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Microhardness of flux grown pure doped and mixed rare earth aluminates and orthochromites

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The results of microhardness measurements on flux-grown crystals of (i) single (pure) rare earth aluminates $RAlO_3$ (R = Eu, Gd, Dy, Er) and rare earth orthochromites $RCrO_3$ (R = Y, Gd, Yb), (ii) rare earth aluminates doped with neodymium, erbium, ytterbium and holmium, and (iii) mixed rare earth aluminate crystals of the type $(La_{(1-x)}\,Pr_{(x)})AlO_3$ (x = 0, 0.25, 0.75 and 1.00) are presented. The variations in the microhardness value with load are non-linear in all cases. Kick's law fails to explain the observed variations. Instead, they are best explained by the application of the idea of materials resistance pressure in the modified law proposed by Hays and Kendall. The results indicate that the doping does not increase the hardness value of crystals in all cases. The hardness instead depends on the composition of the parent material as well as the dopant entering into the crystal lattice. Mixed rare earth aluminate crystals are shown to be harder than those of single rare earth aluminates.

1. Introduction

Hardness is one of the most important properties of crystals. It is, however, very difficult to define express in terms of analytical approach. The ability of a crystal to resist permanent deformation is, in general, taken as the definition of hardness. It is expressed as a ratio of P/A where P is load (kg) and A is the area of the indentation (mm^2). There are several types of mechanical tests used to study this property. Different types of such tests are described by Hayden *et al.* [1]. In one of the most important methods, use is made of a Vickers microhardness tester. The hardness test measures the resistance of a material to an indentor or cutting tool. The indentor is usually a ball, pyramid or cone made of a material much harder than that being tested, e.g. hardened steel, sintered tungsten carbide or diamond.

Hardness is a complex property which shows dependence on a large number of factors which control growth and structure of crystals, namely impurities, dislocations, vacancies, temperature, composition, etc. Hardness studies have been reported on pure [2–11] and doped [2, 12, 13] crystals, mixed crystals [14–16] and alloys [17, 18].

The work reported on hardness has been with different aims and objectives. The dependence of microhardness on load is an important property which needs to be thoroughly investigated in order to gain information concerning the laws governing the mechanical properties of materials. Kotru *et al.* [19–21] and Pratap and Hari Babu [2] showed that the hardness results follow the Hays and Kendall law [22]. However, their study has been confined to pure crystals. It is interesting to investigate whether the law governing microhardness is applicable to doped and mixed crystals of flux-grown rare earth aluminates and orthochromites. To understand the mechanical properties of these materials, the results of indentation-induced hardness testing studies on pure rare earth aluminates ($RAlO_3$, R = europium Eu; gadolinium Gd; dysprosium Dy; erbium, Er) and rare earth orthochromites ($RCrO_3$, R = yttrium Y; gadolinium Gd; ytterbium, Yb); doped rare earth aluminates and orthochromites (lanthanum aluminate $LaAlO_3$, doped with neodymium Nd, erbium Er, ytterbium, Yb; europium aluminate $EuAlO_3$, doped with neodymium Nd, and holmium Ho; gadolinium aluminate $GdAlO_3$, doped with erbium Er; and yttrium orthochromite, $YCrO_3$, doped with erbium Er) and mixed rare earth aluminates of the type $(La_{1-x}:Pr_x)AlO_3$ where x = 0.0, 0.25, 0.75 and 1.00. It may be mentioned that no significant data regarding the mechanical properties of these crystals have been reported.

2. Experimental techniques

The crystals used in the present investigation were grown by the flux technique [23, 24]. Table I gives a summary of the starting composition. Crystals of suitable size (approximately $4 \times 2 \times 1.5\,mm^3$) were used for microhardness measurements at room temperature (32° C), using a Vickers microhardness tester mhp 100 attached to a metallurgical microscope (Neophot-2, Carl Zeiss, Germany). Crystals with plane surfaces were selected for the study and then mounted with cement. Loads ranging from 10 to 100 g were used for indentation, keeping the time of indentation at 2 sec in all cases. The load was applied slowly by pressing the indentor at right angles to the surface being tested.

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TABLE I Starting compositions of crystals (g)

Crystals	PbF_2	PbO	PbO_2	B_2O_3	MoO_3	R_2O_3		
1. $LaAlO_3$ + 3% Nd	5.0	5.0	–	–	–	1.0 La_2O_3	0.03 Nd_2O_3	0.3 Al_2O_3
2. $LaAlO_3$ + 0.6% Er	5.0	5.0	–	–	–	1.0 La_2O_3	0.006 Er_2O_3	0.3 Al_2O_3
3. $LaAlO_3$ + 1% Yb	5.0	5.0	–	–	–	1.0 La_2O_3	0.01 Yb_2O_3	0.3 Al_2O_3
4. $LaAlO_3$	5.0	5.0	–	–	–	1.0 La_2O_3	–	0.3 Al_2O_3
5. $(La_{0.75}:Pr_{0.25})AlO_3$	30.0	90.0	8.0	1.5	4.0	7.5 La_2O_3	2.5 Pr_4O_7	3.0 Al_2O_3
6. $(La_{0.25}:Pr_{0.75})AlO_3$	20.0	90.0	8.0	1.5	4.8	2.5 La_2O_3	7.5 Pr_4O_7	3.0 Al_2O_3
7. $PrAlO_3$	50.0	49.0	1.0	–	–	–	10.0 Pr_4O_7	3.0 Al_2O_3
8. $EuAlO_3$	12.0	36.0	3.2	0.4	1.8	3.4 Eu_2O_3	–	0.9 Al_2O_3
9. $EuAlO_3$ + 1%Nd	12.0	36.0	3.2	0.4	1.8	3.4 Eu_2O_3	0.03 Nd_2O_3	0.9 Al_2O_3
10. $EuAlO_3$ + 2% Ho	12.0	36.0	3.2	0.4	1.8	3.4 Eu_2O_3	0.07 Ho_2O_3	0.9 Al_2O_3
11. $GdAlO_3$	178.0	140.0	6.0	6.0	–	72.0 Gd_2O_3	–	22.0 Al_2O_3
12. GdAlO + 3%Er	178.0	140.0	6.0	6.0	–	72.0 Gd_2O_3	2.16 Er_2O_3	22.0 Al_2O_3
13. $DyAlO_3$	44.0	80.0	1.5	2.5	–	11.9 Dy_2O_3	–	3.2 Al_2O_3
14. $ErAlO_3$	28.0	91.2	8.0	1.0	4.8	10.7 Er_2O_3	–	2.7 Al_2O_3
15. $YCrO_3$	75.3	–	0.7	2.1	–	6.4 Y_2O_3	–	4.3 Cr_2O_3
16. $YCrO_3$ + 5% Er	71.5	9.5	0.8	–	–	6.2 Y_2O_3	0.32 Er_2O_3	4.6 Cr_2O_3
17. $GdCrO_3$	107.0	–	1.0	3.0	–	15 Gd_2O_3	–	6.2 Cr_2O_3
18. $YbCrO_3$	215.0	–	1.0	6.0	–	32.0 Yb_2O_3	–	12.3 Cr_2O_3

The distance between any two consecutive indentations was kept at more than three times the diagonal length of the indentation mark. This ensured the surface effects were independent of one another. These tests are never taken near the edge of a sample. The thickness of the specimen should be at least ten and one-half times the depth of impression. The impression of the indentation mark was square and at least five indentations were made on each sample for each load. The diagonal lengths of each indentation were recorded and the averages of the diagonal lengths were computed for calculations. The diameter of the indentation mark was measured with the help of a filar eye piece with a minimum count of 0.25 μm (× 500). The microhardness value was calculated using the formula $H = 1.8544P/d^2$ kg mm^{-2} where P is the applied load (kg) and d is the diagonal length of the indentor impression (mm). The microhardness value of a particular sample was taken both by averaging the different values of microhardness at various loads as well as the value obtained at higher loads where near constancy in the value of hardness is achieved. Etching experiments were performed using 75% HNO_3 at 95° C for pure or doped $LaAlO_3$ and mixed $(La_{0.75}:Pr_{0.25})AlO_3$ crystals.

3. Results

None of the rare earth aluminates or orthochromites exhibit perfect cleavages along any plane, and so plane habit faces, microscopically free from signs of any damage, were selected for the indentation purposes.

From the data recorded on measurements of microhardness at different loads, the microhardness values in kg mm^{-2} were computed both by taking the average values as well as at a point where saturation of microhardness with load is just achieved. The data so obtained are given at the relevant places.

3.1. Rare earth aluminates (pure, doped and mixed crystals)

The data on microhardness value for lanthanum aluminates (pure $LaAlO_3$, $LaAlO_3$ doped with 3% Nd, 0.6% Er and 1% Yb), europium aluminates (pure $EuAlO_3$, $EuAlO_3$ doped with 1% Nd and 2% Ho), gadolinium aluminates (pure $GdAlO_3$, $GdAlO_3$ doped with 3% Er), pure $DyAlO_3$ and $ErAlO_3$ and mixed crystals of the type $(La_{1-x}:Pr_x)$ AlO_3 (x = 0, 0.25, 0.75, and 1.00) are given in Table II (all wt %). The materials are quite hard as could be seen by comparing their values with those of alkali halide crystals [2, 25, 26]. The hardness value for the aluminates ranges from 1124 to 1867 kg mm^{-2} (if average values are taken) or from 972 to 1809 kg mm^{-2} (if saturation values are taken), whereas the hardness values for alkali halide crystals range from about 9 to 20 kg mm^{-2}.

The microhardness varies with load in the case of rare earth aluminates as shown in Figs 1 to 3. From these curves the following points emerge.

1. Variation of microhardness with load has more or less the same form in all cases, irrespective of whether the crystal is pure or doped rare earth aluminate or is a mixed rare earth aluminate crystal of the composition $(La_{1-x}:Pr_x)AlO_3$ (where x = 0, 0.25, 0.75, 1.00). The curves are non-linear.

2. From Fig. 1a it is revealed that doping of $LaAlO_3$ with other rare earths (Nd, Er and Yb) hardens the

TABLE II Vicker's hardness numbers (kg mm^{-2})

Sample	Average VHN	VHN at 100 g
1. $LaAlO_3$ + 3% Nd	1572	1288
2. $LaAlO_3$ + 0.6% Er	1717	1550
3. $LaAlO_3$ + 1% Yb	1674	1402
4. $LaAlO_3$	1413	1211
5. $(La_{0.75}:Pr_{0.25})AlO_3$	1424	1211
6. $(La_{0.25}:Pr_{0.75})AlO_3$	1539	1315
7. $PrAlO_3$	1367	1211
8. $EuAlO_3$	1755	1623
9. $EuAlO_3$ + 1% Nd	1725	1550
10. $EuAlO_3$ + 2% Ho	1698	1433
11. $GdAlO_3$	1400	1340
12. $GdAlO_3$ + 3% Er	1124	972
13. $DyAlO_3$	1597	1498
14. $ErAlO_3$	1867	1809
15. $YCrO_3$	1056	981
16. $YCrO_3$ + 5% Er	1694	1498
17. $GdCrO_3$	1084	999
18. $YbCrO_3$	1618	1532

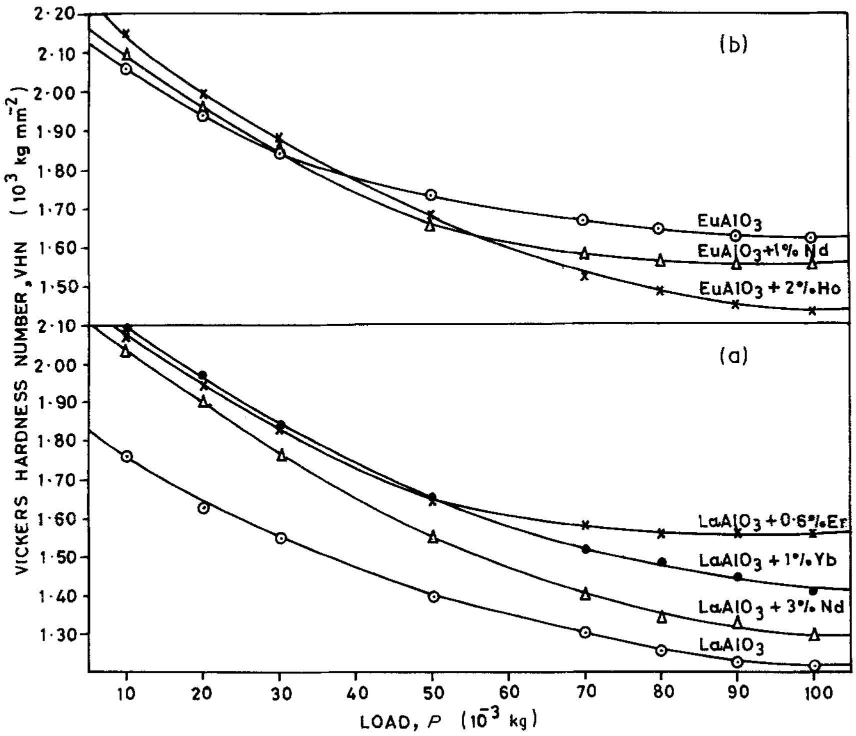


Figure 1 Variation of Vickers hardness number with applied load in the case of (a) pure $LaAlO_3$ and $LaAlO_3$ doped with 3% Nd, 1% Yb and 0.6% Er, (b) pure $EuAlO_3$ and doped with 1% Nd and 2% Ho.

crystal at higher loads (say from 70 to 100 g). In this particular case doping of $LaAlO_3$ with 0.6% Er hardens the material most. Addition of 1% Yb gives the next amount of hardening in the $LaAlO_3$ crystal. The results are quite opposite in the case of $EuAlO_3$ (see Fig. 1b). Here doping of $EuAlO_3$ with 1% Nd or 2% Ho lowers the microhardness in the higher load regions (70 to 100 g). The same is true for $GdAlO_3$ when it is doped with 3% Er (see Fig. 3a).

3. From the results of mixed crystals obtained from the curves of Fig. 2, it is indicated that the mixed rare earth aluminate crystals are harder than the pure ones; $[La_{0.75}:Pr_{0.25}]AlO_3$ or $[La_{0.25}:Pr_{0.75}]AlO_3$ (mixed rare earth aluminates) having hardness values greater than those of $LaAlO_3$ or $PrAlO_3$ (pure rare earth aluminates) crystals. This supplements the results obtained from Fig. 1a where it is indicated that doping also increases the microhardness of $LaAlO_3$ crystals.

3.2. Rare earth orthochromites (pure and doped crystals)

Fig. 3b shows variation of microhardness of $YCrO_3$ (pure as well as doped with 5% Er), $GdCrO_3$ and $YbCrO_3$ with load. Here also the variations exhibit a form similar to those obtained for rare earth aluminate crystals (Section 3.1). It is significant to note that doping of $YCrO_3$ with 5% Er increases its microhardness quite appreciably. In other words, $YCrO_3$ doped with 5% Er is harder than the pure $YCrO_3$ crystals. This result leads to the same conclusion as derived from Fig. 1a but opposite to that of Fig. 1b. In the former case the doped crystals become harder whereas in the latter case they become softer. The microhardness value of $GdCrO_3$ is lower than that of $YbCrO_3$ crystal. However, variation of microhardness with load retains almost the same form in all cases. The curves are non-linear.

4. Discussion

The results reported in Section 3 show that as the applied load increases the hardness of the materials decreases, whether they be pure, doped or mixed rare earth aluminates or pure and doped rare earth orthochromites. Fig. 4 shows the impression of indentations made on $LaAlO_3$ + 3% Nd crystal at loads of 30, 50 and 90 g. These are representative photomicrographs

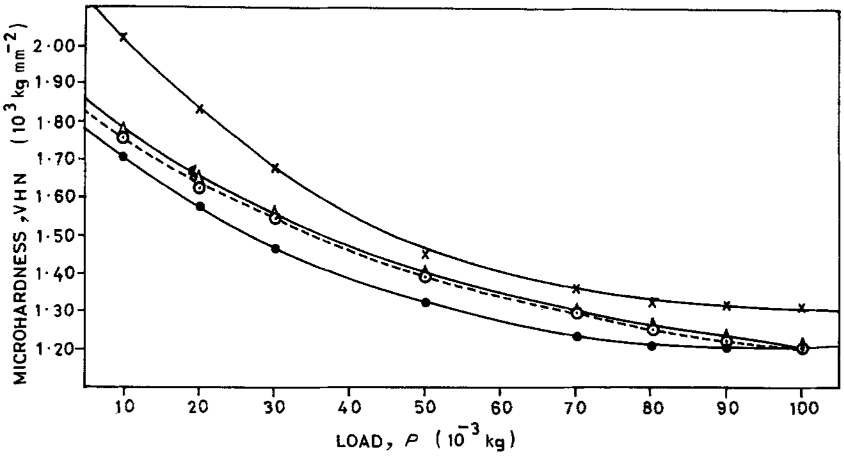


Figure 2 Variation of microhardness with applied load in the case of mixed aluminates of the type $[La_{1-x}:Pr_x]AlO_3$ where x = ⊙ 0, (△) 0.25, (×) 0.75 and (●) 1.0.

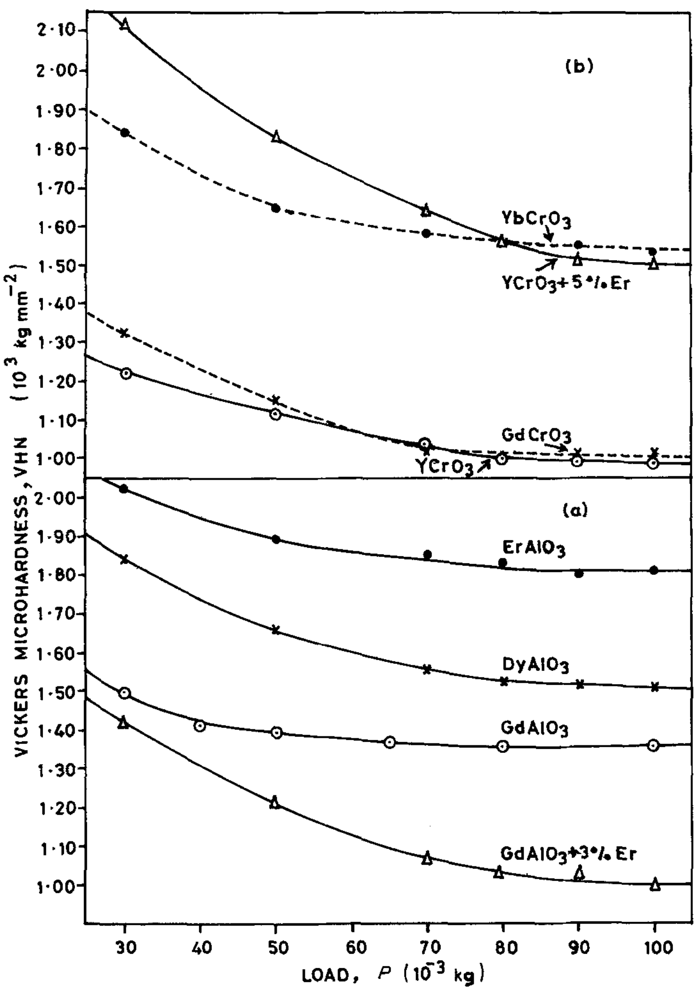
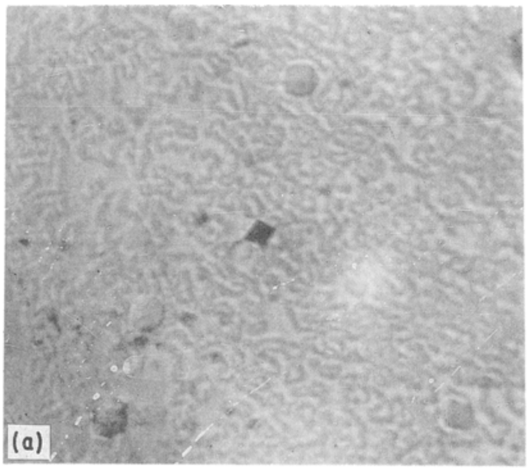
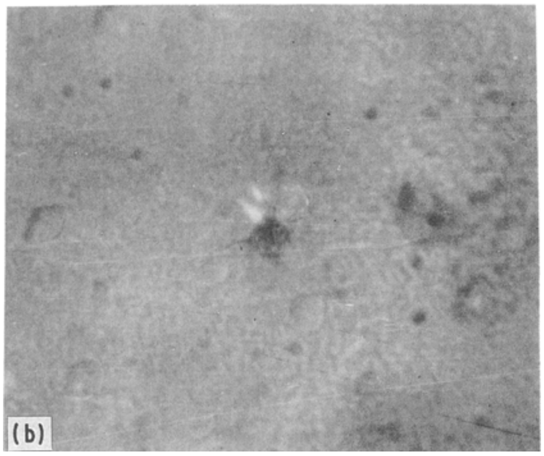


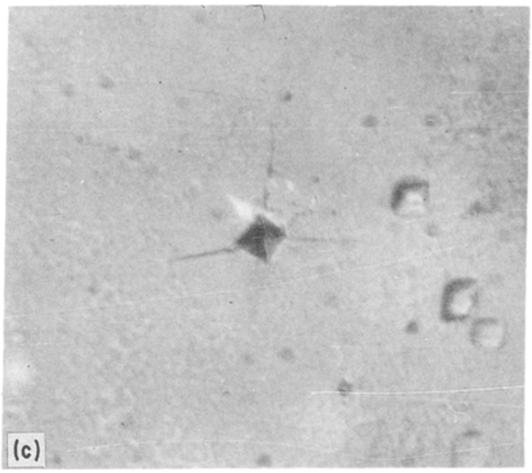
Figure 3 Variation of Vickers microhardness with load in the case of (a) pure rare earth aluminates and $GdAlO_3$ doped with 3% Er, (b) pure rare earth orthochromites and $YCrO_3$ doped with 5% Er.

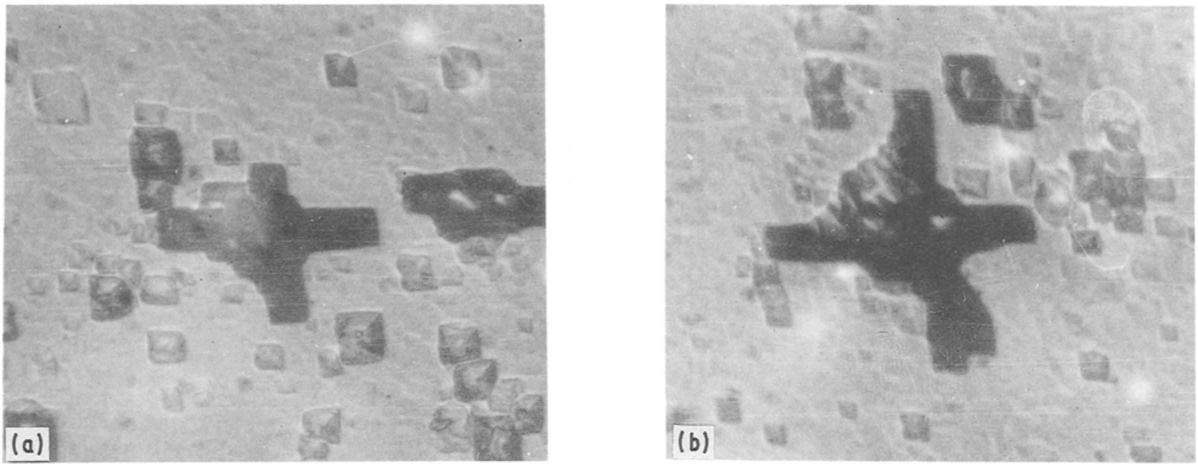


which show that the size of the indented impression increases with the load. The same indented regions are shown in Fig. 5 after etching the crystal in 75% HNO_3 for 0.5 h at 95° C. HNO_3 is a dislocation etchant for $LaAlO_3$ crystals [27]. There is a noticeable increase in the length of the "rosette" arm as the load is increased. The size of the dislocation rosette formed around an indentation mark is a useful and convenient test for the determination of mechanical strength of single crystals [28]. The arm lengths of the dislocation rosette correspond to the distance travelled by the dislocation, which increases as the hardness decreases

Figure 4 Vickers indentor impressions at different loads on the $LaAlO_3$ + 3% Nd crystal surface. The impressions of loads of 30, 50 and 90 g are shown in (a), (b) and (c), respectively (× 500).







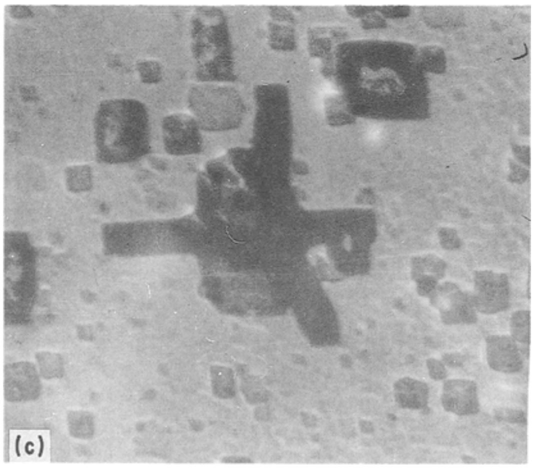


Figure 5 Corresponding rosette pattern of Fig. 4 after 30 min etching (× 500).

(i.e. as the load increases), because the mobility of the dislocation lines increases as the load increases. This is one of the main reasons why microhardness decreases with increase in load. It is confirmed that a further etching of the same surface for a longer period in the same etchant, as shown in Fig. 5, maintains the rosette pattern. However, the pattern thickens on successive etching, because of repeated preferential etching along the strain pattern caused by the indentation.

The results have indicated that the microhardness varies with load non-linearly, irrespective of whether the crystals are pure or doped rare earth aluminates or orthochromites or mixed rare-earth aluminates. The non-linear behaviour is common, as reported previously by Pratap and Haribabu [2], Kotru *et al.* [19–21], Hays and Kendall [22], Buckle [29], and Upit and Varchanya [30]. The non-linear variations for any of the materials investigated here are not in accordance with what is indicated by Kick's law.

As early as 1885, Kick [31] proposed an analysis of hardness results leading to the relation

$$P = K_1 d^n \tag{1}$$

where P is the applied load (kg) K_1 is a constant, d the observed length of the indentation (mm) and n a constant. According to Kick's analysis for hardness, $n = 2$ for all indentors that give impressions geometrically similar to each other. Equation 1 was further corroborated by Schultz and Hanemann [32] who proposed that Vickers microhardness and macrohardness are thereby comparable. Kick's law, Equation 1, has not been widely accepted because n usually has a value of less than 2, especially in the low-load hardness regions. Considerable experimental proof exists which opposes the unlimited utilization of Kick's law in applications concerning Vicker's hardness results [29, 33–44]. Saraf [45] obtained two different values of n for higher and lower load regions in the case of baryte crystals. Hays and Kendall [22]

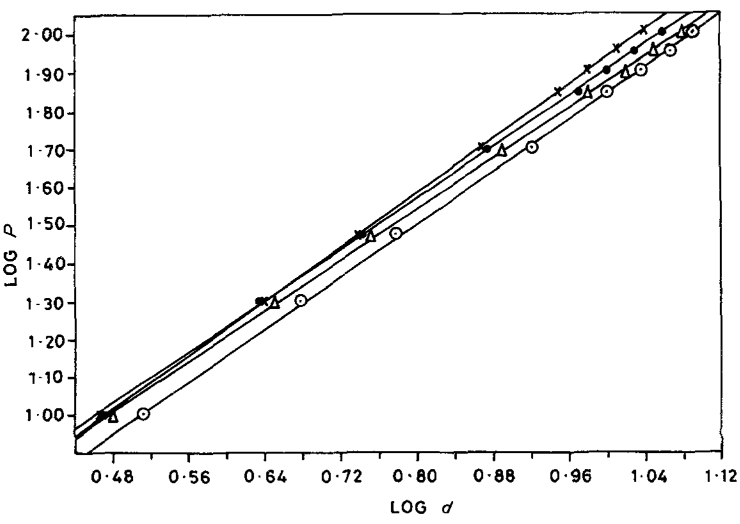


Figure 6 The relationship between logarithm of applied load (log P) with logarithm of Vicker's diagonal (log d) for pure and doped $LaAlO_3$ crystals. (⊙) $LaAlO_3$, (△) $LaAlO_3$ + 3% Nd, (x) $LaAlO_3$ + 0.6% Er, (●) $LaAlO_3$ + 1% Yb.

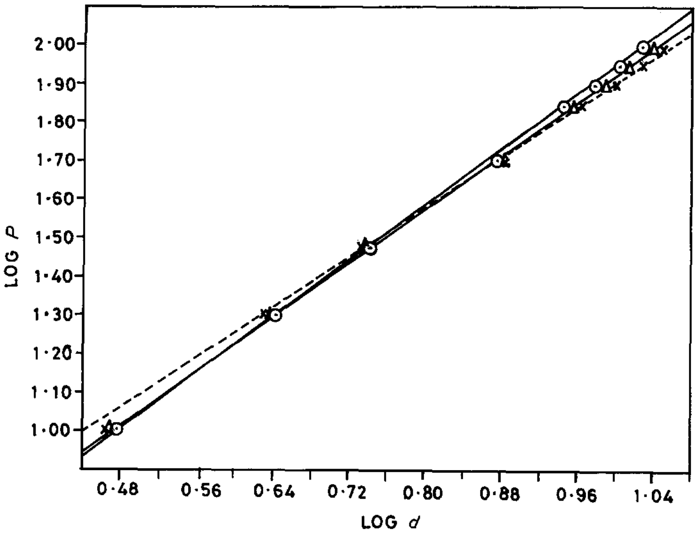


Figure 7 Variation of log P with log d for pure and doped $EuAlO_3$ crystals. (⊙) $EuAlO_3$, (△) $EuAlO_3$ + 1% Nd, (x) $EuAlO_3$ + 2% Ho.

made an attempt to overcome this difficulty by proposing a modified version of Kick's law.

Hardness is known as the resistance of a material to permanent deformation. If it is assumed that a portion of this resistance to deformation can be evaluated as a Newtonian resultant pressure of the specimen itself, then it is possible to analyse Vickers microhardness data without undue concern as to the applied load. Hays and Kendall [22] assumed that as load, P, is applied to a crystal sample, P would be partially affected by a smaller resistance pressure, w, which is a function of the material being tested or a routine test variable. According to them, the measured length of an indentation is not equal to $f(P)$ but a lesser quantity, say $f(P - W)$, instead. Here W is the minimum applied load required to cause an indentation, as loads less than W should, by definition allow no plastic deformation.

Considering Equation 1 on the basis of sample resistance pressure W, it follows that

$$P - W = K_2 d^2 \tag{2}$$

where K_2 is a constant, and $n = 2$ is a logarithmic index. Here n is expected to be equal to 2, because it is proposed that the factor of W allows the limiting case to prevail where hardness is not markedly dependent on the load.

In order to evaluate the function W for a particular solution, one can solve the two equations, thus

$$W = K_1 d^n - K_2 d^2 \tag{3}$$

or

$$d^n = K_2/K_1 d^2 + W/K_1 \tag{4}$$

From these equations, the analysis is completed by simple graphical methods.

A logarithmic study of Equation 1, where log P is plotted against log d, gives the value of n and K_1 for any set of data. The index n is given by the slope and log K_1 is noted by the intercept of the graph log P against log d.

Figs 6 to 10 represent the logarithmic relation of Equation 1 for the hardness data obtained on pure rare earth and doped rare earth aluminates, orthochromites and mixed rare earth aluminates. The values of K_1 and n obtained from these figures are included in Table III for different materials as indicated. It will be noted there that $n < 2$ and, as such, the Vickers hardness number is dependent on the applied load.

Cartesian plots of Equation 4 suggest that d^n against d^2 should yield the slope K_2/K_1 and the intercept W/K_1. Knowing the value of K_1 from the logarithmic plot of P and d, the values of K_2 and W can be calculated. Plots of d^n against d^2 yield straight

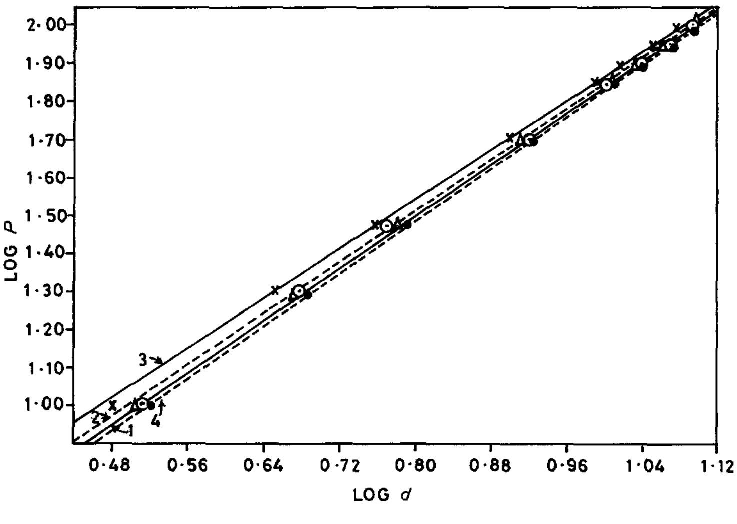


Figure 8 Variation of log p with log d for mixed rare earth aluminates of the type $[La_{1-x}:Pr_x]AlO_3$. 1, (⊙) $x = 0$, 2, (△) $x = 0.25$; 3, (x) $x = 0.75$; 4, (●) $x = 1.0$.

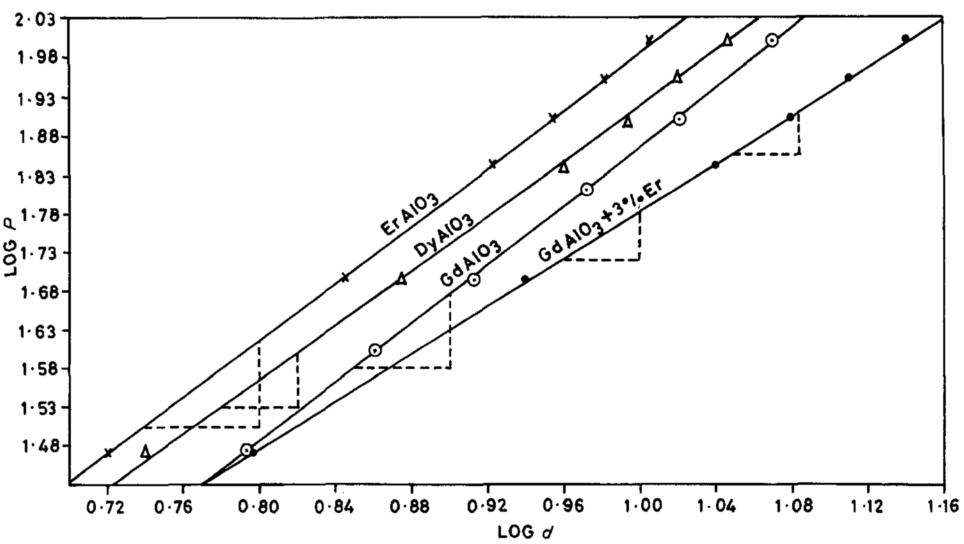


Figure 9 The relationship between log P and log d in the case of pure and doped rare-earth aluminates.

lines for the materials under investigation. Figs 11 and 12 are plots of Equation 4 for the pure, doped, and mixed rare earth aluminates and orthochromites. The values of K_2/K_1 obtained from the slope, and W/K_1 from the intercept, are given in Table III. All the key data for this investigation are included in this table.

Figs 13 and 14 are plots of log $(P - W)$ against log d, which show that the theory of resistance pressure as proposed by Hays and Kendall [22] is valid for flux-grown pure, doped and mixed rare earth aluminates and orthochromites. It is noted here that a family of parallel lines where $n \simeq 2$ is the result of these studies. This modification of Kick's law in the form of the Hays and Kendall law has been held valid for alkali halide crystals [2], pure rare earth orthoferrites $RFeO_3$ (R = Gd to Er and Yb), orthochromites, RC_rO_3 (R = La, Eu and Dy) and rare earth aluminates, $RAlO_3$ (R = La, Sm, Eu, Gd and Ho) [19] and $LaBO_3$ [21] crystals.

The present study leads to the conclusion that irrespective of changes in microhardness values for pure, doped and mixed rare earth aluminates and orthochromites, the theory of resistance pressure proposed by Hays and Kendall [22] is applicable for these materials also. Hardness is a property which is understood in terms of resistance offered to dislocation motion. The general contribution to this resistance is mainly of two types: (i) the intrinsic resistance, and (ii) the resistance due to imperfections. The magnitude of resistance, however, is a factor whose dependence on the characteristics of a crystal can be complex and needs to be thoroughly investigated. There are, however, reports of dependence of microhardness on the composition of KCl–KBr mixed crystals [15], the type of cations in alkali halides [46–50], Peirels–Nabarrow stress [51] which is due to the periodic variation of strain energy as the dislocation moves through the crystal, volumetric lattice energy [52], ionic bonding combined with the theory of plastic deformation [53], and other physical parameters [54, 55]. Changes in the hardness of a material on doping with impurities have also been reported by Pratap and Hari Babu [2], Rao and Hari Babu [12], Reddy *et al.* [13], Patel and Desai [56]; and on mixed crystals by Patel and Arora [14] and Subha Rao and Hari Babu [15, 16]. The hardness of doped or mixed crystals was found to be greater than that of pure ones. This may be due to both retardation of the motion of dislocations at the

TABLE III Results of microhardness analysis

Crystal	$K_1(10^{-3}\,kg)$	$n\ (g\,\mu m^{-1})$	W/K_1	K_2/K_1	$K_2(10^{-3}\,kg)$	$W(10^{-3}\,kg)$
1. $LaAlO_3$ + 3% Nd	1.693 902	1.644 6	3.108 934 3	0.406 275	0.688 19	5.266 23
2. $LaAlO_3$ + 0.6% Er	1.458 833	1.762 7	3.000 135 7	0.549 289 8	0.801 322	4.376 697
3. $LaAlO_3$ + 1% Yb	1.699 468	1.671 0	2.575 333	0.431 515 9	0.733 347	4.376 69
4. $LaAlO_3$	1.312 942	1.726	4.046 865 7	0.482 736 1	0.633 804	5.313 3
5. $(La_{0.75}:Pr_{0.25})AlO_3$	1.370 704	1.710 4	4.198 125 9	0.462 185	0.633 518	5.754 388
6. $(La_{0.25}:Pr_{0.75})AlO_3$	1.733 116	1.625	3.792 008	0.378 074	0.655 246	6.571 99
7. $PrAlO_3$	1.305 834	1.717 6	4.101 355 9	0.471 713 4	0.615 979	5.355 69
8. $EuAlO_3$	1.349 722	1.814 2	2.935 89	0.622 061 5	0.839 61	3.962 64
9. $EuAlO_3$ + 1% Nd	1.520 718	1.740 2	3.365 934	0.515 116 7	0.783 347	5.118 637
10. $EuAlO_3$ + 2% Ho	1.867 967	1.625 4	2.548 048	0.399 449	0.746 158	4.759 67
11. $GdAlO_3$	1.221 4	1.879	2.2	0.724 3	0.884 7	2.687
12. $GdAlO_3$ + 3% Er	1.799 577 7	1.531 8	4.347 237 5	0.271 219	0.488 08	7.823 19
13. $DyAlO_3$	1.475 045	1.75	4.667 589	0.515 152	0.759 871	6.884 904
14. $ErAlO_3$	1.424 091	1.833 333	3.441 151	0.648 649	0.923 734	4.900 512
15. $YCrO_3$	1.159 786	1.698 718	8.440 452	0.410 256	0.475 809	9.789 118
16. $YCrO_3$ + 5% Er	2.552 786	1.514 085	4.551 975	0.281 25	0.717 971	11.620 219
17. $GdCrO_3$	1.553 835	1.583 333	9.306 934	0.285 714	0.443 953	14.461 44
18. $YbCrO_3$	1.365 311	1.791 667	4.119 373	0.576 923	0.787 679	5.624 226

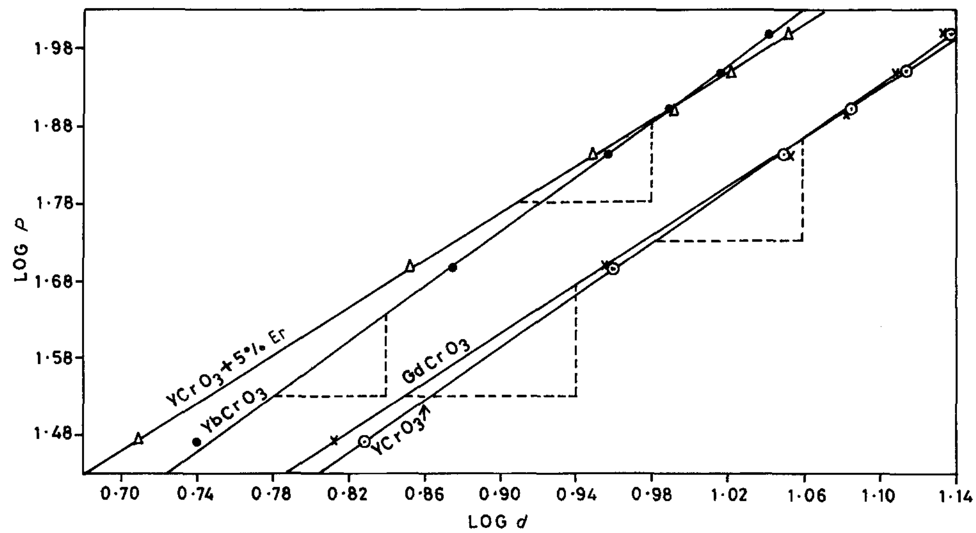


Figure 10 Variation of log P with log d in the case of pure and doped rare earth orthochromites.

impurity sites and other defects caused by the presence of impurity atoms in the crystal, and also to variation in the magnitude of the bond forces in the crystal containing the impurities [56]; the divalent impurities harden the crystal because distortions resulting from impurity vacancy dipoles, are more intense [49, 50]. Internal strains arising from the difference in ionic sizes may be responsible for the formation of dislocations, low-angle grain boundaries and other defects in case of mixed crystals [15, 16], thereby making them harder. It has been shown that the interaction of defect structure of the crystals with dislocations have a decisive role in the hardening mechanism [55, 57–65].

In summary, the results reveal that the addition of 3% Nd, 0.6% Er and 1% Yb make the $LaAlO_3$ crystals harder; addition of 5% Er makes $YCrO_3$ also appreciably harder and the mixed crystals of the type $[La_{1-x}:Pr_x]AlO_3$ are harder than the pure ones. All these observations suggest that doping makes crystals harder than the pure ones. Crystals of mixed rare earth aluminates are also harder than those of pure rare earth aluminates. These observations support the main conclusions drawn from studies

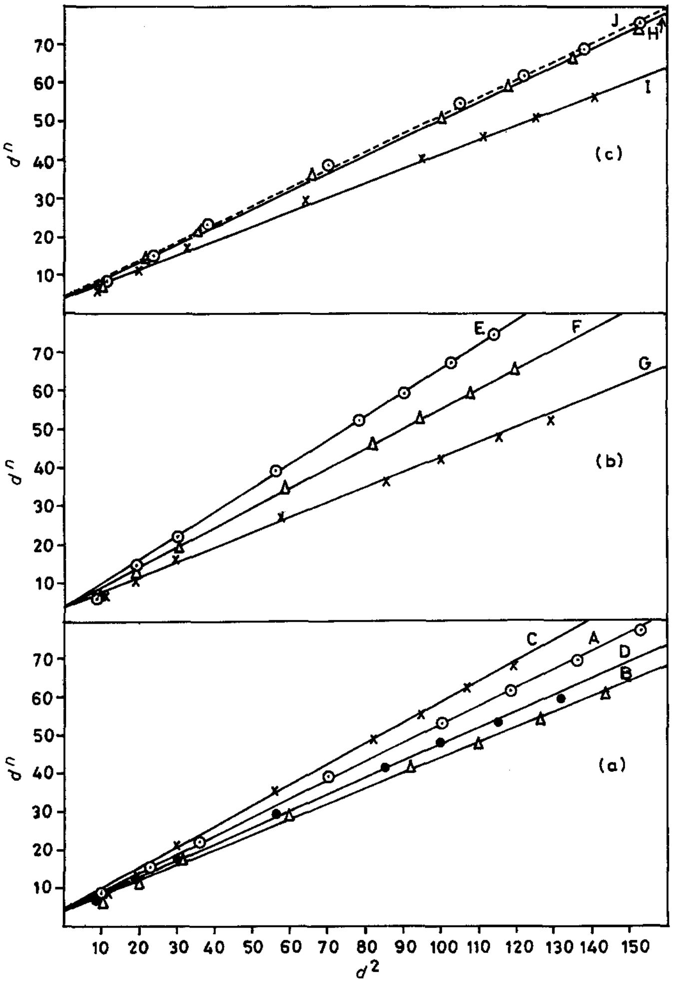


Figure 11 The relationship between d^n and d^2 in the case of pure and doped crystals. (a) (⊙) $LaAlO_3$, (△) $LaAlO_3$ + 3% Nd, (×) $LaAlO_3$ + 0.6% Er, (●) $LaAlO_3$ + 1% Yb; (b) (⊙) $EuAlO_3$, (△) $EuAlO_3$ + 1% Nd, (×) $EuAlO_3$ + 2% Ho; (c) mixed rare earth aluminates (△) $(La_{0.75}:Pr_{0.25})AlO_3$, (×) $(La_{0.25}:Pr_{0.75})AlO_3$, (⊙) $(La_0:Pr_{1.0})AlO_3$.

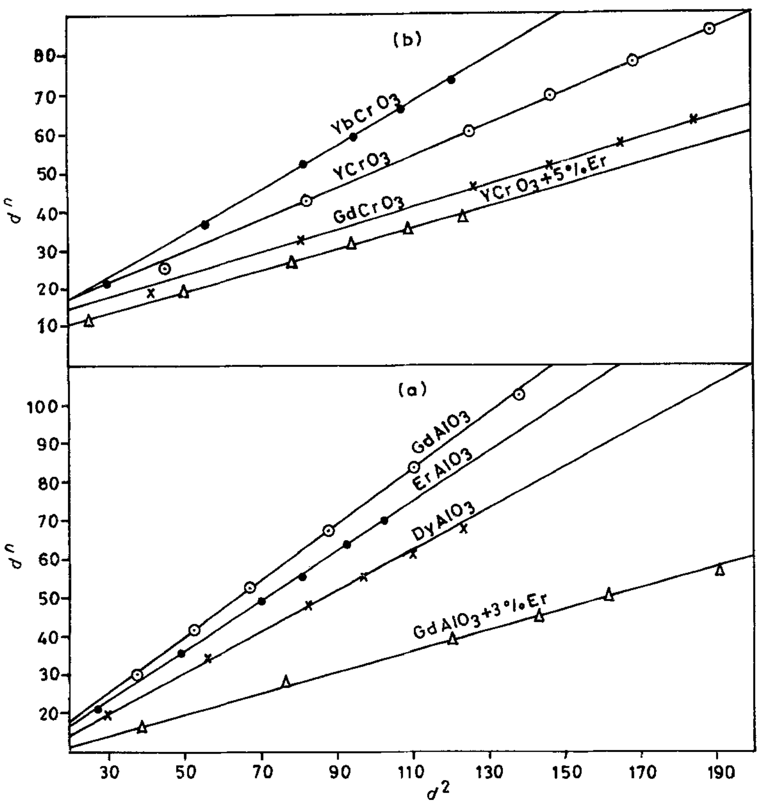


Figure 12 Graph of d^n against d^2 for rare earth pure and doped (a) aluminates, (b) orthochromites.

on other crystals reported in the literature [2, 14–16, 46–50, 55, 57–60].

However, some observations also reveal that $EuAlO_3$ (europium aluminate) crystals become softer if doped with 1% Nd or 2% Ho. $GdAlO_3$ (gadolinium aluminate) crystal also exhibits a decrease in hardness if it is doped with 3% Er. These results thus do not support the general view that doping increases the hardness of a crystal. Hardness is a property whose dependence on physical and chemical imperfections in crystals is very definite but predictions of its exact behaviour may be difficult, because of uncertain corre-

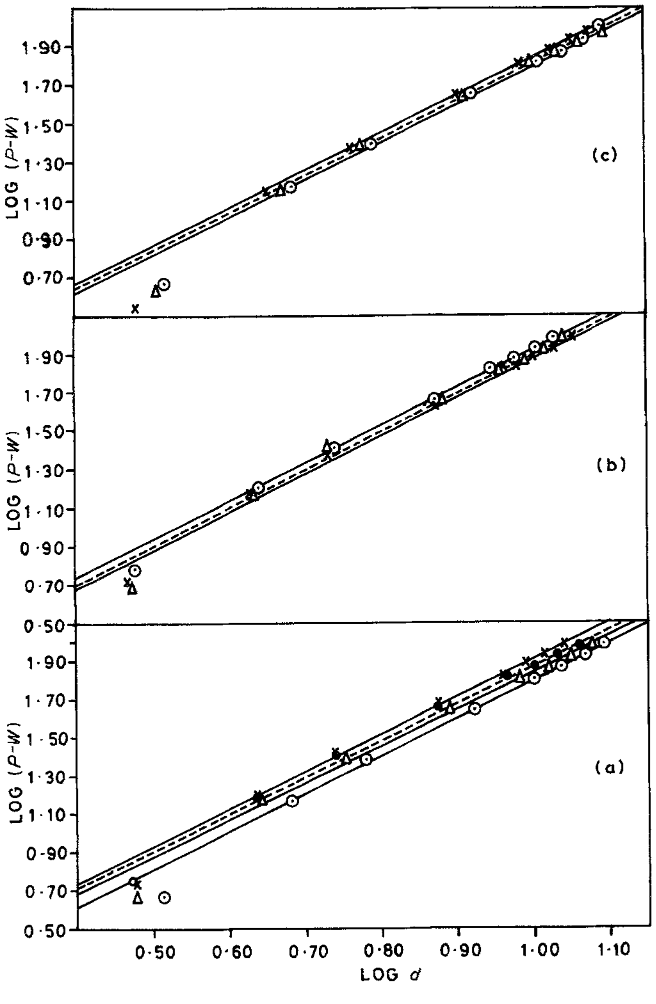


Figure 13 The relationship between the true applied load, log (P–W) and the Vickers diagonal (log d) for pure and doped rare earth crystals of (a) (⊙) $LaAlO_3$, (△) $LaAlO_3$ + 3% Nd, (×) $LaAlO_3$ + 0.6% Ho, (●) $LaAlO_3$ + 1% Yb; (b) (⊙) $EuAlO_3$ (△) $EuAlO_3$ + 1% Nd, (×) $EuAlO_3$ + 2% Ho; and (c) mixed rare earth aluminates of the type $(La_{1-x}:Pr_x)AlO_3$ (△) $(La_{0.75}:Pr_{0.25})$ AlO_3, (×) $(La_{0.25}:Pr_{0.75})AlO_3$, (⊙) $(La_0:Pr_{1.0})AlO_3$.

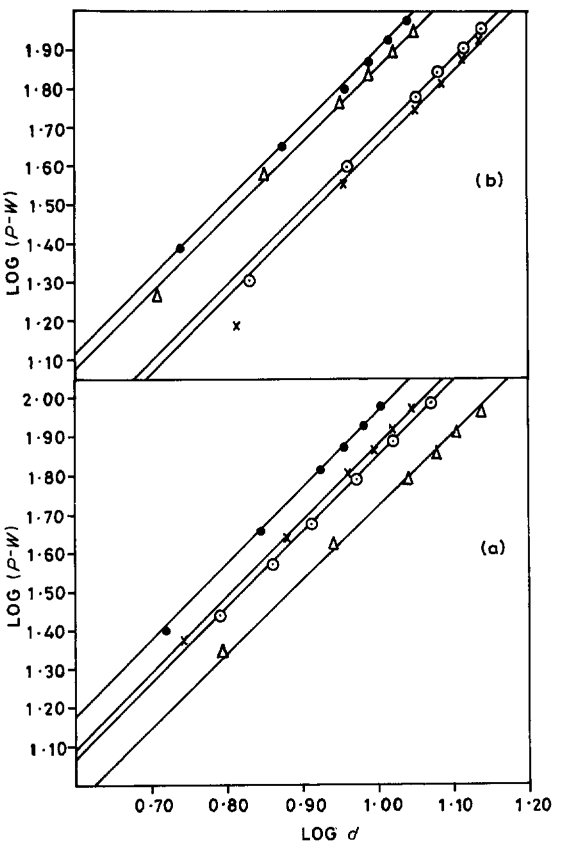


Figure 14 The variation of true applied load, log $(P - W)$, with log d in the cases of pure and doped rare earth (a) aluminates, (⊙) $GdAlO_3$, (△) $GdAlO_3$ + 3% Er, (x) $DyAlO_3$, (●) $ErAlO_3$; (b) orthochromites, (⊙) $YCrO_3$, (△) $YCrO_3$ + 5% Er, (x) $GdCrO_3$, (●) $YbCrO_3$.

lations. Rao and Hari Babu [12] have reported that the addition of impurity increases the hardness until a maximum value for a particular concentration is arrived at; any further increase in the impurity concentration results in a decrease of hardness. This phenomenon may be due to the formation of large visible precipitates [12]. As the precipitate particles increase in size or undergo a change in their crystal structure, it is energetically favourable for dislocations to by-pass the particles by cross-slip or leaving loops around the particles. When dislocations move in this manner, the hardness decreases and softening of the materials results [13]. Chin *et al.* [55] observed such softening in $KCl:Sr^{2+}$ and $KCl:Ba^{2+}$.

The present study demonstrates that the variations in the microhardness value of a crystal depend not only on its own structure but also on which atom or ion goes into the crystal lattice as a dopant.

5. Conclusions

1. The microhardness value of rare earth aluminates and orthochromites ranges from 1124 to 1867 and from 1056 to 1694 kg mm^{-2} respectively, when average values are taken at loads ranging from 10 to 100 g. The value changes from 972 to 1809 kg mm^{-2} for aluminates and from 981 to 1532 kg mm^{-2} for orthochromites at saturation values as recorded from the curves of load against VHN.

2. The variations of microhardness with load are non-linear irrespective of whether the crystals are pure or doped rare-earth aluminates or orthochromites or mixed rare earth aluminate crystals of the composition $(La_{1-x}:Pr_x)AlO_3$ (where $x = 0, 0.25, 0.75, 1.0$).

3. Kick's law ($P = K_i d^n$) fails to explain the observed variations of microhardness value with load not only in the case of pure rare earth aluminates or orthochromites but also in the case of doped or mixed crystals. The hardness results are best explained on application of the idea of materials resistance pressure in the modified law as proposed by Hays and Kendall ($P - W = K_2 d^2$).

4. Doping of crystals does not always increase the microhardness value but may, in certain cases, decrease the microhardness value. The addition of neodymium, erbium and ytterbium makes $LaAlO_3$ crystals harder. Doping of $YCrO_3$ with erbium also hardens the crystal. The mixed crystals of the type $[La_{1-x}:Pr_x]AlO_3$ are harder than pure ones. However, the microhardness value of $EuAlO_3$ crystals decreases if they are doped with neodymium or holmium. This also happens in the case of $GdAlO_3$ if it is doped with erbium.

The variations in the microhardness value of a crystal, therefore, depend not only on its own structure but also on what impurity atom or ion enters the crystal lattice.

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