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Piezoelectricity in Single Crystal of Pentaerythritol Tetranitrate

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ABSTRACT

The piezoelectric constants perpendicular to (110) and (001) of single crystal of pentaerythritol tetranitrate (PETN) are determined to be $(3.2 \pm 0.40) \times 10^{-13}$ and $(1.5 \pm 0.30) \times 10^{-13}$ CN^{-1}. The charge development on these faces under static loading has been confirmed to be true piezoelectric in origin. The crystal seems to experience a quasi permanent deformation under repeated and successive compression with a very long relaxation time. This gives rise to a unique behaviour of individual crystal of PETN under identical stress condition. Mechanical stress relaxation measurements have also been carried out to provide additional evidence on the uniqueness of the crystal. Dielectric constant of the crystal along the directions perpendicular to (110) and (001) are 3.50 ± 0.12 and 4.57 ± 0.17; Young's modulus along the directions are $(1.24 \pm 0.30) \times 10^6$ and $(3.87 \pm 0.7) \times 10^6$ g cm^{-2} respectively. Single crystals of one cm^3 of PETN develops about 10 V cm^{-1} field under a force of 1 kg across (110) face.

1. INTRODUCTION

An important cause of hazards in the storage and handling of explosives is the development of static charge[1-8] on the explosive crystals. A programme of work aiming at understading the nature of charge development on single crystals of high explosives

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was undertaken by Explosives Research and Development Laboratory, Pune as very little information is available in the open literature. Among the very few studies[9-13] carried out in the field of piezoelectricity of high explosive materials, Maycock[8] predicted piezoelectric nature of single crystals of PETN from its crystal structure which was later recorded by Von Liecht[9]. In view of the absence of quantitative data on piezoelectric nature of single crystals of PETN, the authors have attempted to investigate in detail. Further work in this field is extended for tetryl, TNT and RDX also.

2. EXPERIMENT

Single crystals of PETN (2–3 cm) were grown by slow evaporation of the solvent from a saturated solution of PETN in acetone at room temperature. Good blemishless portions were obtained by cutting the large crystals in different crystallographic directions (Fig. 1). They were carefully polished to obtain smooth and plane surfaces. A conducting silver paint was applied on the opposite faces of the crystals in the direction of electrical measurements. The charge developed on (110) and (001) was measured as a function of static load applied perpendicular to those faces.

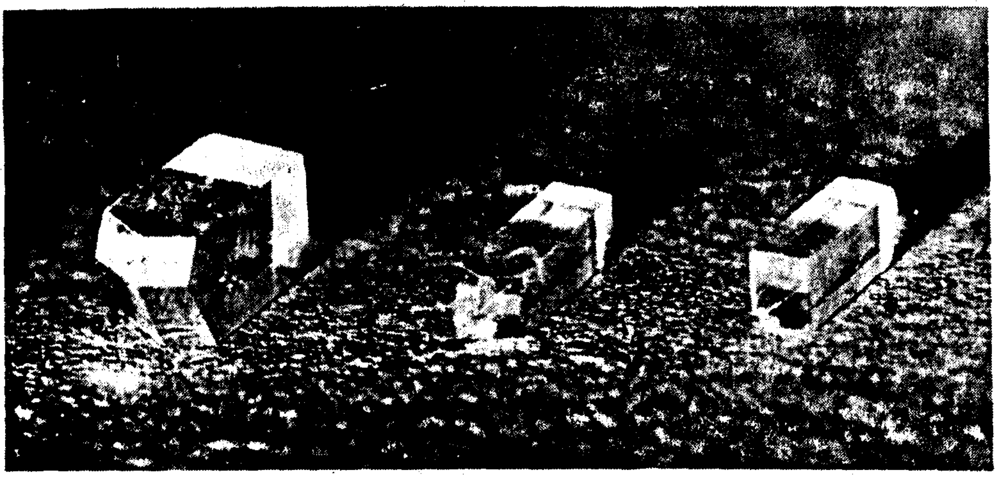

Figure 1. Single crystals of PETN showing natural faces in the front and at the back (left and centre) and cut perpendicular to *c*-axis (right).

The apparatus for the measurement of piezoelectric charge was fabricated out of aluminium metal (Fig. 2). A small sheet of glass epoxy insulator of 10^{12} ohm was fixed to the lower aluminium plate of the apparatus with araldite. One of the steel electrodes (1 cm dia) was fixed on the insulator sheet with araldite and the other steel electrode held at zero potential was fixed to the upper disk of the apparatus. This disk was provided with a 25 cm long aluminium stem which has a provision at the

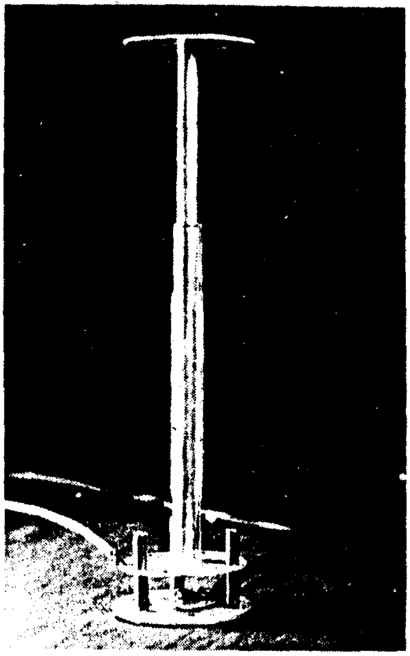

Figure 2. **Crystal holder for piezoelectric charge measurement.**

upper end for applying pressure on the crystal. The bottom plate was provided with three studs which act as guides for the upper disk at zero potential, thus ensuring uniform pressure on the crystal. The necessary precautions were taken to avoid stray current and other electrical pick-ups. The basic measuring instrument was a Kistler dual mode charge amplifier model 503 D146. The charge produced on crystals by progressively varying loads was read out on a photovolt strip chart recorder. This method for piezoelectric charge measurement has been tested with tourmaline crystal for which the value of piezoelectric constant obtained was 17.3×10^{-13} CN^{-1} and is comparable to the reported value of 18.0×10^{-13} CN^{-1}.

The dielectric constants of PETN crystals were measured by holding the crystal between a silver plate-electrode and a platinum point-electrode. The capacitance was determined with the aid of a Waynekerr capacitance bridge with an autobalance adapter model B 642. The capacitance could be measured correct to ± 0.001 pf. The set-up has been tested with tourmaline crystal to determine the value of dielectric constant which was found to be 6.8, in good comparison with the reported value of 7.1.

The measurements on mechanical compression at stress relaxation at constant strain were performed on Instron testing machine, model TTCM. The well polished crystal with flat parallel faces was placed on a load cell of range 0-100 kg CCTM (Fig. 3). The full scale load was adjusted to 0-2 kg. The compression of the crystal was recorded as a function of load on a strip chart recorder. The effect of repeated compression

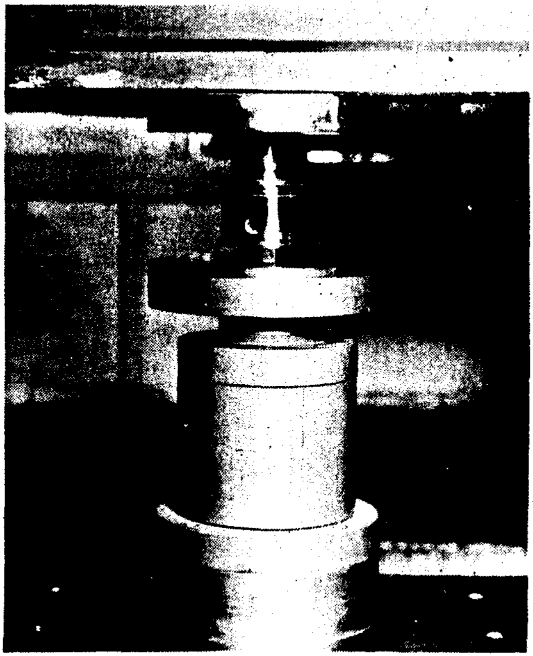

Figure 3. Close-up of the crystal mounted between cross-head and load cell.

on a given crystal was studied by subjecting the crystal to steady value and then allowing the crystal to anneal at atmospheric pressure for 15 to 20 minutes. The crystal was cycled through a compression, stress relaxation and annealing.

3. RESULTS

Figure 4 shows the effect of increasing stress on the charge development on the (110) and (001) faces respectively of PETN single crystals. Table 1 shows the average values of piezoelectric and dielectric constants determined on a number of PETN single crystals for the directions perpendicular to (110) and (001) respectively at 10,000 cycles/s. Table 2 shows the increase in the magnitude of piezoelectric coefficient in both the directions in the second static loading.

Table 1. Average piezoelectric and dielectric constants of single crystal of PETN

Direction ⊥ to	Piezoelectric constant (× 10^{13} CN^{-1})	Dielectric constant
(110)	3.20 ± 0.40	3.50 ± 0.12
(001)	1.50 ± 0.30	4.57 ± 0.17

Table 2. Piezoelectric coefficient for single crystal of PETN in successive experiments along directions

Crystal No.	Direction ⊥ to	Piezoelectric coefficient (× 10^{13} CN^{-1})		
		Direct face		Reverse face
		First expt.	Second expt.	
1	(110)	2.80	3.50	3.00
2	″	3.50	5.00	4.00
3	″	3.50	4.00	2.75
4	″	3.00	4.00	3.50
5	″	2.50	3.50	5.00
6	″	3.45	4.00	4.25
7	″	2.40	3.84	2.72
8	(001)	1.70	2.10	2.80
9	″	1.80	2.40	2.00
10	″	1.36	1.44	2.00
11	″	1.44	1.60	1.68

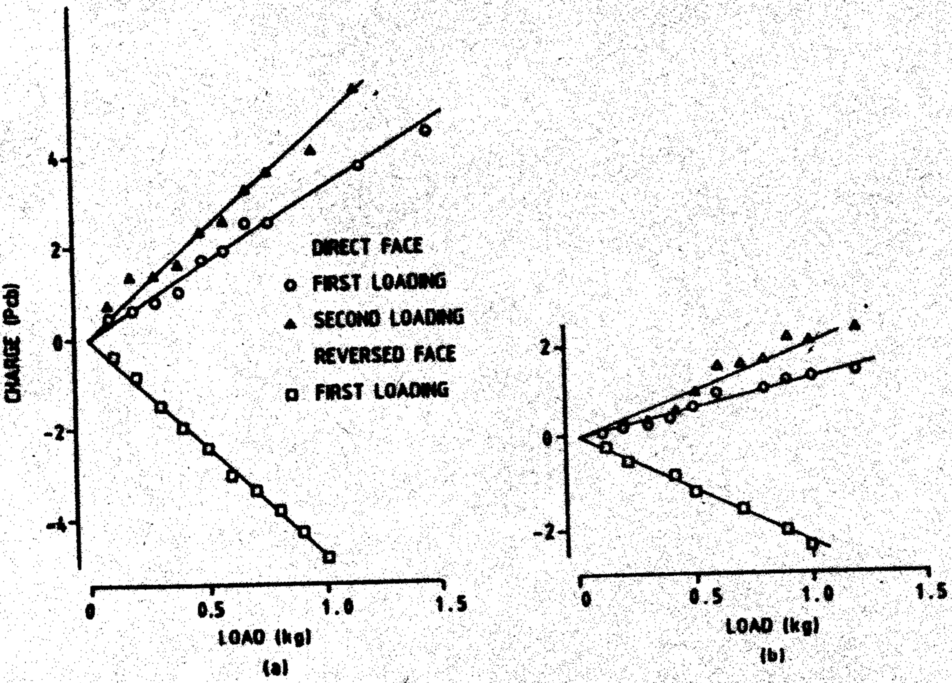

Figure 4. Load dependance of charge developed on a single crystal of PETN along the directions perpendulcular to (a) (110), and (b) (001).

Figure 5 represents the results for the compression and stress relaxation of single crystals of PETN when the stress is applied perpendicular to (110) and (001) respectively. Curve 1 in Fig. 5 is for the first compression and stress relaxation behaviour whereas Curves II and III are for the subsequent compressions. Table 3 presents typical values for a single crystal of PETN of the rate of relaxation in the initial stage within the first fifty seconds, the linear, slow and steady region after fifty seconds, and also the Young's modulii in subsequent loading experiments along the

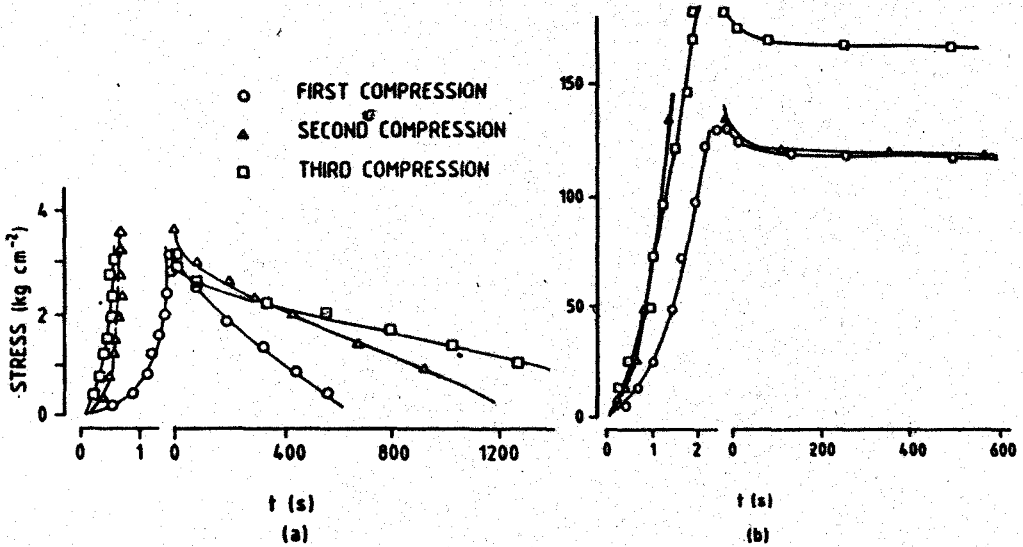

Figure 5. Compression and stress relaxation for single crystal of PETN along the direction perpendicular to (a) (110), and (b) (001).

Table 3: Mechanical properties of single crystals of PETN along directions on repeated compressions

Directions ⊥ to	Compression No.	Stress relaxation during first 50 s (g cm^{-2}s^{-1})	Stress relaxation after a period of 500 s (g cm^{-2}s^{-1})	Young's modulus ($\times 10^{-6}$) (g cm^{-2*})
(110)	1	11.0	4.0	0.95
	2	6.0	2.0	1.05
	3	2.0	1.5	1.00
(001)	1	14.0	1.0	2.8
	2	12.0	2.0	3.6
	3	10.0	1.5	3.3

*To convert into SI units Nmm^{-2}, multiply g cm^{-2} by 9.8065×10^{-5}

directions perpendicular to (110) and (001). Figure 6 represents the stress vs strain relationship for the two directions. The average values of Young's modulii of a large number of single crystals of PETN are found to be (1.24 ± 0.30) × 10^6 and (3.80 ± 0.70) × 10^6 gm cm^{-2} for the directions perpendicular to (110) and (001) respectively.

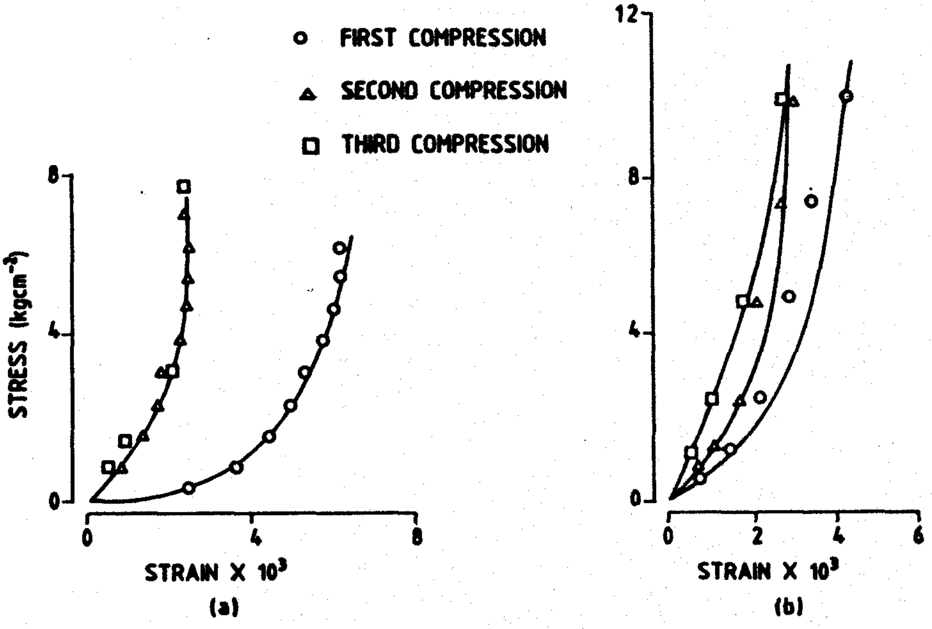

Figure 6. **Stress dependance of strain in single crystal of PETN along the directions perpendicular to (a) (110), and (b) (001).**

4. DISCUSSION

Figure 4 shows that development of charge on the two faces of PETN is a linear function of applied stress and the opposite charges generated on the reverse side of the crystals conform to the true piezoelectric nature of the crystal. The higher charge (3.20 ± 0.40) × 10^{-13} CN^{-1} in the directions perpendicular to (110) face can be attributed to the possibility of greater distortion of molecules by bending with the consequent higher degree of polarisation. This is reflected in the low value of Young's modulus, viz. 1.24 × 10^6 g cm^{-2} perpendicular to (110) as against 3.80 × 10^6 g cm^{-2} along *c*-direction. The (110) face is populated[14] almost entirely by $-ONO_2$ groups which account for the higher value of piezoelectric charge along this direction. The situation is different when viewed[14] along *c*-direction. The $-ONO_2$ groups lie in a plane making an angle 47.5° with the (001) plane. Lower compressibility of the crystal along the direction perpendicular to (001) and lower component of force along the $-ONO_2$ plane accounts for lower value of piezoelectric constants along the direction perpendicular to (001). As viewed along *a*-direction, there is considerable interleaving along the *c*-direction which resists deformation of the crystals under any mechanical force and hence a lower piezoelectric constant.

It is important to note that the magnitude of piezoelectric constant for the two faces increases with the second and subsequent static loadings even though a relaxation and annealing period of half an hour is allowed between successive experiments. This increase indicates that the crystals retain a little part of the electric field gained with earlier loading and thereby manifesting a certain memory. The memory in PETN crystal has also been reflected in the decrease in stress relaxation from the subsequent compression experiment in Fig. 5(a). The relaxation process is very markedly effected by the previous mechanical history of the crystal. The stress relaxation process seems to be extremely slow for compression along the *c*-direction. The Young's modulus along two directions signifies that the compressibility of PETN along the direction perpendicular to (110) is more than that along *c*-direction which is in accordance with the piezoelectric constants observed along the respective directions.

These observations imply that the PETN is more elastic, less compressible and resists permanent or plastic deformation along *c*-direction. The crystal structure as determined by Booth and Llewellyn[14] and refined by Trotter[15] shows a strong interleaving of $CH_2\ ONO_2$ arms along the *c*-direction. These interleaved chains are thus less susceptible to sustain permanent distortion. The packing of atoms being considerably less close along the other directions render the crystal more compressible.

Like other piezoelectric crystals[16] belonging to the space group $P\ 42_1\ c$, PETN also exhibits lower piezoelectric charge along *c*-direction whereas dielectric constant is higher along the same direction. The lower piezoelectric constants along the direction of higher dielectric constants are suggestive of resistance by the electric dipoles to any mechanically induced reorientation process.

An important finding in this study is that individual crystals of PETN can behave differently when subjected to the same applied mechanical forces depending upon the previous history of the crystals. Such behaviour is manifested in the varying values of piezoelectric constants (Table 2) and the different relaxation behaviour along the identical crystallographic directions. It is relevant in this respect to note that even different heats of fusion have been experimentally observed for PETN crystals[17].

An important fact derived from this study is that when a PETN crystal of one cm^3 is considered as a capacitor, the calculated field of 10 $\mathrm{V\ cm}^{-1}$ under a force of 1 kg, is thus produced across (110) comparable with 10 $\mathrm{V\ cm}^{-1}$ under a force of 400 g for δ-HMX. If it is assumed that piezoelectricity on these crystals depend linearly on pressure upto the average primary detonation pressure of 300 kbar, a one cm^3 crystal of PETN may generate about $3 \times 10^6\ \mathrm{V\ cm}^{-1}$ across (110) which is comparable to the value predicted for δ-HMX by Maycock[8] and the observation of high voltage across tetryl pellets at detonation[18].

Such studies should be extended to single crystals of different explosives and allied materials to understand safety limits and the electrical phenomena observed at detonation.

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