Microhardness studies in gel-grown ADP and KDP single crystals

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Abstract. Microhardness studies were carried out on (100) faces of gel-grown ADP and KDP single crystals. Slip lines were observed on (100) face of ADP crystal at the corners of the impressions. Microcracks around the indentation were found on (100) face of KDP crystal from 10 g load which spread out as the load increased. Vickers hardness number H_v decreased with increase in load. ΔH_v at 50 g load for solution-grown crystals and gel-grown crystals (present case) was determined. Work hardening index n for both ADP and KDP crystals was less than 2 showing soft-material characteristics. Using Wooster's empirical relation, values of C_{11} from hardness were calculated and found to be close to the reported ones.

Keywords. Microhardness; elastic constant; ammonium dihydrogen orthophosphate; potassium orthophosphate.

1. Introduction

Single crystal study of ammonium dihydrogen orthophosphate (ADP) and potassium dihydrogen orthophosphate (KDP) has gained considerable importance in recent years because of their important ferroelectric, piezoelectric and electro-optic properties.

As regards mechanical properties, hardness testing provides useful information on the strength and deformation characteristics of materials (Mott 1956) and is correlated with other mechanical properties like elastic constants (Wooster 1953) and yield stress (Westbrook 1958). Meyer (1951) established a relationship between indentation hardness and plastic and work-hardening capacity of a material. The hardness of a material is defined (Ashby 1951) as the resistance it offers to the motion of dislocations, deformation or damage under an applied stress. The most common measurement of hardness is the indentation type. Hardness test methods are used to determine the stress needed to produce plastic flow in the brittle material. It measures the mean contact pressure when a spherical, a conical or a pyramidal indenter is pressed on to the surface of a flat specimen, thus providing a simple and non-destructive means of assessing the resistance of the material to plastic deformation. The general definition of indentation hardness is the ratio of the applied load to the surface area of indentation. The relation between the load and size of indentation, is given by Meyer's law as $p = ad^n$ where p is load in kg, d the diameter of recovered indentation in mm and a and n are constants for a given material. The Meyer index number n gives the value of work-hardening index. The behaviour of indentation hardness at low loads has been a controversial subject. In the light of these, hardness measurements have been made on (100) face of gel-grown ADP and KDP crystals in the load region of 5 to 100 g for ADP and 5 to 50 g for KDP. The literature is scarce and the studies on the (100) face of gel-grown ADP are being done for the first time.

2. Experimental

The crystal growth experiments were performed by slow diffusion in silica gel medium at room temperature (Sengupta *et al* 1990). The microhardness of ADP and KDP crystals was determined using mhp 160 microhardness tester fitted with Vickers diamond pyramid indenter and attached to a Carl-Zeiss (Jenavert) incident light research microscope.

For the static indentation test, load p varying from 5 to 100 g were applied on the selected (100) faces of the crystals over a fixed interval of time (10 s), and removed. The indented impressions were approximately square. The surfaces were indented at different sites. Diagonal lengths of the indented impressions obtained at various loads were measured using a calibrated micrometer attached to the eye piece of the microscope. Several indentations were made on each sample. The average value of the diagonal lengths of the indentation mark for each load was used to calculate the hardness. The Vickers microhardness number H_v was calculated using the relation $H_v = 1.8544 (p/d^2)$ kg mm⁻², where p is the applied load in kg and d the average diagonal length of the Vickers impression in mm after unloading.

3. Results and discussion

Figure 1 shows the indentation marks on the (100) face of ADP crystal at 50 g(b) and 100 g(a) load. Slip lines were observed at each corner of the impression at 100 g load. Maximum indenter load applied for ADP was 100 g. Figures 2(a, b, c) show the indentation marks on (100) face of KDP at 10, 25 and 50 g load. Maximum indenter load applied for KDP was 50 g, because microcracks were observed around the impression. Cracks initiate at 10 g load (figure 2a) and tend to propagate with the

Figure 1. Indentation mark on the (100) face of gel-grown ADP crystal by Vickers indenter ($\times 80$) for (a) 100 g load, (b) 50 g load.

increased load of 50 g, as may be evident from figure 2(c). This implies that the increased hardness of KDP crystals, as also reflected from the increased value of hardness number in figure 3, shows the variation of hardness with indenter load. This variation for solution-grown ADP and KDP crystals, reported by Anbukumar *et al* (1986) is also plotted on the same graph (symbol Δ). ΔH_v at 50 g load for solution-grown and gel-grown crystals is determined from the graph. It turns out to be 31.2 kg/mm² for ADP and 12 kg/mm² for KDP. This shows that the hardness number slightly varies in the same crystal grown by different techniques. The microhardness is found to decrease with increase of indenter load (from 5 to 25 g) for both ADP and KDP, and remains unaffected beyond this load. With gradual

Figure 2. a–b. For caption, see p. 336.

Figure 2. Indentation mark on the (100) face of gel-grown KDP crystal by Vickers indenter ($\times 80$) for (a) 10 g load, (b) 25 g load, (c) 50 g load.

Figure 3. Graph showing variation of microhardness H_v with load P .

increase of the applied stress, the elastic limit of the material can be exceeded and the specimen will not restore its original shape on removal of the stress. In the present case, microhardness number H_v was 99 kg/mm^2 at 100 g load for ADP crystal and 172.5 kg/mm^2 at 50 g load for KDP crystal. This value is also very close to the value

Figure 4. Log-log plot of Meyer for (1) KDP and (2) ADP.

Table 1. Calculated values of n and C_{11} .

Crystal	Work hardening index (n)		Elastic stiffness coefficient (C_{11})		Reference
	Calculated values (gel-grown)	Reported values* (solution grown)	Calculated values from relation $C_{11} = H^{7/4}$ in C.G.S. units	Reported values [†] in C.G.S. units	
ADP	1.991	1.941	3.045×10^{11}	4.725×10^{11}	*Anbukumar <i>et al</i> (1986)
KDP	1.975	1.917	5.119×10^{11}	6.235×10^{11}	[†] Simmons and Wang (1971)

177 kg/mm² reported by Shanmugham *et al* (1986) in the measurement of H_v of gel-grown KDP crystal.

The log-log plot drawn between d and p yields a straight line (figure 4). The slope of the line gives the value of n , the work-hardening index. Table 1 shows the values for ADP and KDP.

Following Wooster's empirical relation ($C_{11} = H^{7/4}$) between elastic stiffness coefficient and hardness of a crystal (Wooster 1953), we calculated the values of C_{11}

(averages of C_{11} and C_{33}) for both ADP and KDP crystals. The calculated values were found to approximate to the reported results (Simmons and Wang 1971) (table 1).

4. Conclusion

On the basis of careful investigations on various substances, Onitsch (1947) and Hanneman (1941) had shown that the value of n comes out to be 1 to 1.6 for hard material and more than 1.6 for soft material, and that microhardness decreases with increase of load when $n < 2$. The decrease in H_v with load, observed in the present case, is in agreement with the theoretical prediction.

Hardness values of solution-grown crystals are less than H_v of gel-grown crystals (as shown in figure 3). This implies that solution-grown crystals are softer than gel-grown crystals which apparently contain more defects. The major problem associated with the gel method lies in the poor control over supersaturation, which varies in the gel from one point to another. Near the growing interface, it is about the same as in solution. Far from the interface, however, the values of the supersaturation must be much higher in gel than in solutions causing fluctuations in growth rate and thereby inducing more crystalline defects. The gel inclusion is also responsible for the generation of defects in these crystals. Further, it has been observed that the hardness value of KDP crystals is greater than that of ADP crystals. This could be attributed to the differences in their molecular structures. Crystallographically, both ADP and KDP are similar in H_2PO_4 network. In ADP crystals, N–H ... O bond occurs between ammonium and phosphate groups, whereas KDP structure is a polar structure consisting of K^+ and $H_2PO_4^-$ ions. The ionic bonding between K^+ and $H_2PO_4^-$ ions in KDP is stronger than N–H ... O bond existing in ADP molecules. As a result, KDP shows increased hardness.

The hardness measurements may be useful in indicating the order of magnitude to be expected for the elastic constant in a new material.

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