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Microhardness studies on as-grown faces of $NaClO_3$ and $NaBrO_3$ crystals

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Abstract. **Single crystals of $NaClO_3$ and $NaBrO_3$ are grown from their aqueous solutions at a constant temperature of 35°C by slow evaporation by using good quality seed crystals. Systematic microhardness studies are made on as-grown faces of these crystals at various loads. Typical cracks are observed at the corners of the impressions in $NaClO_3$ whereas in addition to the cracks at the corners microcracks also appeared in $NaBrO_3$ crystals around the impressions. The impressions formed in $NaBrO_3$ are not very clear as in $NaClO_3$, a possible mechanism for it is discussed. The work hardening index number (n) for both these crystals is around 1·6 suggesting that these are moderately harder samples. The hardness studies point out that $NaBrO_3$ is harder than $NaClO_3$ ($\Delta H \approx 100$ kg/mm^2), this could be due to strong inter ionic forces acting between Na–Br in $NaBrO_3$ crystals. Using Gilman's empirical relation, hardness values are calculated from the values of elastic constants (C_{44}) and are found to be close to the experimental results.**

Keywords. **Microhardness; indentation; $NaClO_3$; $NaBrO_3$.**

1. Introduction

$NaClO_3$ and $NaBrO_3$ are isomorphous crystallizing in enantiomorphic point group 23. Beurskens-Kerssen *et al* (1963) pointed out that $NaClO_3$ and $NaBrO_3$ crystals of same chirality have opposite sense of optical rotation. Further it is interesting to note that $NaClO_3$ grows in cubic form whereas $NaBrO_3$ grows in pyramidal form bounded by (111) faces when grown at room temperature (Holden and Singer 1968). These crystals exhibit some important properties like optical activity (Chandrasekaran and Mohanlal 1976), ferroelectricity and piezoelectricity (Mason 1946).

Although considerable amount of work is reported on physical properties like elastic constants (Bechmann 1951; Radha and Gopal 1967), thermal expansion (Sharma 1950) etc but meagre amount of information is available on hardness, which is an important strength parameter (Haussuhl 1964; Hussain *et al* 1988). Physically speaking hardness is the resistance offered by the crystal for the movement of dislocations and practically it is the resistance offered by the crystal for localized plastic deformation. Hardness testing provides useful information about the mechanical properties like elastic constants (Wooster 1953), yield strength (Westbrook 1958) etc. The most common method of hardness measurements is indentation type. In this, an indenter is pressed on the surface of a specimen, after removal, it leaves an impression according to the indenter used. The hardness is estimated from the ratio of the load applied on indenter to the area of the impression left on the specimen. From this, we are expected to get a constant value for hardness at any load. But in practice, a load dependence is observed showing higher hardness values at low loads and it decreases as the load is increased, finally becomes load independent. Such a load dependence has been observed in a variety of materials like metals (Mott 1956), alkali halides (Pratap and Hari Babu 1980; Rao and Sirdeshmukh 1991) and alums (Sangaiah and Kishan Rao 1993). In some cases, though few, a different trend of initial increase of hardness with increase in load then followed by a decrease and finally hardness becoming load independent at higher loads, was also observed (Pandya and Shah 1981; Seal *et al* 2001). Hence, it is necessary to study the load variation of hardness for every sample to give its actual hardness value. Perhaps this could be the reason to observe different hardness values for the same sample in the literature. Similar observations are made on $NaClO_3$ and $NaBrO_3$ also (table 1). In view of this problem, a systematic study of hardness has been undertaken on these crystals (after procuring the instrument) in this laboratory and this work is in continuation of our programme on growth and characterization of these crystals.

2. Experimental

$NaClO_3$ and $NaBrO_3$ crystals are grown from their aqueous solutions by slow evaporation at 35°C. Deionized

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double distilled water and analytical reagent grade salts supplied by E Merck with 99·5% purity are employed in the present studies. All the crystals are grown by keeping seed crystals on the base of the jar. Crystals of size 8–10 mm are obtained in one week.

It is difficult to make indentations on as-grown (111) faces of $NaBrO_3$ crystals because of its opposite face i.e. apex grows mostly with small $(\bar{1}\,\bar{1}\,\bar{1})$ faces or with sharp tips. Hence the apex part has to be cut and ground parallel to (111) faces. But this process generates a number of dislocations, which affect the true hardness of the samples. Hence a simple gadget has been fabricated with some hard wooden material of size $2{\cdot}5 \times 2{\cdot}5 \times 2{\cdot}0$ cm^3 shown in the line diagram (figure 2). Different sizes of hollow pyramids are made by cutting the top of wooden blocks such that the crystals can fix into the hollow pyramids. In this manner a number of different sizes of hollow pyramidal gadgets are prepared so that the crystals can fix properly into any one of them.

Microhardness measurements are made using Leitz–Wetzlar miniload hardness tester, fitted with a diamond pyramidal Vicker's indenter. Hardness values are estimated from the expression

$$H = 1854{\cdot}4\ P/d^2\ \text{kg/mm}^2,$$

where P is the load applied on indenter in g and d the diagonal length of the impression in μm. In view of the scattering in hardness data, a number of indentations are made for each load and each value is atleast the average of ten close measurements.

Table 1. Hardness data on $NaClO_3$ and $NaBrO_3$ crystals.

	Hardness (kg/mm^2)			
Crystal	Present values	Haussuhl's values	Hussain *et al* values	Work hardening index (n)
$NaClO_3$	135	123	117	1·68
$NaBrO_3$	236	195	215	1·62

3. Results and discussion

3.1 *Load variation of hardness*

Figures 1a–b show the as-grown crystals of $NaClO_3$ and $NaBrO_3$. Figure 1c shows the top view of major (111) face of $NaBrO_3$ crystal. Photograph is taken after grinding and polishing the opposite $(\bar{1}\,\bar{1}\,\bar{1})$ face i.e. apex side. This photograph shows the transparency of $NaBrO_3$ crystals which cannot be revealed in pyramidal form.

Figure 3 shows the load variation of hardness for these crystals. The observed load dependence is similar to the typical load dependence described in § 1. Clear load independence behaviour is observed in $NaClO_3$ beyond a load of 40 g whereas such a clear load independence region could not be reached in $NaBrO_3$ crystals as the measurements were limited to 40 g only due to the indentation problems.

Figure 4a shows the indentation mark on (100) face of $NaClO_3$ at a load of 15 g, the impressions are accompanied by long cracks at the corners. Figure 4b shows typical indentation mark on (111) face of $NaBrO_3$ crystal at a load of 30 g. It is interesting to note that the surface around the indentation is affected by microcracks seen as white spots in the photograph, these are formed in addition to the cracks at the corners of impression. Further, it is important to mention that the microcracks around the impression initiate around a load of 15 g only in $NaBrO_3$ and they tend to increase with increase in load and dominate the region around it. This causes difficulty in the accurate measurement of the diagonals of the impression at higher loads. Hence hardness studies were limited to 40 g only in $NaBrO_3$, due to this reason clear load independent region could not be reached. Yet, a stabilizing trend is observed from a load of 30 g. The present load independent hardness values are 135 and 236 kg/mm^2 for $NaClO_3$ and $NaBrO_3$, respectively.

In view of the discrepancy in the hardness data on these two crystals, indentation studies have been made on atleast fifty crystals of each type in the load independent region. The hardness data is shown by histograms (figure 5).

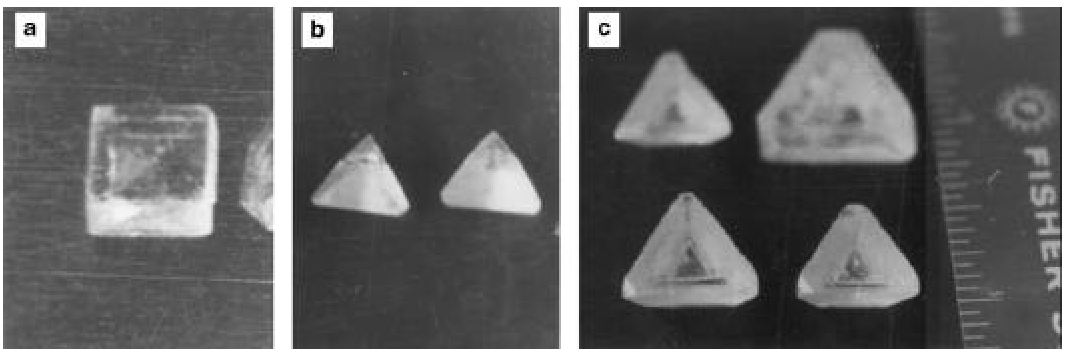

Figure 1. As-grown crystals of **a**. $NaClO_3$ and **b**–**c**. $NaBrO_3$ (**a** & **b** mag × 1·2, **c** top view of (111) face of $NaBrO_3$).

These diagrams show that maximum number lie in the range of 133–136 kg/mm^2 and 233–237 kg/mm^2 in $NaClO_3$ and $NaBrO_3$, respectively. These results suggest that the load independent values are around 135 and 236 kg/mm^2 for $NaClO_3$ and $NaBrO_3$, respectively. Now an attempt has been made to compare these results with the earlier results shown in table 1. It is interesting to note that the present values are higher than the earlier reported values. The present hardness value of 135 kg/mm^2 for $NaClO_3$ is slightly close to the value of 123 kg/mm^2 of Haussuhl (1964) with a deviation of about 9% whereas the present value of 235 kg/mm^2 of $NaBrO_3$ is close to Hussain *et al* (1988) results with a deviation of about 10%. Hence it is necessary to indicate the hardness value from the load independent region only.

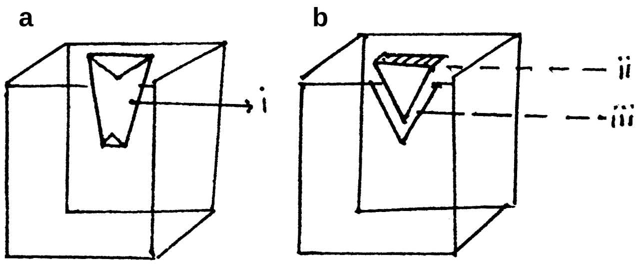

Figure 2. Line diagram of wooden gadgets to hold pyramidal crystals **a**. without crystal and **b**. with crystal (i and iii, hollow pyramidal space and ii, crystal).

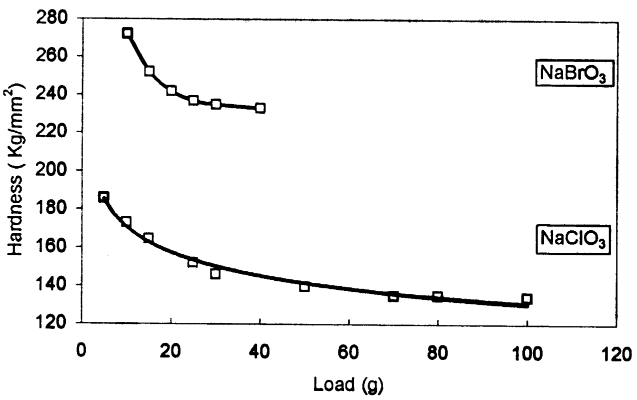

Figure 3. Load variation of hardness on as-grown faces of $NaClO_3$ and $NaBrO_3$.

3.2 *log P vs log d plots*

The relationship between load and size of indentation is given by Meyer's law, $P = ad^n$, where P is the load, d the diagonal length of impression, 'a' and 'n' are constants for a particular material. Figure 6 shows the log P vs log d plot, from the slopes the values of n have been estimated which give the Meyer index number (n) or called as work hardening index. The value of n is expected to be 2 but most of the experimental data show that it is always less than 2. Onitsch (1947) and Hanneman (1941) from careful observations on various materials pointed out that n lies between 1 and 1·6 for hard materials and it is more than 1·6 for soft materials. The 'n' values observed in the present studies are just around 1·6 suggesting that $NaClO_3$ and $NaBrO_3$ are moderately harder substances.

3.3 *Nature of impressions on different crystals*

An attempt has been made here to understand the nature of indentation impressions i.e. why some crystals produce sharp and clear impressions and why some do not. For this, a number of crystals available in this laboratory are taken and indented above load independent region, now the impressions are carefully studied. Then the crystals are divided into different groups depending on their hardness as shown in table 2. It is interesting to note that the crystals in group A show sharp, well defined impressions. The crystals in group B produce moderately good impressions but are accompanied by cracks at their corners, still the measurements can be made accurately. The impressions of group C materials are not well defined as in A and B, apart from the cracks at the corners, microcracks are also formed around the impressions, which may be responsible for disturbance of the material around

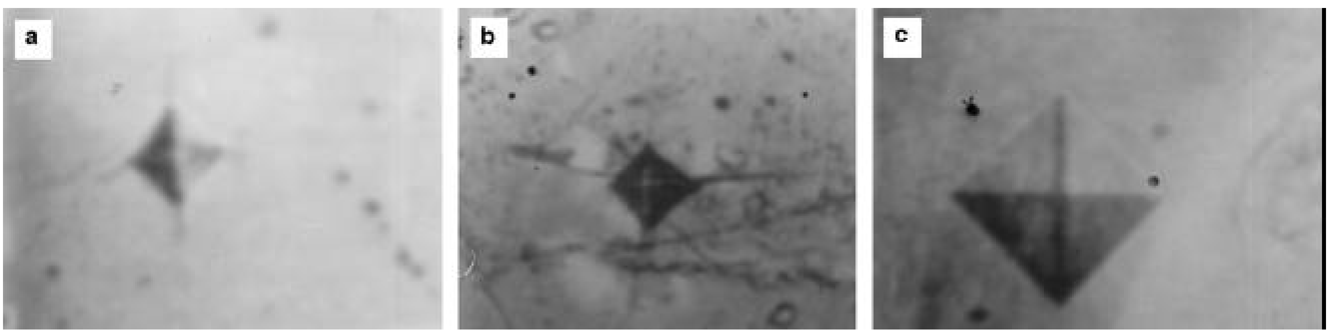

Figure 4. Indentation photographs (magnification **a**–**b**. × 220 and **c**. × 150). **a**. On (100) face of $NaClO_3$, load, 15 g; **b**. on (111) face of $NaBrO_3$, load, 30 g; and **c**. on (100) face of KCl, load, 15 g, given to show the clarity of impression in group A crystals.

it, due to that multiple reflections occur around the impression (figure 4b) and it causes difficulty in the accurate measurement of the impressions.

Initially it was felt that the crystals which possess cleavage planes may produce good impressions (figure 4c). But NH_4Cl and NH_4Br crystals, though they do not possess any cleavage plane still produce good impressions. The possible reason for appearance of good quality impressions in group A samples are (i) as the indenter lands on the surface under a particular load, the material around it is displaced smoothly in softer samples (Boyarskaya *et al* 1975) and (ii) it could be due to the active participation of the slip systems, which helps in easy glide of the material.

The group B crystals show moderate hardness and they are very much harder than group A samples. Perhaps due to this nature, the flow of material under indenter cannot take place uniformly, which could be a reason for the formation of cracks at the corners of the impressions. The hardness of group C crystals is very much higher than A and B samples. When these crystals are indented above a load of 20–50 g, they show number of microcracks around indentation mark. This is very much pronounced in $NaBrO_3$ crystals even at a load of 20 g. The results indicate that these crystals are not only hard but also brittle. Boyarskaya *et al* (1975) pointed out that in harder materials apart from flow of the material some of that under indenter rises above the surface level shown by line diagram (figure 7). This could be responsible for uneven impressions and blunt corners in group C crystals.

3.4 *Correlation of hardness with elastic constants*

An attempt has been made here to estimate hardness from elastic constants and correlate with present experimental results using Gilman's empirical relation which has been proposed for alkali halides ($H = 1{\cdot}4 \times 10^{-3}\, C_{44}$). Although

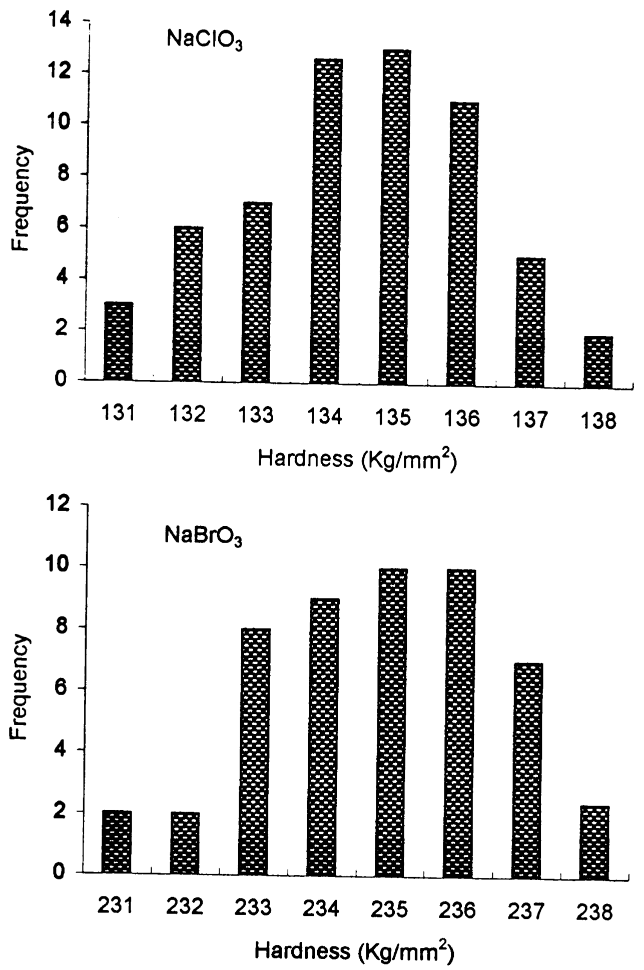

Figure 5. Histograms showing variation of hardness in $NaClO_3$ and $NaBrO_3$ crystals.

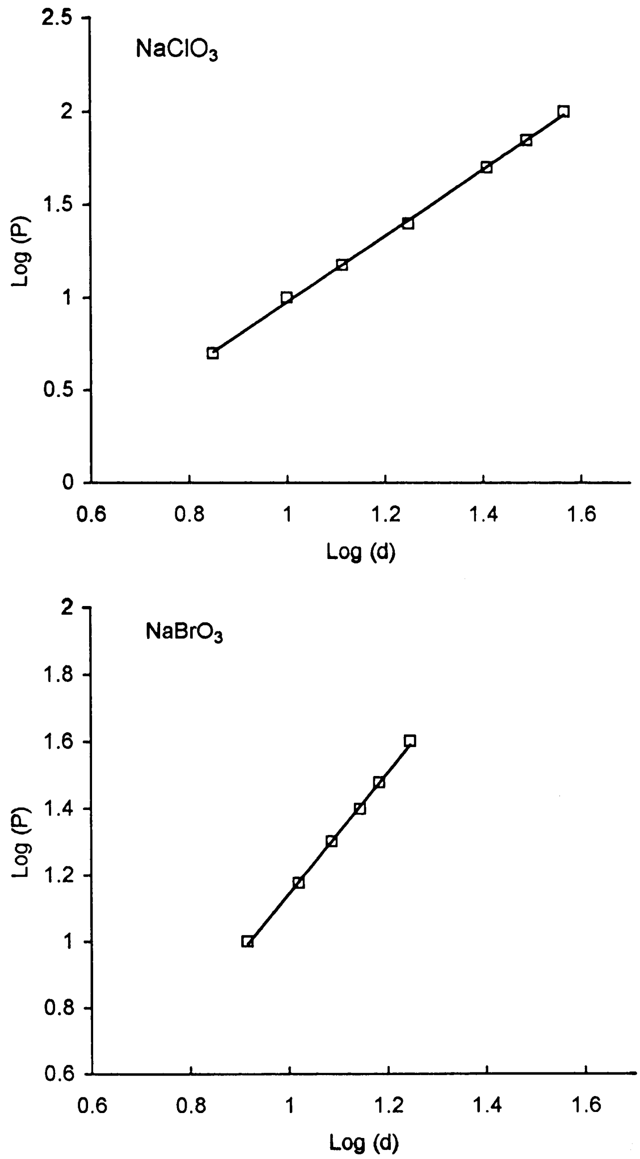

Figure 6. log P vs log d plots on $NaClO_3$ and $NaBrO_3$ crystals.

Table 2. Hardness data on various crystals.

Group A			Group B			Group C		
Crystal	H_V (kg/mm^2)	Remarks of impression	Crystal	H_V (kg/mm^2)	Remarks of impression	Crystal	H_V (kg/mm^2)	Remarks of impression
NaCl	19·5	Indentation impressions are clear with sharp corners	$Ba(NO_3)_2$	64	Impressions are clear. But cracks propagate from corners of impressions	KDP	166	Microcracks form around the impressions, these are apart from cracks at the corners of impressions
KCl	14·0		$Pb(NO_3)_2$	57		KDA	145	
KBr	9·0		K-alum	76		$Sr(NO_3)_2$	106	
RbBr	11·7		NH_4-alum	64		$NaClO_3$	135	
$NaNO_3$	22		ADP	74		$NaBrO_3$	236	
NH_4Cl	2·4		Triammonium citrate	98				
NH_4Br	2·3							

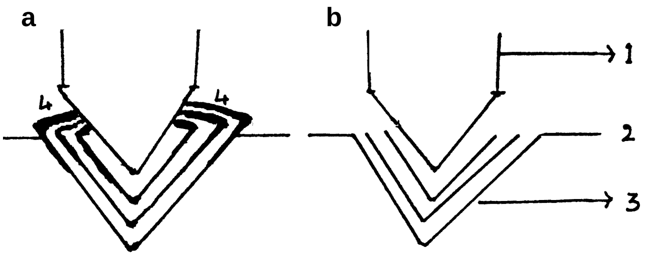

Figure 7. Line diagram showing occurrence of piling-up of the material in **a**. hard materials and **b**. soft materials (1. indenter, 2. surface, 3. flow of material and 4. piling of material above surface).

the structure of $NaClO_3$ and $NaBrO_3$ is not as simple as alkali halides but it can be viewed as consisting of Na^+ and ClO_3^-/BrO_3^- ions. From this approximation hardness values are estimated from C_{44} values (Radha and Gopal 1967). The obtained hardness values are 162 and 227 kg/mm^2 for $NaClO_3$ and $NaBrO_3$, respectively and they are in fair agreement with the present experimental results (table 1).

It is interesting to note that though crystallographically $NaClO_3$ and $NaBrO_3$ are similar but $NaBrO_3$ is very much harder than $NaClO_3$ ($\Delta H \approx 100$ kg/mm^2). Sirdeshmukh *et al* (2001) have pointed out that within a group of related crystals, the lattice constant is a measure of strength of binding, the longer the lattice constant, the weaker the binding. If we look at unit cell dimensions of $NaClO_3$ (a = 6·5758 Å) and $NaBrO_3$ (a = 6·7017 Å), the latter one should be softer. This is completely contrary to the present experimental results. In view of this an attempt has been made to understand the discrepancy by comparing with other strength dependent properties. The studies of thermal expansion (Sharma 1950), elastic constants (Radha and Gopal 1967) and the data on melting points suggest that $NaBrO_3$ structure is stronger than $NaClO_3$. The possible reason for this has been attributed (Radha and Gopal 1967) to shorter Na–Br (3·72 Å) bond distance in $NaBrO_3$ when compared with Na–Cl (4·02 Å) distance in $NaClO_3$. In the present studies also we feel that probably the shorter Na–Br bond distance appears to be responsible for exhibiting higher hardness in $NaBrO_3$ though its unit cell size is large.

4. Conclusions

The microhardness studies on as-grown faces of $NaClO_3$ and $NaBrO_3$ crystals show a clear load dependence. The load independent hardness values are 135 and 236 kg/mm^2 for $NaClO_3$ and $NaBrO_3$, respectively. $NaClO_3$ crystals produce moderately good impressions whereas $NaBrO_3$ cannot. This appears to be due to the more brittle nature of $NaBrO_3$ crystals.

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