Vickers micromechanical indentation and compression testing of ferroelectric lead hydrogen phosphate single crystals

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Ferroelectric crystals of lead hydrogen phosphate (LHP) have been synthesized using the controlled diffusion of lead nitrate into a set gel containing orthophosphoric acid. The variation in the microhardness of LHP crystals has been determined using a Vickers microhardness indentor. The effects of annealing and quenching on the mechanical properties of these crystals have been studied. It is observed that (i) the microhardness of the crystals depends on the applied load and is independent of the duration of loading, (ii) irrespective of the relative orientation of the indentor and the crystal, the median vents initiate at the sharp indentation edges, and (iii) maximum plasticity is observed in quenched crystals. The mechanical behaviour of the crystals has been studied using an Instron compression testing unit. A large anisotropy is observed from experiments on the breaking strength of the crystals and the implications are discussed.

1. Introduction
Hardness is a measure of the resistance to permanent deformation or damage. As the hardness properties are basically related to the crystal structure of the material, microhardness studies have been applied to understand the plasticity of the crystals. All hardness tests measure some combination of various material properties, namely elastic modulus, yield stress, physical imperfections, impurities and work-hardening capacity [1–5]. Boyarskaya *et al.* [6] reported the relation of microhardness to load for NaCl monocrystals. Plendl and Gielisse [7] have correlated the hardness of several crystals with their lattice energy. Julg [8] and Powarjonnych [9] attempted to obtain quantitative information about the bond strength from hardness values. Niyata and Jinno [10] have used the indentation technique for evaluating the fracture toughness of borated glass. Quenching has been found to enhance the hardness and internal stress of potassium chloride crystals [11].

During the past decade, single crystals of lead hydrogen phosphate (LHP), $PbHPO_4$, have become increasingly important in the electro-optical field, as these crystals show many interesting physical properties such as ferroelectricity and piezoelectricity. These crystals are used in transducers and in many linear and non-linear mechanical devices. They are also suitable for testing microscopic theories of ferroelectricity. Desai and Ramana [12] reported that single crystals of LHP can be grown by a gel method. However, information on the mechanical properties of these crystals is meagre. In this paper, studies on the mechanical properties from the plastic deformation of LHP single crystals are reported. The results of Instron compression testing up to the breaking point of the crystal are also described in this paper.

2. Experimental procedure
Single crystals of LHP were grown using a controlled reaction between H_3PO_4 and $Pb(NO_3)_2$ by a diffusion process in silica gels. The crystals were examined by scanning electron microprobe analysis, X-ray diffraction, density measurements and thermogravimetric analysis. These techniques confirmed that they were LHP (monoclinic, space group P2/a). The crystals were cleaved with a sharp blade along the [1 1 0] planes. The freshly cleaved (1 1 0) surfaces and as-grown (0 1 0) and (1 1 0) surfaces were indented using a Vickers microhardness indentor, Model 6270 (Cooke, Troughton and Simms, U.K.). The samples were mounted on a flat aluminium or ebonite circular disc. A Vickers pyramidal diamond was used to make the indentations and a filar micrometer eyepiece on the microscope allowed the diagonals of the resulting diamond-shaped indentations to be measured with an estimated accuracy of $\pm 0.5\,\mu m$.

A load (p) varying from 10 to 100 g was applied for a fixed interval of time, i.e. 30 sec. In another set of experiments, a constant load of 50 g was used and the time of indentation (t) was varied from 5 to 50 sec. These experiments were repeated at least five times for each loading and for each time interval on cleaved (1 1 0) and as-grown (0 1 0) and (1 1 0) surfaces. Measurements were made of the two diagonals of an indentation mark, and from mean values of the diagonals and applied load, the Vickers Hardness Numeral (VHN) was computed using the relation

$$\mathrm{VHN} = 1.854p/d^2 \qquad (1)$$

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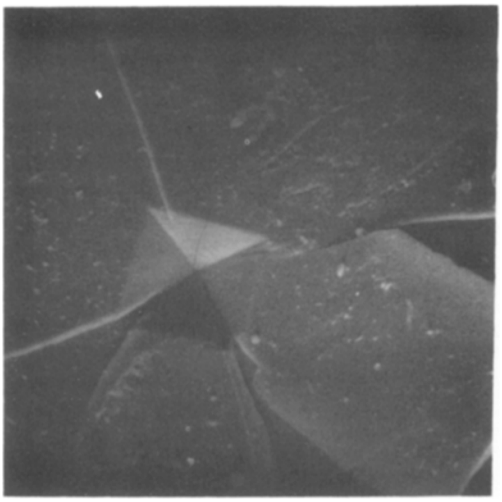

Figure 1 Typical indentation mark and crack pattern on (1 1 0) cleaved surfaces (× 200).

where p = applied load in kilograms and d = mean diagonal length in millimetres.

The probable error was calculated for the mean VHN based on ten indentations for a given plane and environment. However, it was observed that due to slight deviations from normal incidence of the indentor on the crystal surface, two of the four vertices of the indentation mark on some of the samples were not well defined, and in such cases the measurements of the diagonal lengths were not accurate. To minimize errors, half-diagonals were measured. Samples were maintained at 200° C for 24 h and cooled down to room temperature at the rate of 5.0° C h^{-1}, in order to anneal the crystals. The crystals were kept at different quenching temperatures for a fixed time and quenched to room temperature.

For Instron compression testing, visible transparent LHP crystals were selected and their dimensions were carefully determined using a travelling microscope. The crystal was placed between the two compression heads of the Instron machine, the upper head being slowly moved downwards at a uniform speed of 0.5 cm min^{-1}; the record chart speed was 50 cm min^{-1}. The weight applied and the resulting compression were noted on the recorder for various crystals along two directions, namely perpendicular to (0 1 0) and (1 1 0) planes. The compression upper head was moved until the crystal was crushed at the end of the plastic limit.

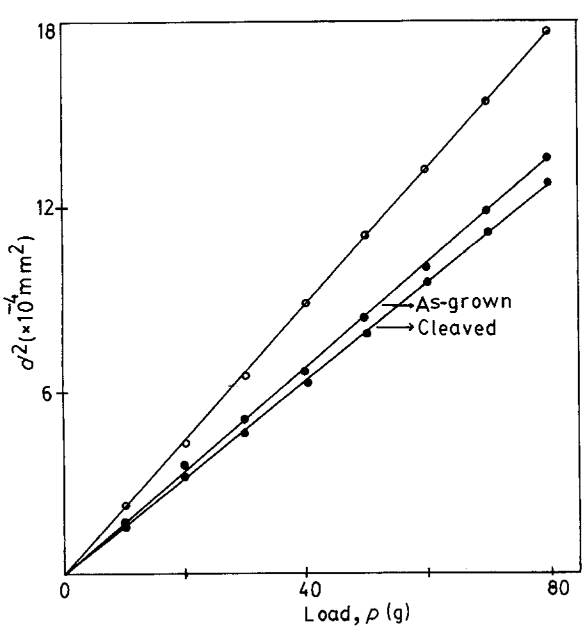

Figure 2 Plots of the square of the diagonal against the applied load on (○) (0 1 0) as-grown and (●) (1 1 0) as-grown and cleaved surfaces.

3. Observations and discussion

3.1. Microhardness testing

A typical indentation mark with a load 50 g is shown in Fig. 1. It is clearly seen from this figure that several cracks or median vents grow simultaneously from the concentration points, the sharp indentor edges. No preferred directions of venting were observed, as in the case of anisotropic materials where vents tend to have preferred orientations [13]. Even for low loads, the deformation was observed to be too severe and, near the indentation mark, displaced matter chipped off as is observed frequently on minerals. However, this chipping off does not change the size of the indentation mark if the diagonal ends can still be observed.

The basic sequence of crack propagation events is explained as follows: the sharp point of the indentor produces an elastic deformation and, at some threshold, a deformation-induced flow suddenly develops into a small crack, the median vent on a plane containing the contact axis, and an increase in load causes further stable growth of the median vent. On unloading, the median vents begin to close but do not heal. Relaxation of deformed material within the contact zone, just before removal of the indentor, superimposes intense residual tensile stresses upon the applied load and sideways-extending cracks, called "lateral vents" begin to appear. The lateral vents continue to extend and cause chipping.

The plots of the square of the diagonal length, d^2, against load P gave straight lines passing through the origin for both (0 1 0) and (1 1 0) as-grown and cleaved surfaces as shown in Fig. 2, indicating that the error in loading is nil in the studied range of loadings.

It may be mentioned that the graphs of log P against log d (Fig. 3) gave straight lines with slopes of 2, 1.9 and 1.95 for (1 1 0) cleaved and (1 1 0) and (0 1 0) as-grown faces, respectively, which proves the validity

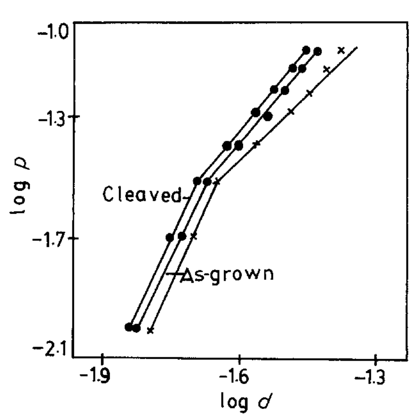

Figure 3 Plots of log ϱ against log (diagonal) for (×) (0 1 0) as-grown and (●) (1 1 0) as-grown and cleaved surfaces.

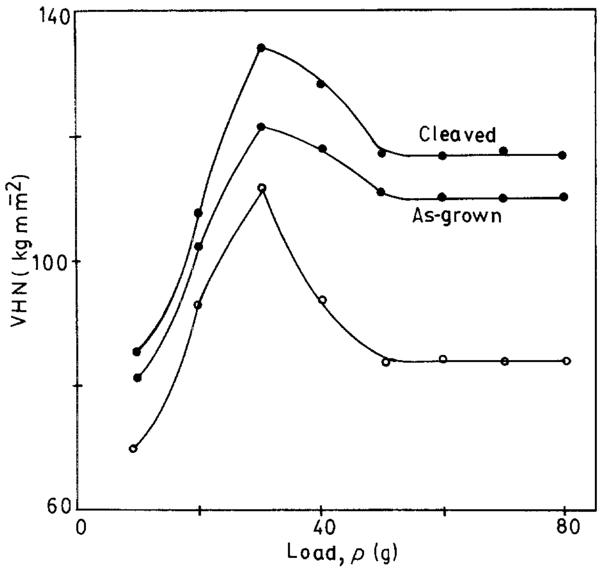

Figure 4 Plots of Vickers hardness numerals (VHN) against the applied load (p) for (○) (0 1 0) as-grown and (●) (1 1 0) as-grown and cleaved surfaces.

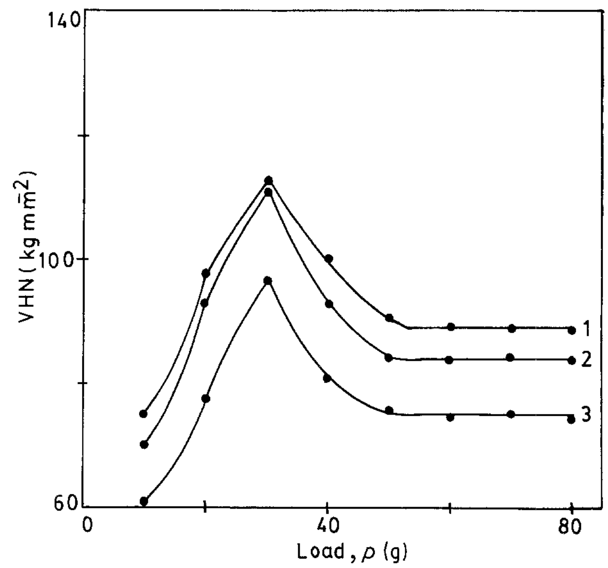

Figure 5 Plots of VHN against load for quenched and annealed (0 1 0) as-grown surfaces: (1) quenched at 373 K, (2) at room temperature (303 K), (3) annealed at 373 K.

of the relation

$$P = ad^n \quad (2)$$

where $n = 2$.

Microhardness measurements revealed that the VHN is independent of loading time or dwell time, but is a function of the indentor load. The variation of VHN with the load for cleaved and as-grown surfaces is shown in Fig. 4. The following special features should be noted:

(i) In all cases, it is found that the microhardness increases with load, giving a sharp maximum at 30 g.
(ii) In all cases, consistency in VHN is revealed after 50 g.
(iii) The absolute value of VHN in the case of cleaved (1 1 0) surfaces is greater than for (1 1 0) and (0 1 0) as-grown surfaces.

During the process of indentation, the indentor penetrates to a depth comparable with, or greater than, the thickness of the distorted zone. Since this zone is pierced by the indentor, its effect will be marked at comparatively low loads. Consequently, a noticable increase in VHN is observed in the beginning, when the chipping of the material from the surface is very intense. As the depth of impression of the diamond pyramid increases, the effect of the distorted zone decreases and hence the load dependence of microhardness is less. This explains that the variation of VHN with load is almost zero beyond 50 g load. For larger loads (above 50 g) when the indentor reaches a depth at which undistorted material exists, the microhardness is independent of load. The indented surfaces were etched in 1.0 M HCl acid solution for 10 min. It is observed that the rosette arms run along ⟨0 0 1⟩ direction and the pit density along them is more or less uniform.

Fig. 5 shows that annealing decreases the hardness whereas quenching increases the hardness for all loadings for (0 1 0) planes. The same behaviour was also observed for (1 1 0) as-grown surfaces; this may be attributed to quenching, as it introduces a large number of line and point defects and also result in the creation of internal stresses. Annealing, on the other hand, is a thermally activated process which leads to arrangements of existing dislocations and other defects into low-energy configurations or the total or partial annihilation of these. Annealing also leads to recovery by the following mechanisms operating singly or in conjunction: (i) vacancy migration by diffusion, (ii) climb of dislocations, (iii) polygonization, (iv) crystal boundary migration, and (v) recrystallization. The activation energy needed for all mechanisms is supplied thermally during the maintenance at an elevated temperature during annealing.

Interestingly, it was observed that the increase in distance from the gel interface tends to decrease the microhardness of the crystal. These can be correlated as in growth systems which depend on the diffusion of one reactant through a gel incorporating the other reagent; it is observed that the growth rate is greatest near the gel–solution interface, where the concentration gradients are high, while away from the interface the gradients are relatively low. Corresponding to different growth rates, the dislocation density is also different. This strongly suggests that the growth rate itself determines the number of defects grown into the crystal, even in the absence of foreign impurity; this in turn affects the hardness of the crystal.

3.2. Instron compression testing

The Instron compression recorder plot obtained for LHP single crystals has been traced and is shown in Fig. 6. It is revealed when the crystal is pressed perpendicular to the (0 1 0) plane that Hooke's law is obeyed in the complete region up to the breaking point, without passing through a plastic region before the catastrophic event. On the other hand when the crystal is presssed in a direction perpendicular to the (1 1 0) cleavage plane, the crystal suffers catastrophy under pressure by a smaller factor when compared with destructive forces applied to (0 1 0) as-grown surfaces. This difference in the breaking strength (Load applied)

TABLE I Young's modulus of LHP crystals

Crystal plane	Thickness of the crystal, t (cm)	Area of the crystal, A (cm^2)	Compressibility, Δl ($\times 10^{-3}$ cm)	Load applied, L (kg)	Strain, $e = \Delta l/t$	Stress, $\sigma = L/A$ ($kg\,cm^{-2}$)	Young's modulus, $Y = \sigma/e$ ($\times 10^3\,kg\,cm^{-2}$)
(0 1 0)	0.154	0.0842	10.0	14.2	0.0649	168.64	2.597 15
	0.135	0.0797	8.6	13.2	0.0637	165.48	2.597 3
(1 1 0)	0.196	0.0812	7.2	6.4	0.0367	78.82	2.147 6
	0.186	0.0771	6.6	5.8	0.0354	75.22	2.125 1

(Table I) observed for the cleavage plane, which is the hardest plane, is probably to be explained by a slight deviation from the assumed perpendicular direction of the applied force causing the planes to slip. This argument can be supported by an observation made on a crushed crystal. For this purpose, motion of the upper moving head was arrested immediately after the breaking point was just reached. The crystal with its cleavage plane (1 1 0) in contact with the compressing head was found to be cleaved to thinner pieces, whereas the crystals with the other planes, (0 1 0), taken individually under the compression head, were just randomly crushed into small fragments.

We have attempted to compare the results of the microhardness study (Fig. 4) with the compression testing (Table I). The inference seems to be consistent despite two entirely different ways of applying pressure to the LHP crystals. These results, of point-indentation and surface compression testing, differ in the damage patterns under different conditions. It may be noted that

(i) (0 1 0) planes, which require the higher pressure per unit area for breaking, are characterized by the smallest value of VHN; and

(ii) the (1 1 0) cleavage plane having the lower breaking strength exhibit the higher VHN.

4. Conclusions

1. LHP crystals are highly brittle because even at low indentation loads fracture occurs at stress concentration points.

2. Irrespective of the relative orientation of the indentor and the crystal, the median vents are initiated at the sharp indentation edges.

3. Microfracture is more predominant on the (1 1 0) cleavage plane even at low loads, and the (0 1 0) and (1 1 0) as-grown faces are fracture-resistant.

4. The VHN of LHP crystals is dependent on the applied load, but is independent of the duration of loading.

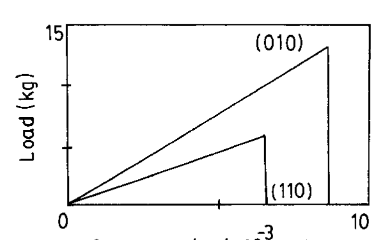

Figure 6 Instron plot of applied load against compression for (0 1 0) and (1 1 0) as-grown surfaces.

5. The VHN for (1 1 0) is greater than that of (0 1 0) as-grown surfaces.

6. The VHN for (1 1 0) cleaved surfaces is greater than that of (1 1 0) as-grown surfaces.

7. Quenching increases the hardness whereas annealing decreases the hardness of LHP crystals.

8. Compresion testing, using the Instron, gave the breaking strength of the crystals. The (1 1 0) cleavage plane required only a small fraction of the pressure for breaking, when compared with the other (0 1 0) as-grown planes.

9. The plane with the lowest breaking strength shows the highest value of VHN and vice versa.

10. The comparison of the results of compression testing and indentation is conclusive through the different mechanisms involved for the application of external forces.

Acknowledgements

The authors are thankful to the Council of Scientific and Industrial Research (CSIR), New Delhi, for sanction of the project, entitled "Growth and characterization of ferroelectric crystals". One of us (C.C.D.) is very grateful to Dr Yogesh Desai and Mrs Hina Desai (Nutley, New Jersey) for their keen interest in the present work.

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Received 15 April and accepted 6 July 1987