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Hardness anisotropy and its dependence on composition in sodium tungsten bronzes and rhenium trioxide single crystals

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Hardness anisotropy measurements using a Knoop diamond indenter on {0 0 1} and {0 1 1} surfaces of Na_xWO_3 ($0.4 < x < 0.8$) and ReO_3 single crystals with the cubic perovskite structure show that hardness is determined by slip on {1 1 0}⟨1 1 0⟩. Room temperature slip is produced by Knoop and Vickers microhardness indentations on polished crystals and confirms the active slip system identified from a consideration of anisotropy. The hardness anisotropy is more pronounced as the sodium content of the crystals increases. The data suggests that hardness of Na_xWO_3 is dependent on both plane and direction.

1. Introduction

In a concurrent study concerned with the relationship between electron band filling and microhardness in cubic sodium tungsten bronzes, Na_xWO_3, ($0.4 < x < 0.75$), it was found that only single crystal samples revealed any such relationship. Only when the Knoop diamond long axis was aligned along the ⟨1 1 0⟩ direction on {0 0 1} planes was the hardness sensitive to composition [1]. Thus in order to investigate the dependence of hardness on composition for the cubic sodium tungsten bronzes with the perovskite structure it was necessary to study the variation in hardness anisotropy of {0 0 1} crystal faces. It is known in other systems that changes in slip plane preference do occur as the degree of non-stoichiometry changes, for example TaC_x changes preference from {1 1 1} to {1 1 0} with decreasing carbon content [2].

Brookes *et al.* [3], who have modified the Daniels and Dunn equation [4], have shown that in favourable cases active slip systems in crystals can be identified by consideration of anisotropy behaviour. Later work [5–7] has confirmed the agreement between hardness anisotropy and mean effective resolved shear stress, τ_e, calculated as a function of indenter orientation for the active slip system. By pointing to a correlation between hardness anisotropy and τ_e for a wide range of crystals the method of Brookes seem quite general. Apparent anomolies noted by Chin [7] who found different anisotropy behaviour for 2 groups of crystals all with the same crystals structure and slip mode have been explained by Brookes [8] as an indentation creep phenomenon. It was thought that an extension of such studies to another cubic system, namely the perovskite sodium bronzes, might further help to demonstrate the general nature of the Brookes analysis.

The sodium tungsten bronzes are interesting materials with which to probe relationships between properties, structure and composition since the structure is governed by the WO_3 matrix. Tungstic oxide itself has a distorted version of the cubic ReO_3 structure which in turn is represented as a corner-shared framework of ReO_6 octahedra. The distortions are of two kinds: ferroelectric-type displacements of tungsten atoms from the cubic positions and tilting of the octahedra, so that at room temperature the symmetry of WO_3 is monoclinic [9, 10]. As the temperature increases the distortions are gradually removed and the lattice becomes orthorhombic at about 320° C and tetragonal at 720° C [11]. There is also a less well

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authenticated transition at a higher temperature [12]. Each structure modification has a unit cell which is a multiple of the basic 3.8 Å cubic ReO_3-type unit cell.

The increase in the symmetry of the WO_3 structure is also accomplished by the insertion of sodium atoms so that above $x = 0.37$ in Na_xWO_3 all the bronzes so formed have the cubic perovskite structure. Such a wide composition range within the same structure type makes the system very suitable for studies concerned with the variation of physical properties with composition. As the sodium content is increased through the cubic region the WO_3 matrix expands gradually. The dependence of lattice parameter on sodium content has been shown to be linear [13] and bronze compositions can be determined from the relationship

$$a_0 = 0.0819x + 3.7846 \text{ Å}$$

Having prepared a number of crystals of the sodium bronzes it was the aim of the present work first to extend the data available on hardness anisotropy of cubic crystals and to test the applicability of the Brookes method for determining the slip systems in these materials. Second to determine how the hardness anisotropy varies with the degree of non-stoichiometry and finally to see if the microhardness depends on the plane of indentation as well as the direction of the long axis of the indenter.

2. Experimental

Sodium bronze single crystals were prepared by electrolytic reduction of sodium tungstate–tungstic oxide melts by the method already described [1]. ReO_3 single crystals were prepared by an iodine transport method in a manner similar to that of Ferretti [14].

Sodium content of the bronzes was determined from the lattice parameters by using the Brown and Banks equation [13]. Nickel filtered copper radiation and an 11.46 cm Debye–Scherrer camera or a back reflection Guinier camera using a tungsten powder internal standard were used to obtain the cubic lattice parameters. Orientation analysis was achieved by the back-reflection Laue X-ray technique using Mo radiation.

Microindentations were made on polished crystal faces with a Leitz Miniload hardness tester using a Knoop diamond indenter and measured directly with a calibrated eyepiece. A load of 200 g was chosen as the standard for all tests after a study had been made of the effects of load and surface treatment on the consistency of hardness results. The average Knoop hardness data collected were derived from between 4 and 20 measurements for each orientation using up to four bronze crystals for each composition. Use was also made of a Vickers diamond indenter in order to add to the evidence for slip system orientation based on observation of slip lines around indents.

3. Results

All the bronze crystals examined showed marked anisotropy. For $\{0\,0\,1\}$ faces this was of a simple nature with $\langle 1\,1\,0\rangle$ directions being harder than $\langle 1\,0\,0\rangle$, the difference in H_K being about 45%. For $\{0\,1\,1\}$ faces the behaviour was more complex demonstrating the two-fold symmetry of these planes as opposed to the four-fold symmetry of $\{0\,0\,1\}$ planes. Hardness increased in the sequence $\langle 1\,0\,0\rangle$:$\langle 2\,1\,\bar{1}\rangle$:$\langle 1\,1\,\bar{1}\rangle$ and $\langle 0\,1\,\bar{1}\rangle$ with the last two being approximately equal. The average hardness values for important directions are shown in Table I.

TABLE I Knoop hardness data for crystals examined

Composition x in Na_xWO_3	Hardness H_K (kg mm^{-1})									
	$\{0\,0\,1\}$		$\{0\,1\,1\}$				$\{0\,3\,2\}$			
	$\langle 1\,0\,0\rangle$	$\langle 1\,1\,0\rangle$	$\langle 1\,0\,0\rangle$	$\langle 2\,1\,\bar{1}\rangle$	$\langle 1\,1\,\bar{1}\rangle$	$\langle 0\,1\,\bar{1}\rangle$	$\langle 1\,0\,0\rangle$	$\langle 2\,2\,\bar{3}\rangle$	$\langle 1\,2\,\bar{3}\rangle$	$\langle 0\,2\,\bar{3}\rangle$
0.515	475 ± 52	707 ± 57	445 ± 18	617 ± 25	685 ± 27	693 ± 28	–	–	–	–
0.601	500 ± 55	758 ± 68	391 ± 27	604 ± 42	671 ± 47	653 ± 46	–	–	–	–
0.691	501 ± 45	782 ± 63	452 ± 47	575 ± 61	718 ± 53	766 ± 33	–	–	–	–
0.707	491 ± 12	796 ± 70	–	–	–	–	532 ± 20	758 ± 19	748 ± 19	753 ± 33
0.750	497 ± 50	844 ± 34	–	–	–	–	–	–	–	–
0.800	547 ± 19	809 ± 36	–	–	–	–	–	–	–	–
ReO_3	555 ± 30	579 ± 40	–	–	–	–	–	–	–	–
WO_3*	142 ± 40	–	–	–	–	–	–	–	–	–

*WO_3 has monoclinic symmetry and since only twinned crystals were obtained it was not possible to orient them. This result represents the average of 36 indents made at random on polished crystal faces at 10° increments.

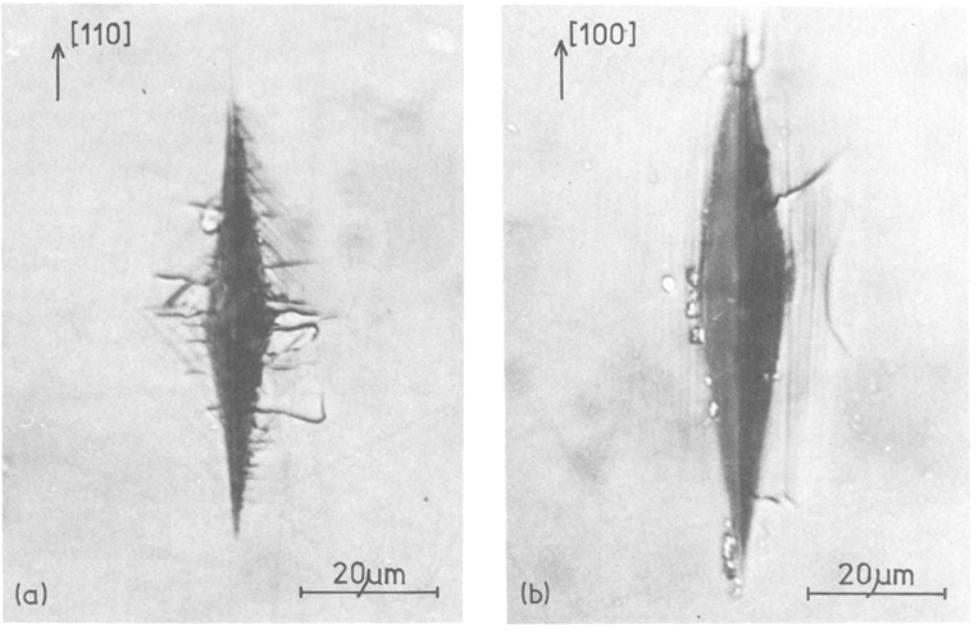

Figure 1 Knoop indents produced by a 200 g load on a (0 0 1) crystal face of $Na_{0.75}WO_3$. (a) Along [1 1 0]. (b) Along [1 0 0].

In several cases for {0 0 1} faces cracking and conchoidal fracture were sometimes observed when the indenter was oriented in the hardest direction, while for {0 1 1} faces cracking occurred when oriented in the softer directions, within about 45° on either side of [1 0 0]. Cracks in {0 1 1} often lay in ⟨0 $\bar{1}$ 1⟩ directions. Micrographs of cracked indents on a (0 0 1) face of $Na_{0.75}WO_3$ are shown in Fig. 1. These also show slip lines produced by the indentation process.

Hardness versus orientation plots such as those shown in Fig. 2 revealed that for {0 0 1} faces the hardness of the ⟨1 1 0⟩ directions and the degree of anisotropy increases with the value of x in Na_xWO_3. No variation in $H_{K\langle 1\,0\,0\rangle}$ with composition could be discerned however. The composition dependence of H_K is shown in Fig. 3. Data for ReO_3, which has the same structure as the hypothetical cubic WO_3 (with only a 1% decrease in cube parameter) and the same electronic structure as $Na_{1.0}WO_3$, is also given in Fig. 3. It appears to be almost isotropic and to have a mean hardness value close to that extrapolated for cubic WO_3.

4. Discussion

The observed anisotropy on {0 0 1} and {0 1 1} faces illustrated in Fig. 2 is very similar to that found by Brookes *et al.* [3] for crystals with the rock salt structure and {1 1 0}⟨1 $\bar{1}$ 0⟩ slip systems. On {0 0 1} faces MgO showed a difference in H_K between ⟨1 1 0⟩ and ⟨1 0 0⟩ directions of about 65%, whereas LiF only showed a 10% difference. The bronze crystals in this investigation showed a 40 to 50% difference. Of the six cubic slip systems treated theoretically by Brookes only one, {1 1 0} ⟨1 $\bar{1}$ 0⟩, gives the type of anisotropy observed for the sodium bronze crystals.

The visual evidence from the slip lines apparent in Figs. 1 and 4 is not at variance with the assignment based on anisotropy. All slip lines lie in ⟨1 0 0⟩ directions irrespective of indenter orientation and in the examples of Figs. 1 and 4 with (0 0 1) faces and ⟨1 0 0⟩ slip traces, the slip planes must belong to a (1 0 0) zone. Of the various possibilities the most likely low-index slip planes are of the type {0 1 1} or {0 1 0}.

Dekker and Rieck [15] have suggested that crack directions around indenters are determined by directions of intersections of sets of slip planes and therefore this might provide further evidence as to which slip systems operate. However in this work such a relationship could not always be confirmed, as shown in Fig. 4b.

A notable feature of the bronze results is the way that the hardness anisotropy becomes more

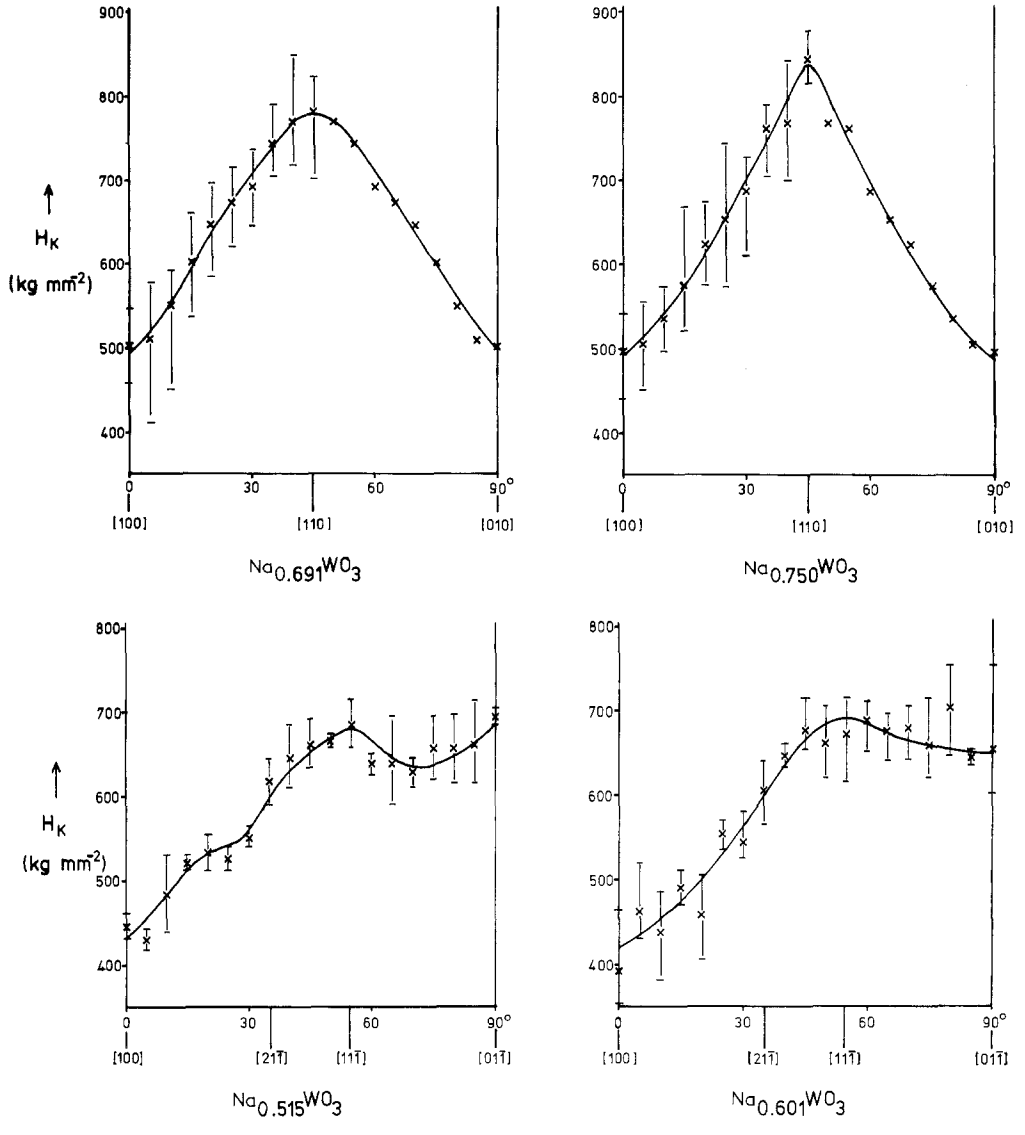

Figure 2 Knoop hardness versus orientation plots for $Na_{0.691}WO_3$ and $Na_{0.75}WO_3$ on $\{0\,0\,1\}$ planes and $Na_{0.601}WO_3$ and $Na_{0.515}WO_3$ on $\{0\,1\,1\}$ planes.

obvious as the sodium content of the crystals is increased. When the sodium content is reduced to zero as in the isostructural ReO_3, which is furthermore isoelectronic with $Na_{1.0}WO_3$, the degree of anisotropy becomes very small. These observations have been explained in terms of the electronic band structure of these oxides [1].

The most likely slip planes in a structure are those with the densest packing of atoms, so for the perovskite $NaWO_3$ the most likely are $\{1\,0\,0\}$, $\{1\,1\,0\}$ and $\{1\,1\,1\}$. Similarly the most likely slip directions are those in which atoms are most closely spaced. For $NaWO_3$ the shortest Burgers vectors for perfect dislocations are $\langle 1\,0\,0\rangle$, $\langle 1\,1\,0\rangle$ and $\langle 1\,1\,1\rangle$. Only six combinations of these slip planes and directions are possible and lead to the following slip systems: $\{1\,0\,0\}\langle 0\,1\,0\rangle$; $\{1\,0\,0\}\langle 0\,1\,1\rangle$; $\{1\,1\,0\}\langle 0\,0\,1\rangle$; $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$; $\{1\,1\,0\}\langle \bar{1}\,1\,1\rangle$ and $\{1\,1\,1\}\langle 1\,\bar{1}\,0\rangle$. Consideration of these systems in terms of the relative configurations that the atoms have to pass through before movement along the lattice vector is completed and the structure becomes continuous across the slip plane again leads to an order of probability. In order to achieve this the distances of closest approach must be calculated. A cubic cell parameter of 3.867 Å

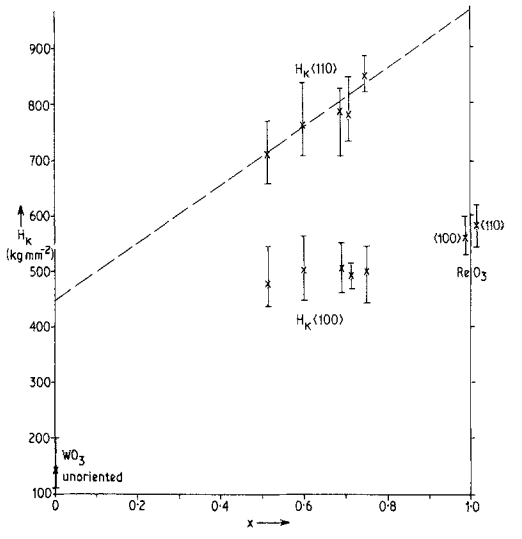

Figure 3 Knoop hardness of $\{0\,0\,1\}$ faces of Na_xWO_3 and ReO_3 crystals.

for $NaWO_3$ is assumed on the basis of the Brown and Banks equation. Shannon and Prewitt [16] give 1.40 Å and 0.58 Å as the ionic radii of six coordinate O^{2-} and W^{6+} respectively. The effective radius of Na^+ in a bronze 12-coordinate site was calculated by subtracting the O^{2-} ion radius from the lattice vector $\frac{1}{2}\langle 1\,1\,0\rangle$ which gives 1.33 Å and compares well with Shannon and Prewitt's value of 1.32 Å for 9-coordinate Na^+. Using these values the critical ionic radii sums shown in Table II are obtained.

Slip of the type $\{1\,0\,0\}\frac{1}{2}\langle 0\,1\,0\rangle$, $\{1\,1\,0\}\frac{1}{2}\langle 0\,0\,1\rangle$ and $\{1\,1\,0\}\frac{1}{2}\langle \bar{1}\,1\,1\rangle$ all produce Na^+–O^{2-} and O^{2-}–O^{2-} distances of $\frac{1}{2}\langle 1\,0\,0\rangle = 1.93$ Å which is considerably less than the critical values in Table II. $\{1\,1\,0\}\frac{1}{2}\langle 0\,1\,1\rangle$ and $\{1\,1\,1\}\frac{1}{2}\langle 1\,\bar{1}\,0\rangle$ slip produce

TABLE II Critical ionic radii sums for ions in sodium tungsten bronzes

Ion pair	Distance* (Å)
O^{2-}–O^{2-}	2.80
Na^+–O^{2-}	2.73
Na^+–Na^+	2.66
Na^+–W^{6+}	1.91
W^{6+}–W^{6+}	1.16

*Values of [16] used.

Na^+–W^{6+} distances of 1.93 Å which is very close to the critical value of 1.91 Å but this involves bringing Na^+ and W^{6+} into close conjunction. The remaining system is $\{1\,1\,0\}\frac{1}{2}\langle 1\,\bar{1}\,0\rangle$ which produces Na^+–Na^+ distances at $\frac{1}{2}\langle 1\,1\,0\rangle = 2.73$ Å which although approaching the radii sum of 2.66 Å appears to provide the least steric or repulsive hindrance to slip.

Even though derived for stoichiometric $NaWO_3$, bronzes with $x < 1.0$ should not produce a different conclusion than that $\{1\,1\,0\}\langle 1\,\bar{1}\,0\rangle$ is the most likely active slip mode for the cubic sodium bronzes. This choice coincides with the choice indicated by the experimental results and comparisons with calculated effective resolved shear stress curves.

A final observation that can be made from a consideration of these results is that Knoop hardness of cubic tungsten bronzes is probably dependent on both the plane and direction. The results for the $x = 0.601$ sample definitely show this whilst the other crystals are only equal for $\langle 1\,0\,0\rangle$ at the limit of their uncertainties. This is in contrast to the more commonly observed feature in Knoop hardness studies that hardness is dependent only on the direction of indentation. This feature

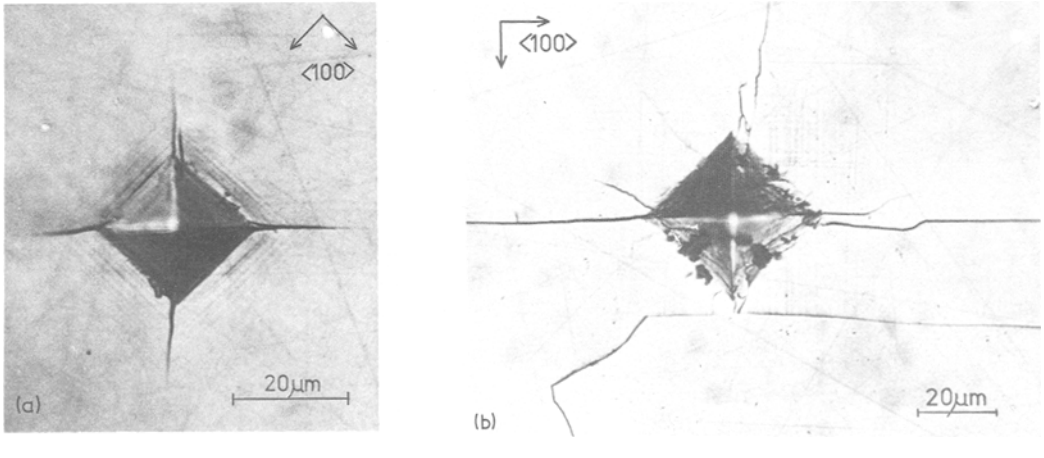

Figure 4 Vickers indents on a (0 0 1) face of $Na_{0.75}WO_3$ showing slip traces and cracks. (a) 200 g load; (b) 500 g load.

was first reported by Garfinkle and Garlick [17] and later confirmed by studies on LiF, MgO, CaF_2, Al_2O_3 [3] and SrF_2, BaF_2, NaCl, AgCl [7]. However more recent work, together with the present study, has shown that this may not be a universal rule, in that $LiNbO_3$, $LiTaO_3$ [18] and InP [6] show variations in hardness of up to 18% for the same directions on different planes. In fact even Garfinkle and Garlick's data for titanium shows a similar variation.

5. Conclusions

(1) The Knoop hardness anisotropy of sodium tungsten bronze crystals becomes more apparent as the sodium content increases in the range $0.4 < x < 0.75$. This is a reflection of the fact that hardness is only sensitive to composition when measured in $\langle 1\,1\,0 \rangle$ on $\{0\,0\,1\}$.

(2) Single crystals of ReO_3 show only a small degree of anisotropy in KHN.

(3) The active slip system in the crystals as obtained by comparison of observed anisotropy with calculated τ_e versus indenter orientation plots is $\{1\,1\,0\}\langle 1\,\bar{1}\,0 \rangle$.

(4) The slip lines visible on polished single crystals support a $\{1\,1\,0\}$ assignment and a simplistic consideration of the perovskite crystal structure leads to a $\{1\,1\,0\}\langle 1\,\bar{1}\,0 \rangle$ assignment.

(5) The Knoop hardness is dependent on both the direction and plane of indentation.

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