Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 685–688
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Electron emission from $Pb_{0.88}La_{0.08}(Zr_{0.65}Ti_{0.35})O_3$ ferroelectric ceramics

Lei Liu, Zhuo Xu *, Yujun Feng, Guoqiang Zhang, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

Available online 29 September 2007

Abstract

The electron emission characteristics of PLZT 8/65/35 ferroelectric are studied. High current density has been obtained from PLZT 8/65/35 ferroelectric cathode. The source of the disturbance in the experiment is discussed and several methods to reduce the disturbance are proposed. It is discovered that there is a voltage threshold, and the electron emission will not occur until the amplitude of the pulse exceeds the threshold. Moreover, there are two current peaks in the FE electron emission curves, the primary peak remains stable in location and intensity, while the secondary one shows instability during repeating experiments.

Keywords: Electron emission; PLZT; Ferroelectric cathode

1. Introduction

Electron emission from ferroelectric materials during the switch of spontaneous polarization was first noted by Miller and Savage in 1960 [2] and early experimental results of that period were mainly weak electron emission (varying from 10^{-12} to 10^{-17} A/cm^2) [1] from some ferroelectrics like $LiNbO_3$ and PbG_3O_{11}. Later on strong electron emission from PZT and PLZT ferroelectrics was detected, and the reported value varied from several A/cm^2 to tens of A/cm^2 [1,3,5,7]. Since then many groups [4] have studied strong electron emission mechanisms. Compared with traditional cathodes, ferroelectric cathodes have several advantages. For example, there is no need for heating during activation, low vacuum requirement and low cost, easy manufacturing, they can be activated without external accelerated fields, and have large electron emission density. Possessing these advantages mentioned above, ferroelectric cathodes have been one of the most promising cathode materials in generating high current density.

Till now, the main explanation for ferroelectric emission is a theory about fast polarization switch [6], which is shown in Fig. 1. And this allows the usage of one pre-poled sample by applying a high-voltage pulse to its rear side which is covered by full electrode, and making its front side which is covered by striped electrode grounded. Then polarization reversal occurs, giving rise to the generation of uncompensated polarization charge at the gridded surface of the ferroelectric [3,4] and the uncompensated polarization charge is responsible for a intense electric field which then causes the electron emission from the bulk of the ferroelectric. Many electron emission density results were received from PLZT ceramics, which were regarded as intense electron beam sources with high brightness, and with easy spontaneous polarization switching. In this paper, it is discovered that there is a voltage threshold, and electron emission will not take place until the amplitude of the pulse exceeds this threshold. Moreover, the corresponding electric field of this voltage threshold is much bigger than coercive field in value, and some suppositional explanation will be discussed later.

2. Experimental procedure

In this experiment, PLZT 8/65/35 with a general formula of $Pb_{0.88}La_{0.08}(Zr_{0.65}Ti_{0.35})O_3$ was synthesized from high-purity ingredients, namely, PbO, ZrO_2, TiO_2, and La_2O_3. The sample was prepared by the conventional mixed oxide method. Ball-milled powders were calcined, pressed, and sintered at 1260 °C for 2.5 h. Then the sintered pellets with a diameter of 20 mm were cut to a thickness of 1–2 mm. Fig. 2 shows the electrode configuration for two sides of the sample, and the electrode stripes and exposed stripes in the front side had widths of 600 μm and 300 μm, respectively.

* Corresponding author.
E-mail address: xuzhuo@mail.xjtu.edu.cn (Z. Xu).

0272-8842/$34.00 © 2007 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2007.09.050

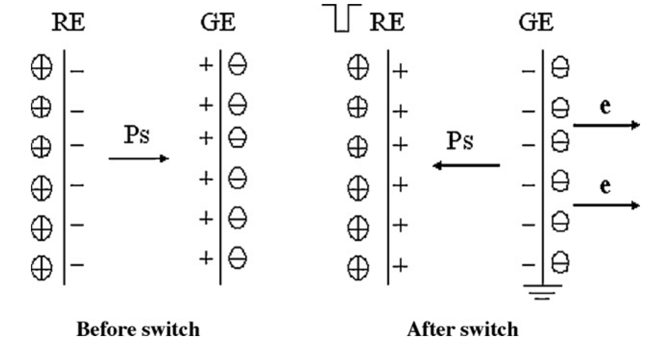

Fig. 1. Charge distribution before and after polarization reversal (RE, rear electrode; GE, gridded electrode).

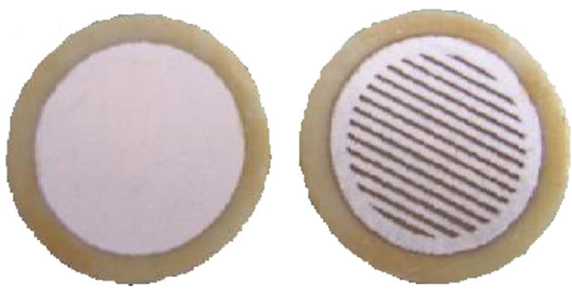

Fig. 2. Electrode (Ag) configuration on rear (left) and front (right) sides of the sample.

Fig. 3 shows the equivalent circuit for generating a negative high voltage pulse in this experiment. The rise time of the high voltage pulse could be easily controlled by the value of R_f. The schematic diagram for this FE emission experiment is shown in Fig. 4 where a negative high voltage pulse was applied to the rear side of the sample and the front side was grounded. The experiment was carried out under vacuum condition with a vacuum degree of 10^{-3} Pa. Graphite electrode was used to collect the emitted electron with a distance of 3–15 mm from the emitted surface of the sample, and then emission current was measured via a current view resistor. For detecting the narrow pulsed current signal, many methods have been applied to avoid or decrease the inductance effect. For example one non-inductive resistor was used for this experiment, and this resistor was fixed inside one iron box as a shield. In this way, current passing the resistor and the shield box were in opposite

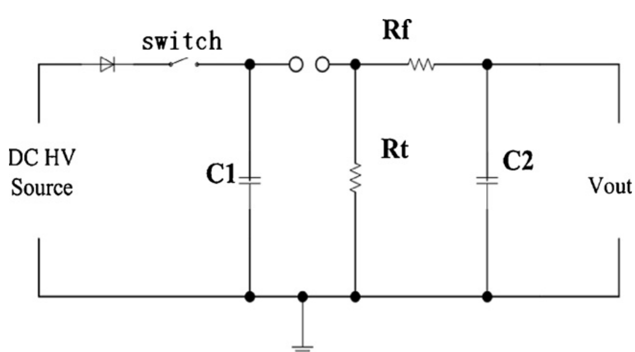

Fig. 3. Equivalent circuit for generating negative high voltage pulse in this experiment (R_t, tail resistor; R_f, forward resistor; C_1, charging capacitor (10^{-2} μF); C_2, adjusting capacitor (10^{-3} μF)).

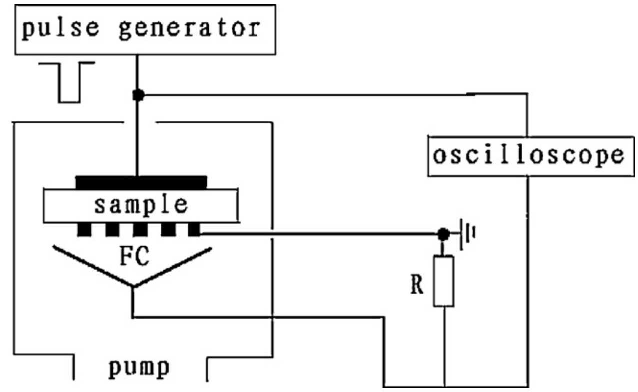

Fig. 4. Experimental setup for FE emission.

direction from each other. Then the disturbance which came from fast falling edge of the pulse could certainly be restrained. Moreover, the bigger resistance was employed to enforce SNR (signal to noise ratio). All the measuring wires used in this experiment were coaxial line with lengths as short as possible.

3. Results and discussion

Fig. 5 shows a typical temperature dependence of relative dielectric constant curve from PLZT 8/65/35 under different frequencies. It is shown that T_c (Curie temperature) increases slightly with the increase of the frequency. Generally, spontaneous polarization intensity of ferroelectrics will strengthen with the increase of polarization temperature. However, if the temperature goes too high over T_c, spontaneous polarization intensity may then decrease just because of the phase transition (from ferroelectric to paraelectric). So a polarization temperature of 120 °C is selected in this experiment.

It was discovered that the best polarization efficiency could be achieved in this way. Firstly the PLZT 8/65/35 sample was pre-poled by a DC electric field of 1000 V/mm at 120 °C for about 10 min. After that, the sample was cooled down without removing the DC electric field. An average value of piezoelectric coefficient (d_{33}), which equated to 560 was obtained by using this method.

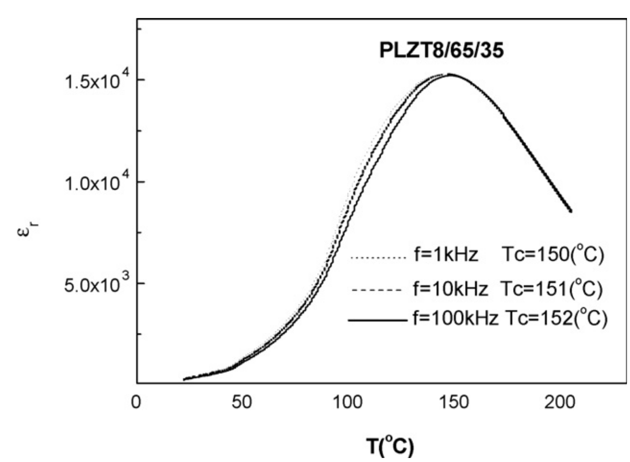

Fig. 5. Temperature dependence of relative dielectric constant curve from PLZT 8/65/35 under different frequencies.

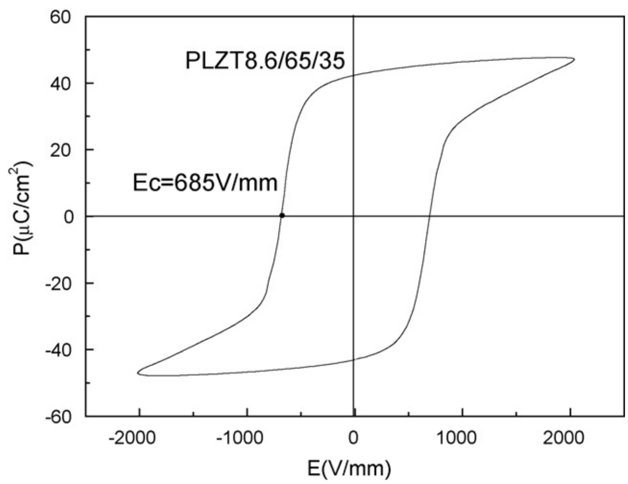

Fig. 6. Hysteresis loop of PLZT 8/65/35 ferroelectric.

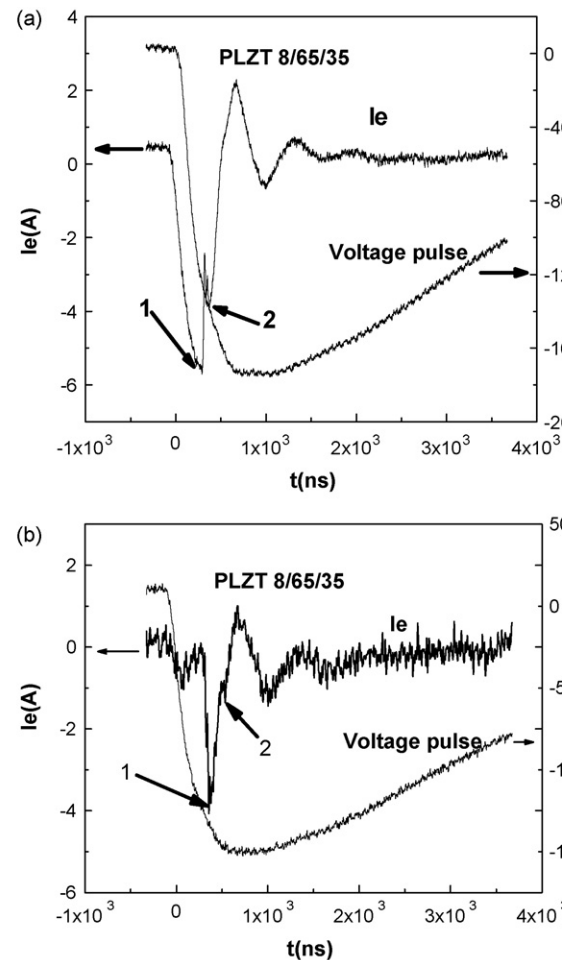

Fig. 7. Electron emission curves from PLZT 8/65/35, there are two current peaks in both graphs (a) and (b) 1, primary peak; 2, secondary peak.

Fig. 6 shows a typical hysteresis loop of PLZT 8/65/35 ferroelectric. The measurement was performed by applying a 1 Hz sine voltage. After measuring several PLZT 8/65/35 samples, the maximum coercive field (E_c) with a value of 685 V/mm was achieved. From original thinking, as long as the amplitude of the external voltage pulse exceeded this E_c value, polarization would certainly occur. However, after trying for several times, no obvious signals were obtained except for some tiny disturbed signals, unless a much higher external voltage pulse was applied.

It was discovered that there was a voltage threshold, and the electron emission from FE would not happen until the amplitude of the pulse exceeded this threshold. After repeating experiments, it was found that the threshold was around 1750 V/mm when an exciting voltage pulse with rise time of 350 ns was applied. As long as a higher amplitude of voltage pulse was applied, obvious electron emission signals would be obtained. Here is one suppositional explanation for this phenomenon. In a hysteresis loop experiment, a slow sine voltage signal (1 Hz) was applied to the sample, so there was plenty of time for this sine voltage to react on the polarization switch. This was why the external voltage (1 Hz) need not be too high. The pulse used in electron emission experiment was much faster (with rise time of 350 ns), so a much higher electric field induced by the pulse had to be applied to the sample just to achieve the same functionality. From this point, a further conclusion might be drawn. For the exciting pulse to trigger FE emission, a higher amplitude is required if a higher voltage ramping rate is applied.

Fig. 7 shows two typical electron emission curves of PLZT 8/65/35 under the application of a negative high voltage pulse. The electron emission current density could be evaluated by dividing the value of primary current peak by the total area of the exposed stripes, which are surrounded by electrode. And here the maximum current density is approximately 11.4 A/cm^2.

There are two current peaks during the leading edge of the exciting pulse. After repeating experiments it was discovered that the first current peak remained stable in location and amplitude, while the second peak showed instability in time and intensity. This phenomenon was also shown in Fig. 7(a) and (b). The first current peak was generated by fast spontaneous polarization switching. First of all, the ferroelectric sample started to change its spontaneous polarization during the leading edge of the exciting voltage pulse. The polarization charge which had little time to compensate with others was responsible for a high electric field. This electric field then caused the electron emission from the bulk of the ferroelectric. Since all electrons were emitted from the exposed area of the surface, this would then give rise to a strong enhancement of electric potential in this area, while the area which was covered by electrode always remained grounded at the same time. Hence, an intense tangential field which was parallel to the surface would be generated in the border of these two areas. Then electrons and ions which had opposite charge drifted in the opposite direction from each other, which then caused the formation of surface plasma. The plasma might be helpful for the energetic electrons to overcome the space charge barrier and arrive at the anode, and this might be the origin for the secondary current peak.

4. Conclusions

High current density has been obtained from PLZT 8/65/35 ferroelectric cold cathodes. Although the maximum coercive field (E_c) for PLZT 8/65/35 samples is only 685 V/mm, the electron emission from FE does not happen until a much higher exciting pulse is applied. The threshold for the electric field induced by the pulse is approximately 1750 V/mm. After repeating experiments it is shown that, there are two current peaks in the electron emission curves, the primary one remains stable, while the secondary one is unstable both in location and intensity.

Acknowledgements

This work was financially supported by the Ministry of Sciences and Technology of China through 973-project (Grant No. 2002CB613307) and the Natural Sciences Fund of China (Grant No. 50472052).

References

[1] G. Rosenman, D. Shur, Y.E. Krasik, A. Dunaevsky, Electron emission from ferroelectrics, J. Appl. Phys. 88 (2000) 6109–6161.
[2] H. Riege, I. Boscolo, J. Handerek, U. Herleb, Features and technology of ferroelectric electron emission, J. Appl. Phys. 84 (1998) 1602–1617.
[3] D. Flechtner, C. Golkowski, J.D. Ivers, G.S. Kerslick, J.A. Nation, Electron emission from lead–zirconate–titanate ceramics, J. Appl. Phys. 83 (1998) 955–961.
[4] Y.T. Kim, J. Park, K.H. Yoon, Electron emission from $Pb(Zr_{0.65}Ti_{0.35})O_3$ film cathode by pulse electric field, Mater. Res. Bull. 37 (2002) 631–639.
[5] Y.T. Kim, K.H. Yoon, T.H. Kim, K.B. Park, Electron emission from Pb-based ferroelectrics, antiferroelectrics, and paraelectrics by pulse electric field, Appl. Phys. Lett. 76 (2000) 3977–3979.
[6] K. Chirko, Y.E. Krasik, J. Felsteiner, A. Sternlieb, Enhanced emission mode of a ferroelectric plasma cathode, J. Appl. Phys. 92 (2002) 5691–5697.
[7] Z.D. Chen, S.R. Zhang, X.M. Cai, S.G. Guo, Experimental study on the mechanism of the ferroelectric emission from PLZT ceramics, Microelectron. Eng. 66 (2003) 670–675.