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Systematic hardness studies on lithium niobate crystals

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Abstract. In view of discrepancies in the available information on the hardness of lithium niobate, a systematic study of the hardness has been carried out. Measurements have been made on two pure lithium niobate crystals with different growth origins, and a Fe-doped sample. The problem of load variation of hardness is examined in detail. The true hardness of $LiNbO_3$ is found to be 630 ± 30 kg/mm^2. The Fe-doped crystal has a larger hardness of 750 ± 50 kg/mm^2.

Keywords. Microhardness; lithium niobate.

1. Introduction

Lithium niobate ($LiNbO_3$) is one of the most prominent nonlinear optical materials. Because of this importance, there is considerable work on all its physical properties (Nikogosyan 1997). One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically, hardness is the resistance offered by a solid to the movement of dislocations. Practically, hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentation. The hardness estimated from the scratch test is on the Moh's scale. The indentation hardness is measured as the ratio of the applied load to the surface area of the indentation (details in § 2). Indentation hardness measurement can, in principle, be carried out at fairly high loads (~ 100 kg). But for materials which have low hardness and which are available as small-sized samples, it is convenient to make measurements at low loads of < 200 g. This low-load hardness is called microhardness. There are discrepancies in the available information on the microhardness of $LiNbO_3$.

Chai (1995) lists a value of 5 on the Moh scale for the hardness of $LiNbO_3$. Using a conversion formula given by Mott (1956), we get a value of 400 kg/mm^2 on the Vickers scale. Brown *et al* (1975) made Knoop hardness measurements on the (001) plane at a single load of 50 g and obtained an average value of 570 kg/mm^2. It may be mentioned that Knoop and Vickers hardness values generally agree to within 5% (Mott 1956). Brown *et al* (1975) also observed that there was no measurable anisotropy in the hardness on the (001) plane. Recently, Dhanraj *et al* (1994) reported measurements of Vickers hardness on the (001) plane, using crystals grown by them, and obtained a value of about 780 kg/mm^2 at a load of 50 g (same load as used by Brown *et al* 1975). Thus there is a scatter of values from 400–800 kg/mm^2 in the reported microhardness values.

The other discrepancy is related to the load dependence of hardness of $LiNbO_3$ observed by Dhanraj *et al* (1994). In ideal circumstances, measured hardness values should be independent of the applied load. But in practice, a load-dependence is observed. Typically, the measured hardness has a high value at very low loads. As the load is increased, there is a steep fall in the hardness. At still higher loads, the rate of fall in hardness with load decreases and, finally, the hardness becomes load independent. The load vs hardness curve is smooth. The cause of such load-variation, and the method to obtain the true hardness will be discussed later. Suffice it to mention that such load dependence is due to a systematic factor which is equivalent to a load correction. This correction, may vary from sample to sample, but is not related to the deformation mechanism in the crystal. Such load dependence has been observed in a variety of materials like metals (Mott 1956), ionic crystals (Pratap and Hari Babu 1980; Thirmal Rao and Sirdeshmukh 1991; Sirdeshmukh *et al* 1995; Sangaiah and Kishan Rao 1993), and minerals (Thirmal Rao and Sirdeshmukh 1994). Dhanraj *et al* (1994) observed that the microhardness of $LiNbO_3$ has a value of 700 kg/mm^2 at a low load of 20 g. In the load range 20–30 g, they observed a steep increase in hardness to nearly 900 kg/mm^2. At higher loads they observed a decrease in hardness with a value of 600 at 100 kg/mm^2. The increase in hardness in the 20–30 g load range was attributed to work-hardening and the decrease at higher loads to plastic flow. Thus, the load-dependence observed by Dhanraj *et al* (1994) is at variance with several earlier observations. Furthermore, the interpretation of the observed behaviour as due to two different deformation mechanisms in different load regions would have new implications on the indentation process in $LiNbO_3$.

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In view of these two discrepancies with regard to the true hardness of $LiNbO_3$ and the load dependence of hardness in $LiNbO_3$, it was considered desirable to undertake a systematic study of the hardness of $LiNbO_3$. In the present communication, we report a detailed study of the load-dependence of hardness on two crystals of $LiNbO_3$ of different origins, one of the crystals being from the same batch as used by Dhanraj *et al* (1994). A crystal of Fe-doped $LiNbO_3$ has also been included in the study.

2. Experimental

Pure lithium niobate ($LiNbO_3$) crystals (labelled A) were grown at the Indian Institute of Science, Bangalore, by the Czochralski method. The details of crystal growth are given elsewhere (Dhanraj *et al* 1994). They were oriented, cut and polished to reveal the (001) plane. Crystals of pure $LiNbO_3$ (labelled B_1) and $LiNbO_3$ doped with 0·02 wt% Fe (labelled B_2) were grown by the same method at the Solid State Physics Laboratory, Delhi, and had the same orientation as crystal A. The details of crystal growth are discussed by Thyagarajan (1989). While crystals A and B_1 were colourless, crystal B_2 had a yellowish tinge. These crystals are shown in figure 1. Hardness measurements were made on the (001) plane at several loads in the range 15–200 g using a Miniload Leitz-Wetzlar hardness tester fitted with a Vickers diamond pyramidal indentor. The microhardness was calculated from the relation

$$H_v = 1854{\cdot}4\, P/d^2, \tag{1}$$

where H_v is the microhardness in kg/mm^2, P the load in g, and d the length of the diagonal of the indentation measured in μ. At each load several indentations were made and the mean of the diagonal length was used. Though hard, $LiNbO_3$ crystals are brittle. As a result, cracks show up in indentations made at and above 100 g. Such crack formations have been observed by Brown *et al* (1975) and Dhanraj *et al* (1994). Both linear cracks along the diagonal of the impression and curved cracks along the edges of the indentation were observed. With some care, measurements could be made up to 200 g on samples A and B_1; whereas in sample B_2, the tendency to crack formation was more and measurements were limited to 100 g. The measured hardness values at a given load are consistent among themselves within 2%. In view of the report of Brown *et al* (1975) that there was no evidence of anisotropy of hardness on the (001) plane, no effort was made to maintain any definite orientation of the indentor on the (001) surface while making different indentations.

3. Results and discussion

The variation of hardness with load is shown in figure 2. The observed load dependence is similar to the typical load dependence described in § 1: a high hardness value at low loads, a steep fall at higher loads, followed by a slower decrease with load, and, finally, a practically load-independent behaviour. The load-independent behaviour is seen to occur beyond 100 g in samples A and B_1; in sample B_2, this region is not reached as measurements were limited to 100 g. It is to be noted that in all three samples, the load dependence is smooth.

Load variation of hardness of the type that has been observed can be interpreted in three different ways.

(i) Mott (1956) explains this type of load variation by assuming that the index of d (the Meyer index) in (1) is not 2 but some value less than 2. Equation (1) is obtained by defining hardness as the ratio of the applied load to the surface area of the indentation. A value other than 2 for the index of d strikes at this simple and meaningful definition of hardness.

(ii) Upit and Varchenya (1973) attribute this type of variation to the surface effect. The surface is harder than

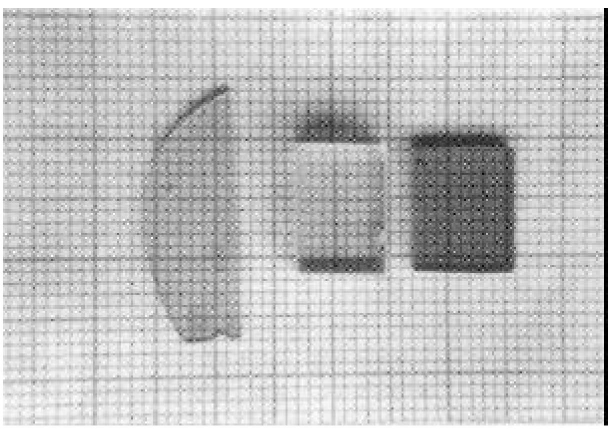

Figure 1. $LiNbO_3$ crystals used for indentation (L–R: sample A, sample B_1 and sample B_2).

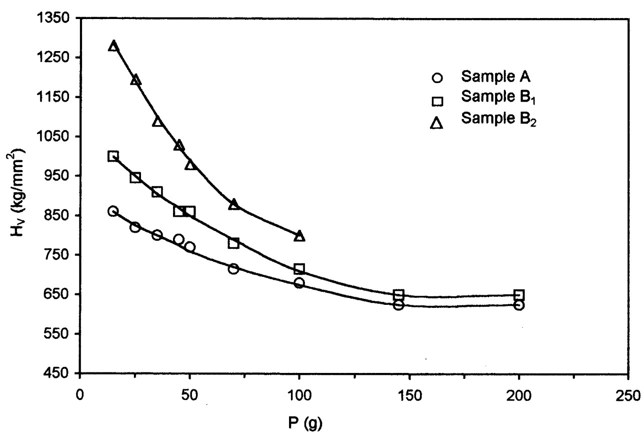

Figure 2. Plots of load P against hardness (H_v).

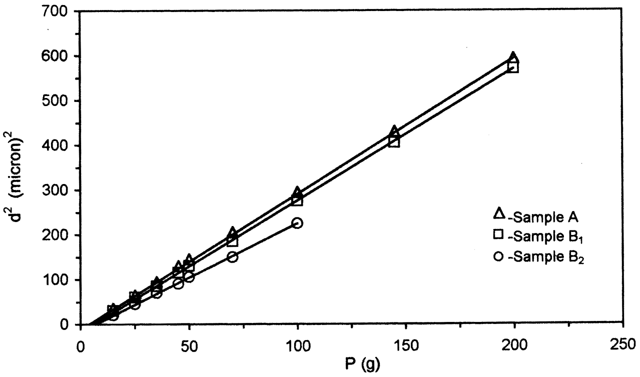

Figure 3. Plots of load P against d^2.

the bulk, and hardness measured close to the surface (low loads) tends to have larger values. The true bulk hardness can be obtained by applying a correction which needs measurement of the depth of the indentation or by making hardness measurements at very high depths (high loads) where the surface effects become negligible and hardness becomes load independent.

(iii) Hayes and Kendall (1973) suggested that the observed load dependence may be due to the fact that the sample offers a resistance to deformation in the form of a Newtonian pressure. This is effectively equivalent to a negative load W acting against the applied load P. Hayes and Kendall interpret W as the minimum load to be applied to cause indentation as at any lesser load plastic deformation will not take place. A plot of P vs d^2 will be a straight line whose intercept on the P-axis represents W. From this the true load-independent hardness (H_v^0) value can be evaluated by modifying (1) to:

$$H_v^0 = 1854{\cdot}4\,(P - W)/d^2. \qquad (2)$$

This last explanation of the observed load variation is simple and leads to meaningful estimates of the true bulk hardness. It reduces the cause of load variation to a systematic loading error. Furthermore, it is applicable to all crystals since it does not assume any particular deformation mechanism during indentation. Thirmal Rao and Sirdeshmukh (1991) have shown that the hardness value obtained from the flat region of P vs H_v curve, and that obtained by the W-correction agree to within 2%. Further, Thirmal Rao and Sirdeshmukh (1994) have also shown that this method can be applied even in cases where the P vs H_v curve does not reach the flat region.

The present results are analysed following the method of Hayes and Kendall (1973). The P–d^2 plots for the three samples are shown in figure 3. The values of the load correction W obtained from these plots are given in table 1. The values of the true hardness (H_v^0) are also given in the same table. It was mentioned in § 2 that each hardness measurement yielded a value with an internal consistency of 2%. However, on the basis of the underlying assumptions behind the method of analysis, a larger uncertainty of 5% in the (H_v^0) values of the two $LiNbO_3$ crystals is allowed. But, a still larger uncertainty of 7% is allowed for Fe-doped $LiNbO_3$, since the measurements were limited to a load of 100 g, and also since the flat region of the P–H_v plot could not be reached.

Table 1. Load correction (W) and true hardness (H_v^0) of $LiNbO_3$.

Material	Sample code	W (g)	(H_v^0) kg/mm^2
Pure $LiNbO_3$	A	4	630 ± 30
Pure $LiNbO_3$	B_1	7	620 ± 30
0·02% Fe-doped $LiNbO_3$	B_2	6	750 ± 50

The type of two-regime P–H_v plot, i.e. H_v increasing up to some load and then decreasing, observed by Dhanraj *et al* (1994), has not been observed in the present measurement. Instead, the P–H_v plots for all the three crystals are smooth monotonous curves showing the same trend viz. a large hardness value at low loads, followed by a steep fall with increasing loads, with a slower fall at still higher loads.

Based on measurements on two crystals of different origin, the true hardness value of $LiNbO_3$ is estimated as 630 ± 30 kg/mm^2 on the Vickers' scale and 5·6 on the Moh scale. The value of 570 kg/mm^2 obtained by Brown *et al* (1975) at 50 g load, and the value of 600 kg/mm^2 obtained by Dhanraj *et al* (1994) at 100 g load reconcile with the present value. The extreme values of 400 and 800 kg/mm^2 referred to in § 1 appear to have resulted from some unidentified error. The Fe-doped $LiNbO_3$ has a larger hardness value of 750 ± 50 kg/mm^2. The Fe impurity entering into the lattice impedes the movement of dislocations, thus enhancing the hardness. Such impurity-enhanced hardness has been observed by other workers (Pratap and Hari Babu 1980).

It is to be noted that though the load vs hardness plots for crystals A and B_1 nearly converge at high loads, there are large differences in the hardness values measured at low loads (note values of 865 and 1000 kg/mm^2 at $P = 15$ g for samples A and B_1, (figure 2)). This re-emphasizes the point made out by Thirmal Rao and Sirdeshmukh (1994) that hardness values of different crystals can be compared only when they have been evaluated from a systematic study of load variation.

4. Conclusions

Our studies on two samples of $LiNbO_3$ of different origins have shown similar load variation of hardness. The load variation is smooth, and is consistent with the idea that the sample offers a deformation resistance pressure which reduces the applied load by a constant quantity. The true hardness value of $LiNbO_3$, as determined, is

630 ± 30 kg/mm^2. The microhardness value of Fe-doped $LiNbO_3$, as determined, is 750 ± kg/mm^2.

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