voltage EL pulses are created as the magnitude of the field and the rate of change of field is such that reversal of a certain number of domains takes place creating a large number of free charges. The reversal of spontaneous polarization (dielectric hysteresis) in $PbTiO_3$ has been observed by Gavrilyanhenco *et al* (1970), Remeika and Glass (1970) and very recently by Deshpande *et al* (1977). At the corresponding points on the other side of the peak of the waveform, the magnitude and the rate of change of field are suitable for reversal of domains and consequently for initiation of EL but now no further reversal of domains is possible as no domains which could be reversed by the combination of E and dE/dt are available and thus no initiating charges needed for EL breakdown are created during the fall of the voltage. Hence there is a non-symmetry in the distribution of pulses with respect to the voltage peak. This non-symmetry continues to exist for a much larger voltage when a large number of EL pulses are observed on the left side of the voltage peak and no pulse is observed on its right side. The non-symmetry is the direct consequence of the dependence of EL on the sudden reversal of domains which create a large concentration of initiating electrons needed for EL breakdown. At sufficiently high fields second or subsequent pulses are created due to the availability of other unswitched hard domains to be reversed at higher fields. The basic observations (i) dependence of EL pulses on dE_l/dt, (ii) non-symmetry of the pulses with respect to voltage peak and (iii) sharp vertically rising EL pulses of very short duration leads to the following EL mechanism.

At a sufficiently high applied field, mobile charges are created in the crystal due to dipole reversal. These charges under the action of the field undergo exciting and/or ionizing collisions with the atoms or molecules while passing through the crystal and photons are created. These photons when impinge on the instantaneous cathode release secondary electrons by the γ_p process. These secondary electrons form further avalanches in the dielectric and the process repeats itself at a very fast rate. Thus there is a self maintained discharge in the dielectric maintained by the γ_p secondary process. The enormous number of positive and negative charges produced by the self maintained discharge in a very small duration of time creates an opposing field which reduces the applied field quenching the discharge. Hence as required by the above mechanism the observed current pulses are of a very small duration and large height. When the electric field is slightly less than the threshold field the initiating electrons produce only Townsend avalanches in the bulk of the dielectric and this gives rise to the observed switching distortion. If the electric field is much smaller than this, switching of the dipoles gives rise to only displacement current and there is no current amplification due to Townsend avalanches as they do not occur, and therefore the current waveform remains sinusoidal.

4.2. *Frequency dependence of EL*

The variation of EL light output with applied field (figure 4) shows a discontinuity at high pd. At high fields the rate of change dE_l/dt is much higher and therefore dipole switching will be faster than at low fields (see figure 6). A study of mechanism of electrodeless discharge in a gas by Kher and Kelkar (1961) and Kher and Ayachit (1964) has shown that a small duration pulse of large height requires a very fast secondary process like the γ_p mechanism for the self maintained discharge during the pulse. When the applied peak voltage is 390 V rms, a cluster of pulses which cannot be resolved is observed. Such a cluster extends up to the peak of the voltage on increasing the applied voltage further. In any particular half cycle there will be a discrete number of sharp pulses close to each other. But in general the pulses will not arise exactly at the same phase instant at various half cycles. Hence the pulse pattern observed on the CRO will be that of an average effect of unsynchronized pulses leading to the observed cluster which increases in duration with applied voltage. The break in the log I vs log $(V-V_0)$ curve and the cluster formation for longer duration occur at nearly the same applied voltage. It may be imagined at this stage that the positive ions (mobility lower than that of electrons) which are left free by the avalanching electrons on striking the instantaneous cathode emit secondary electrons. Electrons produced by the secondary γ_i mechanism help in building further avalanches and the process is repeated leading to a γ_i self maintained discharge. These secondary electrons due to γ_i process along with the secondary electrons due to γ_p process create a very large number of avalanches and helps in increasing the number of photons in the bulk. Thus the break indicates that both the secondary processes are active at high fields and in effect increases rapidly the EL light output.

Increase in frequency reduces the threshold voltage. For a particular E_l the rate dE_l/dt changes with ω (becomes higher as ω increases). The dipoles are switched at a faster rate and the released charges are swept away at an increasing rate. Thus the threshold and the break in $(V-V_0)$ curve shift to a lower value with the increase in frequency. So also the EL light output increases at a faster rate with increase in frequency. Table 2 summarizes the observations of EL dependence on frequency.

4.3. *EL onset variation with temperature*

In general the breakdown voltage increases with increase in temperature of the solid.

In contrast to this the variation of EL onset voltage with temperature shows a decrease with increase in temperature. It is well known that with increase in crystal temperature the coercive field of a ferroelectric crystal decreases. Decrease in coercive field will ease the domain switching. Hence at higher temperatures increase in the number of switching domains at the same initial applied voltage increases the availability of free charges necessary for avalanche breakdown by the γ_p process and thus the threshold voltage decreases with increase in temperature. This decrease continues till the Curie point of the crystal is reached where the coercive field is zero and near the Curie point the threshold voltage will be minimum. Above the Curie point, the threshold voltage increases with increase in temperature which is a similar characteristic of the avalanche breakdown. In normal solids this characteristic is due to decrease in mean free path of the charges at high temperature. In ferroelectrics the increase in the threshold field beyond the Curie point is due to an entirely different cause. Above the Curie point the application of the electric field transforms the crystal from the cubic to the tetragonal phase (Roberts 1952: Deshpande *et al* 1977). Below the Curie point the threshold voltage is higher than that at the Curie point. Hence this electrically forced distortion will increase the threshold voltage. The forced distortion decreases with increase in temperature. To produce the same distortion the applied field has to be increased. Thus the threshold voltage increases beyond the Curie point.

5. Conclusions

The characteristics of EL in $PbTiO_3$ lead to the following conclusions. (i) The non-symmetry in the distribution of EL current pulses is a direct consequence of the switching of domains, (ii) the distortion in the current waveform is connected with Townsend avalanches as well as the space charge formed within the dielectric, (iii) EL onset depends on the rate of change of electric field at the threshold and (iv) EL is originated in the bulk rather than in surface layers due to the avalanche breakdown in the crystal assisted by the secondary γ_p and γ_i processes.

References

Anliker M, Brugger H R and Kanzig W 1954 *Helv. Phys. Acta* **27** 99
Barrett H H 1964 *J. Appl. Phys.* **35** 1420
Bhide V G, Gondhalekar R T and Shringi S N 1965 *J. Appl. Phys.* **36** 3825
Bhide V G and Gondhalekar R T 1966 *J. Appl. Phys.* **37** 810
Bogatko V V, Guro G M, Ivanchik I I and Kovtonyuk N F 1969 *Sov. Phys. Solid State* **10** 1640
Brezina B and Fotchenkov A A 1964 *Czech. J. Phys.* **B14** 21
Callabay D R 1965 *J. Appl. Phys.* **36** 2751
Callabay D R 1966 *J. Appl. Phys.* **37** 2295
Chynnoweth A G 1956 *Phys. Rev.* **102** 705
Desphande D A, Bagree K R, Patki B A and Kher V G 1977a *Indian J. Pure Appl. Phys.* **15** 612
Deshpande D A, Bagree K R, Patki B A and Kher V G 1977b *Indian J. Pure Appl. Phys.* **15** 477
Fang P H 1963 *J. Phys. Soc. Jpn.* **18** 1968
Fatuzzo E and Merz W J 1961 *J. Appl. Phys.* **32** 1685
Gavrilyachenko V G, Spinko R I, Martynenko M N and Fesenko E G 1970 *Sov. Phys. Solid State* **12** 1203

Harman G G 1958 *Phys. Rev.* **111** 27
Ishibashi Y and Stadler H L 1968 *J. Appl. Phys.* **39** 5802
Kanzig W 1955 *Phys. Rev.* **98** 549
Katpatal A G and Deshmukh K G 1972 *J. Phys.* **D5** 1937
Katpatal A G and Deshmukh K G 1976 *Pramana* **7** 95
Kawabe K, Yematsu S and Inuishi Y 1964 *Electr. Eng. Jpn.* **84** 45
Kher V G and Kelkar M G 1961 *J. Sci. Ind. Res.* **B21** 293
Kher V G and Ayachit V G 1964 *Physica* **30** 702
Kher V G, Bagree K R, Patki B A and Deshpande D A 1978 *Indian J. Pure Appl. Phys.* (in press)
Merz W J 1956 *J. Appl. Phys.* **27** 938
Remeika J P and Glass A M 1970 *Mat. Res. Bull.* **5** 37
Roberts S 1952 *Phys. Rev.* **85** 925
Schoijet M 1964 *Phys. Status Solidi.* **4** 639
Ueda I, Takiuchi M, Ikegami S and Sato H 1964 *J. Phys. Soc. Jpn.* **19** 1217
Williams R 1965 *J. Phys. Chem. Solids* **26** 399