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Knoop microhardness measurements on lithium niobate and lithium tantalate

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Knoop microhardness measurements were made on the (11.0), (01.0) and (00.1) planes of the trigonal isostructural compounds lithium niobate and lithium tantalate. The data indicate uniform hardness in the ⟨11.0⟩ and ⟨01.0⟩ directions and greater hardness in the [00.1] direction. In accordance with previous findings of hardness anisotropy in materials with hexagonal crystal structure, the present data indicate preferred slip on basal planes. The ratio of hardness to the shear modulus C_{66} is close to 0.1, which is usually found in covalent-bonded solids.

1. Introduction

The Knoop indenter, because of its geometry, provides a sensitive method of determining the anisotropic hardness of many interesting non-metallic single crystals. Recent studies have been made, for example, of the cubic alkali halides [1], alkaline earth fluorides [1], and certain cubic refractory carbides [2]. Furthermore, many hexagonal materials having the wurtzite structure have also been studied [3, 4]. In contrast, relatively little work has been done on materials crystallizing in the other symmetry groups. Accordingly the isostructural trigonal compounds lithium niobate and lithium tantalate were chosen for this study. Both materials are of current interest and have been extensively characterized as to their crystal structure [5, 6], ferroelectric [7, 8], optical [8], elastic and piezoelectric [9, 10] properties. Some Knoop hardness indentation data for lithium niobate have also appeared in the literature [11].

2. Experimental

A lithium niobate single crystal grown in the [00.1] direction and subsequently annealed at 1200°C was obtained from the Isomet Corporation, Oakland, N.J. Oriented wafers were cut from the boule and polished flat and parallel to within 10 μm. Final polishing using Syton HT-30, obtained from the Monsanto Co., St. Louis, Missouri, provided damage-free surfaces for indentation. The lithium tantalate samples were obtained through the courtesy of D. W. Rudd of the Merrimack Valley Works of the Western Electric Company. These wafers had also been annealed at 1200°C and were given the same final Syton polishing prior to indentation. All wafers were of nominally stoichiometric composition.

All indentations were made on a Kentron microhardness tester equipped with a Knoop diamond indenter and a micrometer eye piece. Preliminary tests using a 25 g load showed that this loading produced suitably long indentations in lithium niobate but was unsatisfactory for lithium tantalate. It was therefore decided to standardize on a 50 g loading with each indentation completed within 30 sec. Indentation lengths were measured at a magnification of × 500.

Indentations were made on the (01.0), (00.1) and (11.0) planes with the long axis of the indenter aligned in 10° increments from a reference direction up to 180° with five indentations for each angular position. In addition, because of scatter in the data, an average of twenty-five indentations were made for the major crystallographic directions. Knoop hardness numbers were calculated from the data and are reported along with their probable errors.

3. Results

Table I summarizes the average hardness measurements of about twenty-five indentations in several major directions. Those planes and directions where subsurface cracking was observed are indicated. These effects probably contributed only a minimal error to the hardness

numbers because of the light loading involved [12].

Table I shows that hardness values in the ⟨11.0⟩ and ⟨01.0⟩ directions on the (00.1) plane are about equal. These data were supported by studying the angular dependence of hardness on the (00.1) plane of both compounds which showed only random variations. The second study showed that the average Knoop hardness over all directions parallel to the basal plane is 600 ± 30 for lithium niobate and 750 ± 30 for lithium tantalate, in reasonably good agreement with the values shown in Table I. The [00.1] direction is thus about 25% harder than the other two directions. The data for $LiNbO_3$ compare quite well with those of Noda and Ida [11] at the 50 g loading, except that their value for the ⟨11.0⟩ direction on the {01.0} plane is 28% lower than our value.

TABLE I Knoop hardness data

System			
Direction	Plane	$LiNbO_3$	$LiTaO_3$
⟨11.0⟩	(01.0)	530* ± 10	660* ± 20
	(00.1)	560 ± 5	780 ± 10
⟨01.0⟩	(11.0)	570* ± 10	775* ± 5
	(00.1)	570 ± 5	760 ± 15
[00.1]	(11.0)	650 ± 15	920 ± 5
	(01.0)	780 ± 10	970 ± 20

Subsurface cracking.

Fig. 1 represents the combined results of several hardness experiments made on the (01.0) prism plane of lithium niobate. Knoop hardness is shown as a function of orientation of the long axis of the indenter from the ⟨11.0⟩ direction. Subsurface cracking was observed within a 30° interval of this orientation. The hardness increases smoothly to a rather broad maximum value of about 900 located near 120° from the ⟨11.0⟩ direction. Thus it appears that [00.1], which is located at 90°, is not the maximum hardness direction. Fig. 2 shows the corresponding plot for lithium tantalate which

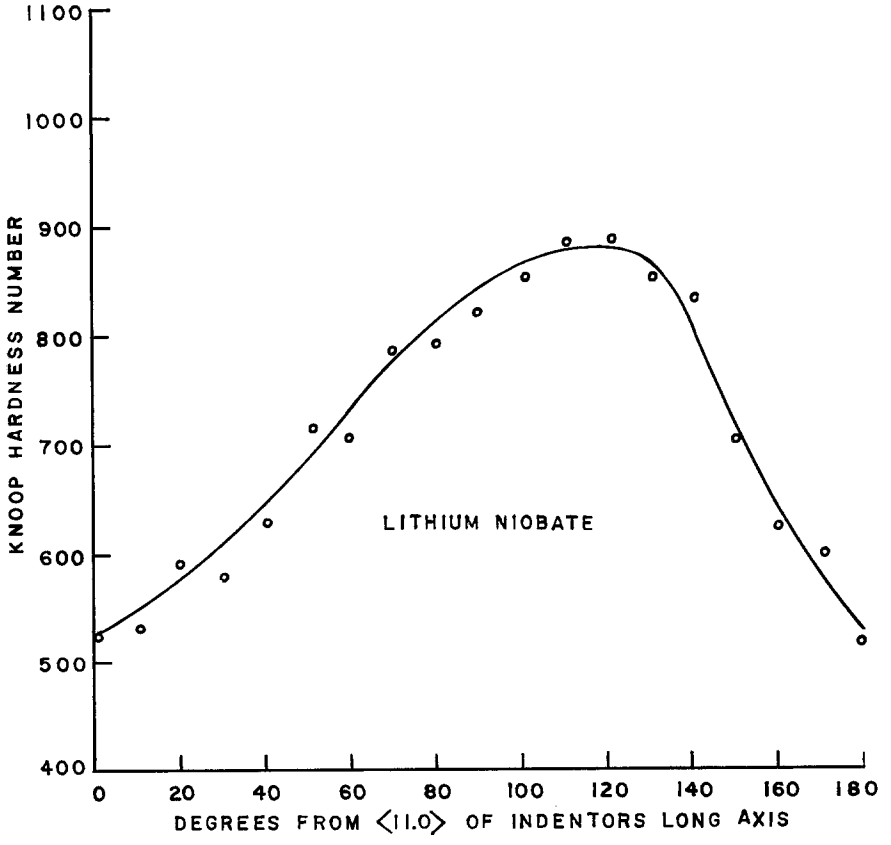

Figure 1 Knoop hardness variation on the (01.0) plane of lithium niobate as a function of angle from the ⟨11.0⟩ direction.

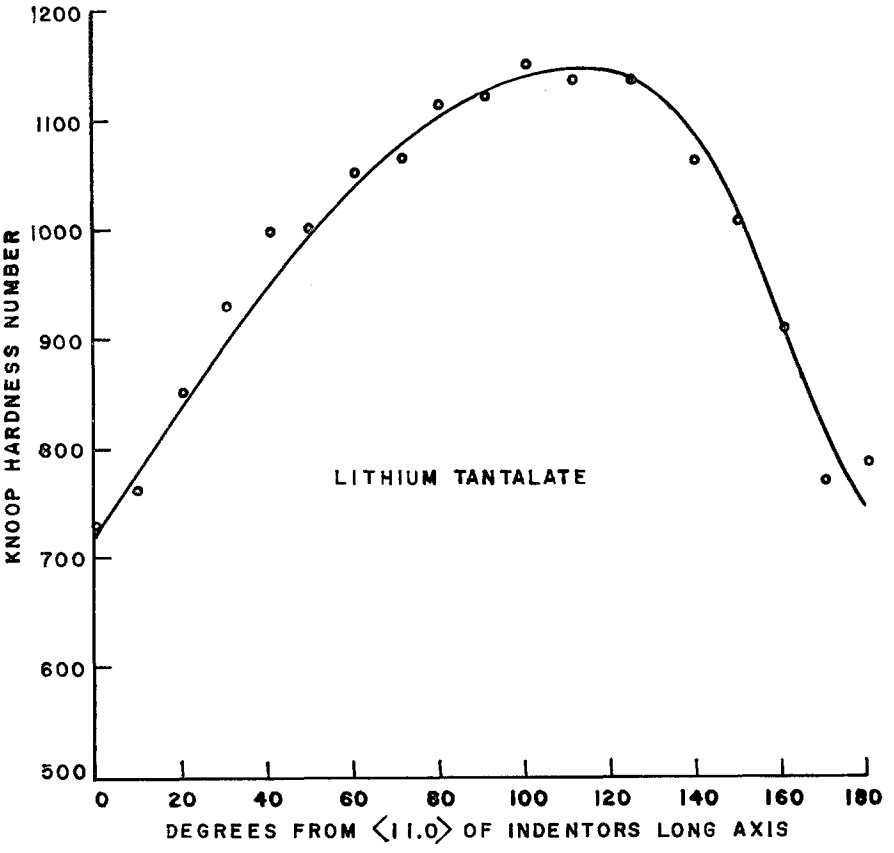

Figure 2 Knoop hardness variation on the (01.0) plane of lithium tantalate as a function of angle from the ⟨11.0⟩ direction.

also has a broad maximum hardness value of about 1100.

4. Discussion

Both lithium niobate and lithium tantalate crystallize in the space group *R3c* and their lattice parameters differ by less than 1% [5]. The nature of the chemical bonding of the Nb–O and Ta–O bonds is highly covalent, with Ta–O more so [13, 14]. This is perhaps reflected in the higher melting point and generally greater values of the elastic constants for $LiTaO_3$. Previously one of us showed that the ratio of hardness to shear modulus is about 0.1 for covalent-bonded solids as compared with a value about 0.001 for metals [15]. The shear modulus C_{66} has a value of $\sim$ 7500 and $\sim$ 9500 kg mm^{-2} for $LiNbO_3$ and $LiTaO_3$ respectively [9, 10]. (The units were chosen to conform with the hardness numbers which are in units of kg mm^{-2}.) Hence for a range of hardness values H = 570 to 800 kg mm^{-2} for $LiNbO_3$ and 770 to 1000 kg mm^{-2} for $LiTaO_3$, the ratio $H/C_{66} \sim$ 0.08 to 0.11. Such a large ratio, as found with other covalent-bonded solids, is in agreement with the theoretical and experimental picture noted above [13, 14].

The observation that there is practically no hardness anisotropy on the basal plane and that the anisotropy is greatest on the prism planes is in general agreement with past findings in solids with hexagonal crystal structure. Brookes *et al.* [16] have pointed out the correlation that the *c*-axis is the hardest direction if deformation occurs mainly by slip on basal planes, whereas it is the softest direction if slip occurs mainly on prism planes. Since the *c*-axis is the hardest direction in both $LiNbO_3$ and $LiTaO_3$, such correlation suggests that basal slip is favoured at room temperature for the two compounds. Basal slip is generally favoured in materials with a large *c*/*a* lattice parameter ratio. This ratio has favourably large values of 2.69 and 2.67 for $LiNbO_3$ and $LiTaO_3$ respectively [5].

5. Summary

(1) The Knoop hardness number of $LiNbO_3$ has an average value of 570 for the basal plane and 800 normal to the basal plane. The corresponding values are 770 and 1000 for $LiTaO_3$.

(2) There is some indication that the hardness maximum occurs in a direction around 30° from the *c*-axis.

(3) In accordance with previous findings in hexagonal materials, the present hardness data suggest preferred slip on basal planes in both compounds.

(4) The ratio of hardness to shear modulus C_{66} is close to 0.1, in line with other covalent-bonded solids.

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