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Secondary electron emission of doped PZT ceramics

A. V. DIXIT, N. R. RAJOPADHYE, S. V. BHORASKAR
Department of Physics, University of Poona, Pune-411 007, India

Secondary electrom emission yield (δ) and the surface work function values (ϕ) were measured for lead zirconium titanate (PZT) doped with lanthanum, strontium, and niobium. The single pulse method was used in LEED/Auger geometry for measuring the secondary electron emission yield δ while the retarding potential technique was employed for measuring the work function. In view of the application of ceramics as continuous dynodes in electron multipliers, the secondary electron emission and electical conductivity data is analysed for reduced PLZT ceramics. Maximum δ of 2.7 was found to remain unchanged after reduction of PLZT. Dionne's equation was used as a basis for analysis of secondary electron emission measurements to estimate escape depth and emission probability.

1. Introduction

There is a growing interest in materials which exhibit significant secondary electron emission (SEE) yield (δ) for various applications. A knowledge of SEE measurements is useful in various fields such as scanning electron microscopy and electron multipliers.

Electron multipliers [1] form the useful particle detectors, widely used in space applications and analytical instruments, due to their small size, light weight and solar blindness in contrast to the conventional photomultiplier tubes. Different kinds of multiplier such as parallel plate electron multiplier, single channel wide bore and microchannel plates (Channeltron) are possible. Basically the device consists of an electron emissive material functioning as a continuous dynode. The charging in these devices is avoided by making use of an appropriate semiconducting (10^7 to $10^9\,\Omega$ cm) emissive dynode material. Presently electron multipliers are commercially produced using PbO glasses. Many new materials can, in fact, be used as continuous dynodes, the potentials of which have not been very well explored on large scale. Ceramic materials are found to be convenient for such applications [2], since they can be easily moulded and extracted in the desired form. Secondly, their properties can be easily changed by changing the composition and constituents of the solid solution. Lead zirconium titanate (PZT) is one of the ceramics which we propose for such application.

In this paper an attempt is, therefore, made to characterize the electronic properties and electron emissive properties of PZT. It is a versatile piezoelectric ceramic widely used as modulating medium in optical modulators [3] and other piezoelectric devices.

PZT in its original form is a highly insulating ceramic ($10^{14}\,\Omega$ cm) and is not suitable as a continuous dynode. It was, therefore, modified to suit the requirements (10^7 to $10^9\,\Omega$ cm) by doping with various dopants and the process of reduction. The effect of these on the secondary emission behaviour is reported in the present paper. Since the work function is an important surface parameter at lower energies and plays a major role in secondary emission process, its measurements were simultaneously recorded. SEE yield δ was measured by single pulse method incorporating a LEED/Auger geometry, while a diode gun assembly was used for the *in situ* measurements of work function at ultra high vacuum.

The variation of SEE yield δ with primary energy (E_P) reveals much information about the electronic properties of emissive materials. Though PZT is widely studied for its piezoelectric applications the electronic properties are rarely studied. In the present context the yield curves were used to estimate various physical parameters by using Dionne's [4, 5] equation. This is based on the assumption that the SEE mechanism consists of two consequent processes; "production" and "emission". Accordingly, the controlling parameters namely the band gap, penetration depth, escape depth, work function and emission probability were included in the expression. The experimental values of maximum SEE yield δ_{max}, energy at which maximum yield occurs E_{pm} and work function ϕ along with the penetration depth, were used to estimate the escape depth and emission probability of doped PZT samples. The results are discussed with the help of electrical conductivity measurements.

2. Experimental details

PZT crystallizes in the perovskite structure. The structure may be described as a simple cubic unit cell with large cation [A] on the corners, a small cation [B] in the body centre and oxygen (O) in the centres of the faces. Its structural and piezoelectric properties are discussed by Jaffe *et al.* [6].

2.1. Preparation method

PZT was prepared adopting the conventional powder method. Samples were prepared in the form of circular pellets of thickness 0.15 cm. Reagent grade oxides

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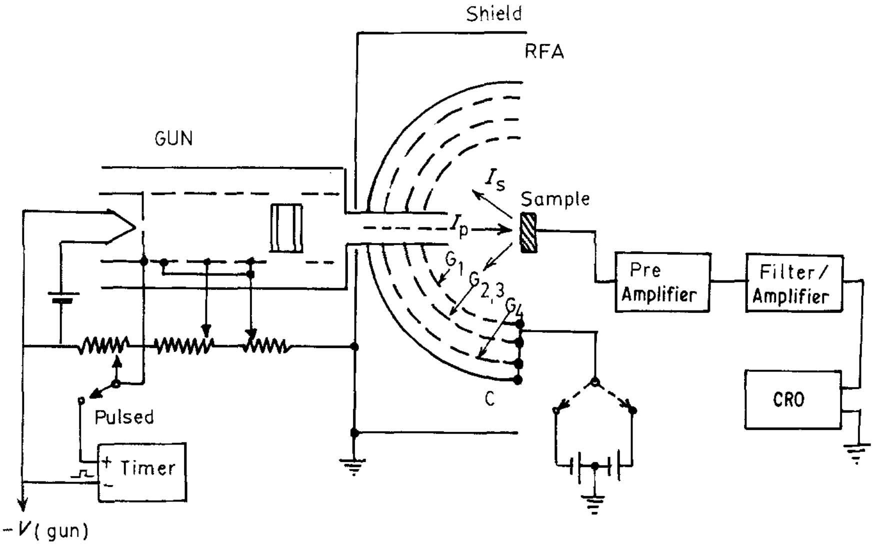

Figure 1 Schematic of the experimental set up used in single pulse method for SEE measurement. Retarding field analyser (RFA) with integral electron gun is shown. A pulse was applied to the extracting grid (G1) of the gun. The pulsed electron current from the sample was monitored on the oscilloscope when the collector was switched to ± 50 V.

PbO, ZrO_2, TiO_2 and the appropriate oxide of the dopant elements were mixed in suitable proportion by weight to obtain

$$Pb_{0.95}D_{0.05}(Zr_{0.53}Ti_{0.47})O_3$$

where D indicates the dopant. After compressing, the pellets were sintered in air at about 1290 to 1300° C for 90 min. Loss of volatile PbO was prevented by adding excess amount of PbO while preparing the batch. Weight losses were always held below 1%. Density of the final product was $7.6 \times 10^{-3}\,kg\,m^{-3}$ which was in agreement with the theoretically calculated density [6]. X-ray diffraction analysis of these pellets showed the typical phase pattern for PZT.

2.2. SEE and work function measurements

All measurements were undertaken in a stainless steel ultra high vacuum system specially designed for SEE and work function measurements and pumped by a sputter ion pump. Samples were mounted on a rotatable sample manupulator with a provision for heating the samples up to 200° C.

The schematic of the set-up used for SEE yield measurements is as shown in Fig. 1. The single pulse method was used to avoid any charging effect during the measurements. It consisted of 4 grid LEED optics, with an integral electron gun, modulated to give pulsed electron beam. The pulser was designed to give an "ON" time varying from a few microseconds to milliseconds and "OFF" time from 0.5 seconds to a few minutes. This became necessary particularly for thick ceramic pellets (~ 1.5 mm) which required a long time to disharge. In these experiments a pulse width of 10 sec with off period of 2 min was used for modulating the electron beam. The primary pulsed electron current was of the order of 1 nA. The primary and secondary electron pulses were measured on the cathode ray oscilloscope (CRO) after proper amplification and switching the collector voltage, respectively, to negative and positive 50 V. However, primary current could also be measured with the help of a Faraday cup placed exactly at the position of one of the samples. Secondary electron current I_s was determined from the measure of the target current I_T instead of measuring it directly on the collector and thereby improving the accuracy of measurement [7]. Secondary yield δ is then given by

$$\delta = I_s/I_p = (I_p - I_T)/I_p = 1 - I_T/I_p \quad (1)$$

In the case of the samples, for which the target current I_T and the primary current I_p are in reverse directions, δ is always greater than 1.

2.3. Work function measurement

The work function measurements were performed by the retarding potential technique, which refers to the modified diode method, using a low energy electron beam collimated by an axial magnetic field. The low energy electron gun is similar to that described by Klauser and Bas [8] and the schematic of the experimental details is shown in Fig. 2. The beam energy was kept at 8 eV and a typical beam current of 10^{-6} A was measured on the target when no retarding voltage applied. The accuracy in measuring the work function was obtained to be ± 0.1 eV.

3. Results and discussion

3.1. Electrical conductivity measurements

As it was mentioned earlier, for an efficient continuous dynode, it is desirable to maintain the resistivity at 10^8 to $10^9\,\Omega\,cm$ for avoiding the surface charging during emission process. Keeping this in view the PZT samples, with different dopants, were subjected to a process of reduction. The effects of this process on the electrical resistivity measured at room temperature is indicated in Table I. It is interesting to note that the resistivity in lanthanum doped PZT (PLZT) and niobium doped PZT have decreased considerably. Out

TABLE I Resistivity changes after reduction in doped PZT samples

Resistivity $\pm 50\,\Omega\,cm$ at 25° C	PZT	PZT(Nb)	PZT(Sr)	PLZT
Before reduction (Ωcm)	1.5×10^{12}	2.3×10^{12}	1.2×10^{11}	1.2×10^{12}
After reduction (Ωcm)	1.8×10^{12}	3.3×10^{6}	2×10^{11}	1×10^{7}

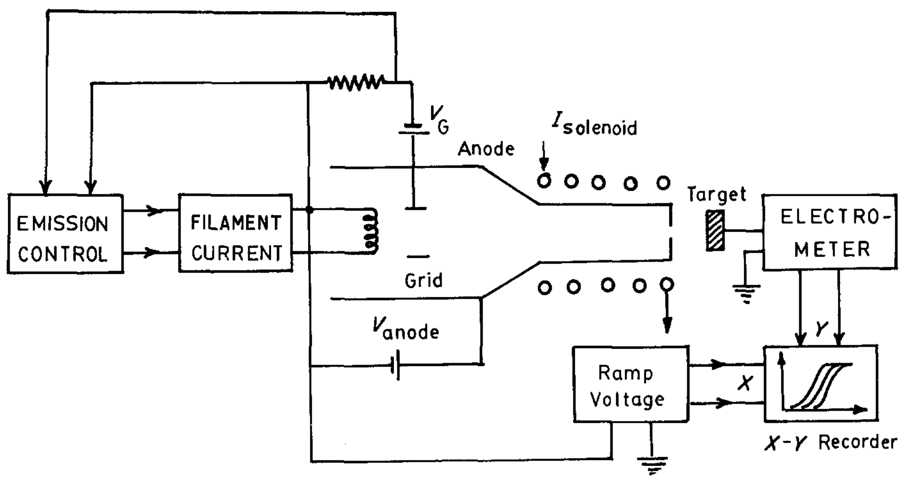

Figure 2 Schematic of the low energy electron gun for work function measurements using retarding potential technique. Current sensed by the grid is used for controlling the electron emission current. V_{anode} defines the beam energy and retarding ramp voltage is applied between a target and the filament.

of these the former was chosen for further analysis, as it is also an important piezoelectric and optoelectronic material and, thus, is manufactured on a large scale.

From the thermoelectric power measurement the virgin PLZT samples were found to be p-type and after reduction they showed n-type behaviour. The first phenomenon, in the process of understanding the effects of reduction, is the loss of oxygen when the PLZT sample is heated in vacuum. In the present experiments the pellets were sealed off inside closed capsules and were then kept in a hot zone at 500° C for a few hours. At this temperature there may be two possibilities. Oxygen can migrate towards the surface and/or lead can evaporate from the surface. However lead loss would result in a p-type semiconductor which has not happened and thus only oxygen vacancies can explain the observed fact. This is also supported because the reaction was observed to be reversible in the sense that the black conducting reduced PLZT returned to a pale yellow non-conducting sample when heated in air above 250° C for about 4 h. The role of oxygen vacancies on increasing the conductivity of PZT samples has also been observed by Dih and Fulrath [9] in their scandium doped PZT.

The reduced PLZT contains some missing O^{2-} ions and in order to have the total electrical neutrality it requires two additional electrons for each mising O^{2-} ion. According to Aitchinson's [10] explanations in such reduced metal oxides the valency of the metal ion should reduce and create additional impurity levels near the conduction band edge, which are ionizable at room temperature. Similar effects are routinely reported for reduced TiO_2 where the valence change occurs with Ti^{4+}. It has been well established [11] that in PLZT La^{3+} ions in all probability, enter sites occupied by Pb^{2+} ions, and excess charge of the trivalent ions is compensated by one lead vacancy for every two La^{3+} ions in the ABO_3 type PZT lattice. This is expressed by the chemical formula

$$Pb^{2+}_{1-x}[\ ]_{x/2}La^{3+}_{x}(Zr^{4+}_{0.5}, Ti^{4+}_{0.5})\ O^{2-}_{3}$$

where [ ] represents the vacancy.

In reduced PLZT the valence change may in principle occur with either lead, zirconium or titanium and may be expressed with the formulae

$$Pb^{2+}_{1-x-2y}[\ ]_{x/2}Pb^{1+}_{2y}\ La^{3+}_{x}(Zr^{4+}_{0.5}Ti^{4+}_{0.5})O^{2-}_{3-y}$$

$$Pb^{2+}_{1-x}[\ ]_{x/2}La^{3+}_{x}(Zr^{4+}_{0.5-2y}Zr^{3+}_{2y}Ti^{4+}_{0.5})O^{2-}_{3-y}$$

$$Pb^{2+}_{1-x}[\ ]_{x/2}La^{3+}_{x}(Zr^{4+}_{0.5}Ti^{4+}_{0.5-2y}Ti^{3+}_{2y})O^{2-}_{3-y}$$

In any of these cases the reduced PLZT can behave like an n-type semiconductor with excess electrons.

3.2. Work function measurements

The anode current variations with retarding field is shown in Fig. 3. Here polycrystalline gold was used as

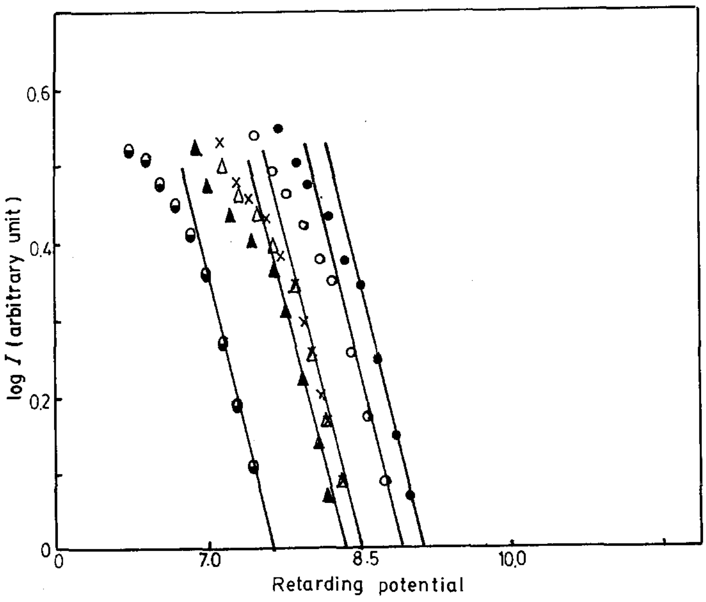

Figure 3 Logarithmic plots of I_t against retarding voltage for the PZT and its doped species. The parallel shift with respect to gold on the voltage axis gives the work function. (ϕ_{gold} = 4.68 eV). (◒) PLZT, (x) reduced PLZT, (●) Nb doped PZT, (○) gold, (△) Sr doped PZT, (▲) PZT.

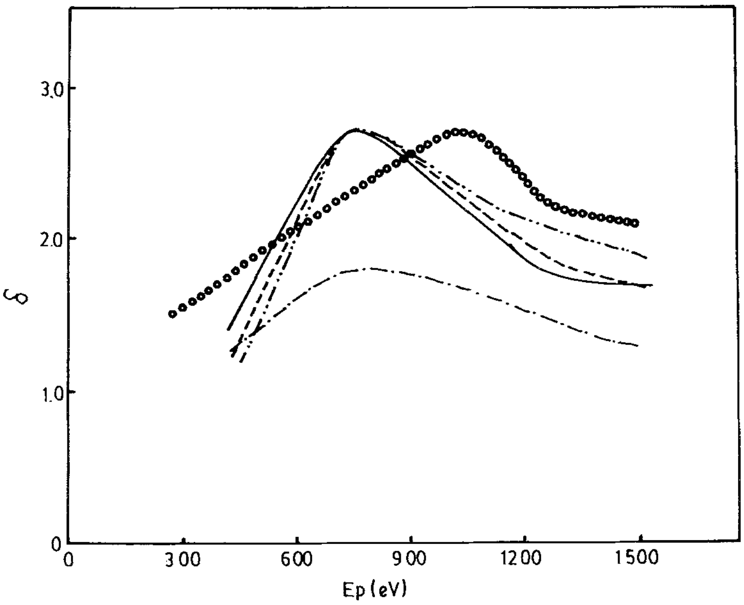

Figure 4 Variation of SEE yield (δ) with primary electron energy E_p for different samples. Maximum yield δ_m is 2.7 for all the samples except strontium doped PZT. E_{pm} for reduced PLZT is shifted by 300 eV with respect to PLZT. (-···-) plain PZT, (○) reduced PZT, (– –) Nb doped PZT, (——) La doped PZT, (-·-) Sr doped PZT.

a reference sample and the relative values of work functions of the various ceramics are indicated in the same figure. Work function in PLZT is seen to decrease as a result of reduction process. This is in agreement with the expectation for an n-type semiconductor. For PZT doped with lanthanum, the work function has increased compared to virgin PZT while for PZT–Nb and PZT–Sr it has decreased. This can be understood more clearly by looking at the shift of the Fermi level by doping with donor [Nb and Sr] or acceptor [La] type of impurities. Similar n-type and p-type behaviour of PZT with the above dopants are reported [9] earlier.

3.3. Secondary electron emission measurements

Fig. 4 shows the variation of secondary yield δ of PZT samples, with primary energy E_p. The maximum yield δ_m for PZT–Sr is seen to be 1.8 while for others it is 2.7. The trend of the curves have almost remained identical for all the samples although E_{pm} is shifted towards the higher energy (1.05 keV) for the reduced PLZT. These values of E_{pm} and δ_m are used in Dionne's equation for estimating other physical parameters. Similar calculations using Dionnes's equation are reported by Khairi *et al.* [12] for few insulators and semiconductors.

Dionne's equation for secondary yield as a function of primary energy E_p can be written as

$$\delta = \left(\frac{B}{\xi}\right)\left(\frac{n\alpha_p}{\alpha_s}\right)^{1/n} (\alpha_s d)^{1/n-1} [1 - \exp(-\alpha_s d)] \qquad (2)$$

where $\xi = E_g + X$. E_g is the band gap and X is the electron affinity. For insulators and semiconductors this can also be obtained as $\xi = \phi + E_g/2$ where ϕ is the work function, B is the emission probability and the parameters α_p and α_s are the absorbtion coefficients of primary and secondary electrons respectively. The term d is the penetration depth corresponding to primary energy E_p and n is the exponent of energy loss power law, which is taken as 1.4 for all the calculations.

The range (or the penetration depth) can be evaluated from Young's [13] energy range relationship applicable for primary energies less than 7.5 keV as

$$d = [1/n\alpha_p]\, E_p^n \qquad (3)$$

where d is in centimetres and E_p is in keV. This can also be defined [14, 15] as

$$d = 2.6 \times 10^{-6}[A(Z_{\text{eff}})/\varrho(Z_{\text{eff}})]\, E_p^n \qquad (4)$$

where ϱ is in g cm^{-3} and

$$Z_{\text{eff}} = \sum n_i Z_i^2 \Big/ \sum n_i Z_i \qquad (5)$$

where n_i is the number of atoms in the compound of species i having atomic number Z_i, $A(Z_{\text{eff}})$ is the atomic weight of the element having atomic number Z_{eff}. From this α_p can be expressed as

$$\alpha_p = 0.4 \times 10^6(\varrho/n)[Z_{\text{eff}}/A(Z_{\text{eff}})] \qquad (6)$$

Taking the density as 7.6 g cm^{-3} for PZT and its doped samples, we can estimate α_p using Equation 6. However in the case of reduced PLZT the density is taken 1.1 times larger than PLZT, since the total amount of lead is increased in the surface region as was observed from our X-ray photoelectron spectroscopy (XPS) analysis. Exact measurements of density becomes difficult because the change takes place only in the surface layer of a few micrometres.

Considering these α_p values, Equation 3 gives a set of energy range relations which is used to calculate d (i.e. d_m) for each E_{pm} values. Now to estimate the escape depth we recall Equation 2 from which it can be shown that the yield is maximum at energy E_{pm} such that the term $\alpha_s d_m$ equals 2.14. This gives us α_s for each sample. The escape depth of secondaries is often required which is defined as $\lambda_s = 1/\alpha_s$ and the corresponding values are listed in Table II.

Substituting these α_p, α_s and experimental δ_m values we get (B/ξ) in (keV)$^{-1}$. The bandgap (E_g) in PZT and its doped species were taken to be 3.1 eV which was obtained from our measurements of photoconductivity. ξ values are calculated using this band gap and experimentally observed ϕ values. Finally we can work out B from the (B/ξ) obtained above. These are listed in Table II. It is worth mentioning here that in

TABLE II Values of $\alpha_p[10^6(\text{keV})^n\,\text{cm}^{-1}]$, λ_s(nm), ϕ(eV), ξ(eV), δ_m, E_{pm}(keV), B/ξ(keV^{-1}) and B for PZT and its doped species

	α_p ± 0.01	λ_s ± 0.1	ϕ ± 0.01	ξ ± 0.01	δ_m ± 0.1	E_{pm} ± 0.25	B/ξ ± 0.4	B ± 0.002
PZT	0.89	2.48	5.35	6.9	2.7	0.750	8.7	0.06
PZT(Nb)	0.89	2.50	4.59	6.14	2.7	0.750	8.7	0.053
PZT(Sr)	0.89	2.50	5.19	6.74	1.8	0.750	5.8	0.039
PLZT	0.89	2.50	6.09	7.6	2.7	0.750	8.73	0.0663
Reduced PLZT	0.98	3.64	5.19	6.74	2.7	1.050	6.2	0.042

Equation 2 three-dimensional scattering has been neglected. For the same reason care should be taken while using the above values of B.

From Table II it can be seen that the effect of doping PZT is to change the value of ξ which represents the ionization energy. However this seems to be insufficient to alter δ_m by an appreciable magnitude. Maximum value of ξ is obtained for PLZT which can be correlated to the increase in ϕ as discussed in section 3.2.

The yield data shows a slightly inferior value for δ_m in PZT(Sr) which is also reflected in the relative B value. This is difficult to explain as there is no clue to this effect from any other experiment.

In the case of reduced PLZT, E_{pm} is shifted towards the higher energy side which has resulted in an apparent increase of escape depth. This should in principle lead to increase in δ_m value. However, from the present data it remained equivalent to that of unreduced PLZT. There may be several possibilities for this to occur. One of which may be understood as possible influence of donor levels on its secondary yield and escape mechanism. This includes the production of secondaries on their way to the surface by ionizing the donors and producing the tertiaries.

This phenomenon would first lead to increase the effective value of escape depth by adding the escape depth of tertiaries into the escape depth of secondaries. As a consequence of this effect in the reduced PLZT, one may expect E_{pm} to shift towards the higher energy side and overall yield to increase. However the present results do not indicate any increase in the yield although E_{pm} shows a shift as expected. This behaviour may be explained on the basis of an increased number of scattering centres, present in the path of the secondaries, due to donor impurities as well as increased amount of lead atoms on the surface. In other words the effect of increase in escape depth is compensated by the process of scattering keeping δ_m unaltered. Finally the combination of all these phenomena lead to the resultant yield energy curve as observed in Fig. 4. From this it appears that the process of tertiary production is effective only on higher primary energies as a result of which the yields at lower energies are governed only by the scattering mechanism.

The maximum yield in PZT (Nb), PLZT and virgin PZT are identical in magnitude and position. This is also clarified by the constancy of λ_s, within experimental error, for these samples indicating that doping has not influenced the escape mechanism. Although the δ_m has remained constant, from the point of utility PZT (Nb) seems to be useful as there is a change in the resistivity of this ceramic by reduction. This system is proposed to be analysed in our future work. The experimental results presented here for various ceramics, confirm that they can be used as potential secondary emitters. Especially our results with the reduced PLZT indicate that this material fulfills almost all the requirements for a suitable continuous dynode in electron multiplier. It is a chemically stable material with δ_m more than 2, and is produced on a large scale giving identical properties. The only drawback which can be realized is the high electron energy (>750 eV) required for producing sufficiently high yield. This needs a large potential to be applied across a dynode for making it effective. We have, in fact, semiempirically calculated the expected gain for a parallel plate electron multiplier. We consider a set of parallel plates with 36 mm length (L) and 15 mm width separated apart by 0.04 cm so that an optimum L/D ratio of 90 is obtained. By applying a d.c. voltage of 6 kV across this set of multiplier a gain of $\sim 10^5$ is calculated using the relations given by Anderson and Berg [1]. This gives fairly good chances for reduced PLZT to be used in electron multipliers. More effective multipliers can be produced by obtaining higher yield at lower energies, which is being attempted.

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References

1. L. P. ANDERSON and S. BERG, *J. Phys. E, Sci. Instr.* **12** (1979) 1015.
2. T. MASUOKA, *Rev. Sci. Instr.* **48** (1977) 1284.
3. G. MARIE, *Philips Res. Rep.* **22** (1967) 110.
4. G. F. DIONNE, *J. Appl. Phys.* **46** (1975) 3347.
5. *Idem, ibid.* **44** (1973) 5361.
6. B. JAFFE, R. S. ROTH and S. MARZULLO, *J. Res. NBS* **55** (1955) 239.
7. V. E. HENRICH, *Rev. Sci. Instr.* **44** (1973) 456.
8. S. J. KLAUSER and E. B. BAS, *J. Phys. E, Sci. Instr.* **12** (1979) 841.
9. J. J. DIH and R. M. FULRATH, *J. Amer. Ceram. Soc.* **55** (1972) 230.
10. R. E. AITCHISON, *Aus. J. Appl. Sci.* **5** (1954) 10.
11. K. H. HARDTLE and D. HENNINGS. *J. Amer. Ceram. Soc.* **55** (1972) 230.
12. I. KHAIRI, K. I. GRAIS and A. M. BASTAWROS, *J. Appl. Phys.* **53** (1982) 5239.
13. J. R. YOUNG, *ibid.* **28** (1957) 524.
14. I. M. BRONSTEIN and A. N. PROTSENKO, *Rad. Eng. Elect. Phys.* **15** (1970) 677.
15. *Idem, ibid.* **6** (1971) 347.

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