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Systematic hardness measurements on some rare earth garnet crystals†

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Abstract. Microhardness measurements were undertaken on twelve rare earth garnet crystals. In yttrium aluminium garnet and gadolinium gallium garnet, there was no measurable difference in the hardness values of pure and nominally Nd-doped crystals. The hardness values were correlated with the lattice and elastic constants. An analysis of hardness data in terms of the interatomic binding indicated a high degree of covalency.

Keywords. Microhardness; rare earth garnets.

1. Introduction

Rare earth garnets have a cubic structure [O_h^{10}–$Ia3d$] with eight molecules per unit cell. They have the general formula $C_3A_2D_3O_{12}$, where C, A and D denote cations and O the oxygen ion. They are hard gem-quality materials. Because of their magnetic properties, they are useful as microwave and magnetic bubble devices. When doped with Nd, some of the rare earth garnets act as excellent laser hosts. Their photoemission spectra are sensitive to pressure, making them useful as optical pressure sensors (Hua *et al* 1996).

There is an enormous volume of literature on the physical properties of rare earth garnets (see for example, Khattak and Wang 1984; Nikogosyan 1997). But still, there are areas where further studies are desirable. This laboratory has a comprehensive on-going programme on the study of various physical properties of rare earth garnets. As a part of this programme, the results on Debye temperatures (Nagaiah *et al* 1979), thermal expansion (Hussain and Sirdeshmukh 1993) and dielectric properties (Krishna Kumar *et al* 1994, 1998; Sirdeshmukh *et al* 1998) have been reported.

The purpose of the present communication is to report the results of systematic measurements of the microhardness of rare earth garnets. Khattak and Wang (1984) have listed values of hardness for only three rare earth garnets (YAG, YIG and YGG) from two reports while Nikogosyan (1997) has quoted a single value for $Gd_3Sc_2Ga_3O_{12}$. In the present study measurements have been made on twelve rare earth garnet samples including pure, doped and mixed crystals. The systematics are analysed and information is derived regarding the binding in these materials.

2. Experimental

Rare earth garnet crystals are grown by the flux or Czochralski technique depending on their melting type (incongruent or congruent, respectively). The origin of the crystal samples used, their purity and colour are described in table 1. All samples were in the form of parallel-faced plates of 1–2 mm thick and had polished surfaces revealing the (111) plane.

Microhardness measurements were made on the (111) face of the crystals using a miniload Leitz-Wetzlar microhardness tester fitted with a Vicker's pyramidal indentor. Indentations were made at several loads in the range 25–200 g. At each load, the Vicker's microhardness, H_V was calculated from the formula

$$H_V = (1854{\cdot}4)\, P/d^2, \qquad (1)$$

where P is the load in g and d the length of the diagonal of the impression measured in μm; H_V is in units of kg/mm^2. The measured hardness shows a load variation, decreasing with increasing load up to 100 g and thereafter becomes nearly load independent. A typical load vs hardness plot is shown in figure 1. The possible causes of load variation have been discussed in detail and the procedure to evaluate the true load independent hardness, H_V^0 from the data on load variation has been described in a recent paper by Subhadra *et al* (2000). However, the superscript 0 will be dropped and hereinafter H_V will represent the Vicker's hardness corrected for load variation. The true hardness values are accurate to 5%. In some cases,

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†Dedicated to the memory of Dr R Thyagarajan, eminent Solid State Physicist.

because of brittleness the indentations showed distortion at higher loads. In such cases indentation was limited up to 100 g and a larger uncertainty of 7% is not ruled out in the values of H_V. The Moh hardness, H_M is obtained from the Vicker's hardness using the conversion formula (Mott 1956):

$$H_M = 0{\cdot}675\ (H_V)^{1/3}. \quad (2)$$

3. Results and discussion

3.1 *Hardness of pure, doped and mixed garnets*

The Vicker's and Moh hardness values of the pure, doped and mixed rare earth garnet crystals are given in table 2. The hardness values of pure YAG, YIG and EuGG crystals agree well with earlier values quoted by Khattak and Wang (1984) and Nikogosyan (1997). In the case of YAG and GGG, measurements were made on pure and Nd-doped crystals. As can be seen from table 2, the difference in hardness values is of the same order as the experimental error. Although doping of a crystal generally leads to a larger hardness (Subhadra *et al* 2000), in the case of these garnets, any change in hardness due to the incorporation of a nominal concentration of Nd as dopant seems to be small and within the limits of experimental error. Therefore, where pure garnet crystals are not available for measurement, we may consider the hardness values

Table 1. Description of the rare earth garnet samples.

Sample no.	Formula	Short symbol	Purity	Colour	Shape of plate	Origin
1.	$Gd_3Ga_5O_{12}$	GGG	Pure	Colourless	Circular	Litten/Airotron (US)
2.	$Gd_3Ga_5O_{12}$	GGG (Nd)	0·5% Nd	Violet	Circular	Litten/Airotron (US)
3.	$Y_3Al_5O_{12}$	YAG	Pure	Colourless	Circular	Solid State Physics Laboratory (India)
4.	$Y_3Al_5O_{12}$	YAG (Nd)	0·5% Nd	Violet	Circular	Solid State Physics Laboratory (India)
5.	$Gd_3Sc_2Ga_3O_{12}$	GSGG	0·5% Nd 0·3% Cr	Green	Rectangular	Solid State Physics Laboratory (India)
6.	$Eu_3Ga_5O_{12}$	EuGG	Pure	Colourless	Irregular	Bell Labs (US)
7.	$Y_3Fe_5O_{12}$	YIG	Pure	Violet	Semicircular	Philips Labs (Germany)
8.	$Nd_3Ga_5O_{12}$	NdGG	Pure	Pink	Circular	Philips Labs (Germany)
9.	$Y_3Ga_5O_{12}$	YGG (Nd)	0·5% Nd	Colourless	Irregular	Philips Labs (Germany)
10.	$Tb_3Ga_5O_{12}$	TbGG	Pure	Colourless	Circular	Philips Labs (Germany)
11.	$Pr_{2\cdot96}Mn_{1\cdot34}Mg_{0\cdot4}Zr_{0\cdot4}Ga_{2\cdot9}O_{12}$	Pr(Mn, Mg, Zr) GG	Mixed	Green	Circular	Philips Labs (Germany)
12.	$Sm_{2\cdot6}Ca_{0\cdot31}Zr_{0\cdot32}Ga_{4\cdot68}O_{12}$	Sm(Ca, Zr) GG	Mixed	Brown	Circular	Philips Labs (Germany)

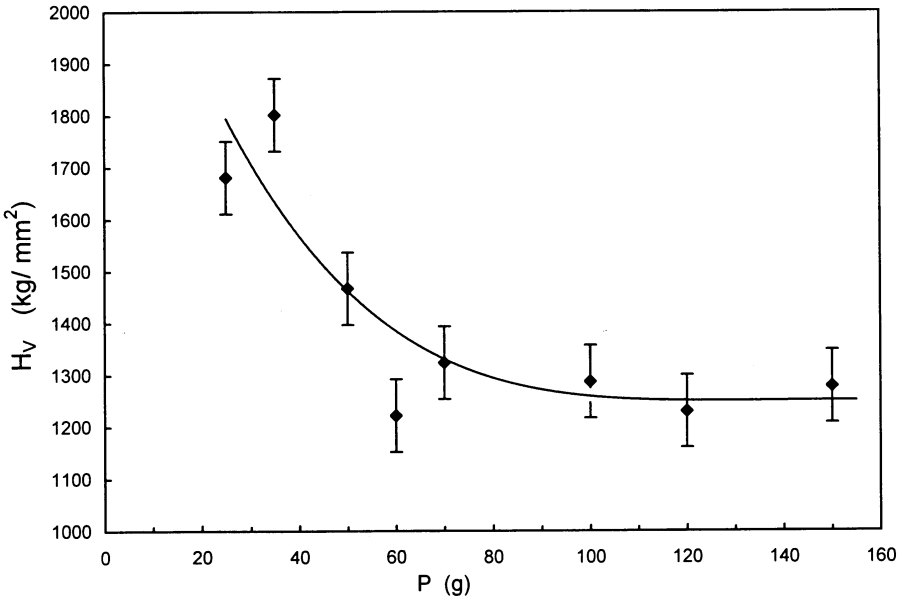

Figure 1. Plot of hardness (H_V) against the applied load (P) for sample no. 5.

obtained from measurements on nominally doped crystals as representative of the hardness of pure crystals with an uncertainty of ± 100 kg/mm^2.

The concentrations of Ca and Zr in Sm(Ca, Zr)GG and of Mn, Mg and Zr in Pr(Mn, Mg, Zr)GG are substantial and so these crystals are to be treated as mixed crystals rather than as doped crystals. The hardness of mixed crystals is generally larger than that of the pure components (Thirmal Rao and Sirdeshmukh 1991). In the case of Sm(Ca, Zr)GG and Pr(Mn, Mg, Zr)GG, it is not possible to compare the mixed crystal hardness values with those of the corresponding pure garnets as pure crystals were not available for measurements.

3.2 *Hardness and nature of binding in garnet crystals*

The microhardness of the group of rare earth garnet crystals studied in this work is in the range 1100–1700 kg/mm^2 (7·1–7·8 on the Moh scale) which by itself is indicative of strong interatomic binding. Within a group of related crystals, the lattice constant is a measure of the strength of binding, the larger the lattice constant, the weaker the binding. Correlation of hardness with lattice constant has been carried out by Thirmal Rao and Sirdeshmukh (1991) for alkali halides and by Sirdeshmukh *et al* (1995) for divalent and tetravalent crystals with NaCl structure by plotting the hardness against the lattice constant. In both the cases the data points were scattered about smooth curves which indicated decreasing hardness with increasing lattice constant i.e. decreasing strength of binding. Figure 2 shows a hardness vs lattice constant plot for the rare earth garnets. Here, again, the data points are closely scattered about a curve (in fact, a line) indicating decreasing hardness with increasing lattice constant. Thus the variations of hardness and lattice constant within the group are mutually consistent. The H_V vs a plot does not yield any further information.

Gilman (1973) pointed out that the ratio of microhardness, H_V and the shear constant, C_{44} is nearly constant for a group of related crystals. Chin (1975a) considered the value of this parameter (H_V/C_{44}) for a variety of crystals with simple structures and found that the ratio has characteristic values of ~ 0·01 for ionic crystals and ~ 0·1 for covalently bonded crystals. Kishan Rao and Sirdeshmukh (1983) calculated the value of the ratio H_V/C_{44}, for several compound crystals to draw inferences regarding the type of binding. Sirdeshmukh *et al* (1995) have termed this ratio (H_V/C_{44}), the Gilman–Chin parameter. The values of the Gilman–Chin parameter for the rare earth garnets, for which elastic constant values are available, are given in table 2. The values are in the range 0·14–0·15. This indicates a high degree of covalency in binding in these garnets.

The Gilman–Chin parameter merely helps to distinguish between different bond types. A different approach makes it possible to estimate the degree of ionicity (or the degree of covalency) from hardness values. Julg (1978) proposed the equation:

$$H_M = k\,[1 - (2/3)I^4], \tag{3}$$

where I is the ionicity and k a constant. Though the formula appears simple, the evaluation of the constant k

Table 2. Values of the Vicker's hardness, H_V, Moh hardness, H_M, lattice constant, a, shear elastic constant, C_{44}, Gilman–Chin parameter (H_V/C_{44}) and the ionicity, I.

Sample no.	Short symbol	H_V (kg/mm^2)	H_M	a[c] (Å)	C_{44}[d] (kg/mm^2)	H_V/C_{44}	I (4)
1.	GGG	1350 ± 70	7·28	12·38	9220	0·146	0·75
2.	GGG (Nd)	1300 ± 60	7·23				
3.	YAG	1700 ± 120 1730[a]	7·86	12·00	11730	0·145	0·71
4.	YAG (Nd)	1740 ± 120	7·91				
5.	GSGG (Nd, Cr)	1250 ± 60	7·06 7[b]	12·53			0·77
6.	EuGG	1150 ± 50	6·91	12·50	7770	0·142	0·78
7.	YIG	1200 ± 60 1230[a]	7·0	12·38	7810	0·154	0·77
8.	NdGG	1300 ± 65	7·19	12·50	8550	0·152	0·76
9.	YGG (Nd)	1500 ± 90 1490[a]	7·54	12·27	9740	0·154	0·73
10.	TbGG	1600 ± 110	7·70	12·35			0·72
11.	Pr (Mn, Mg, Zr) GG	1050 ± 50	6·70				
12.	Sm (Ca, Zr) GG	1250 ± 60	7·10				

[a]Khattak and Wang (1984); [b]Nikogosyan (1997); [c]a for GSGG from Hua *et al* (1996) and for TbGG from Shannon *et al* (1990) and rest as in d; [d]C_{44} and a for YIG and NdGG from Haussuhl *et al* (1976) and for the rest from Haussuhl and Mateika (1972).

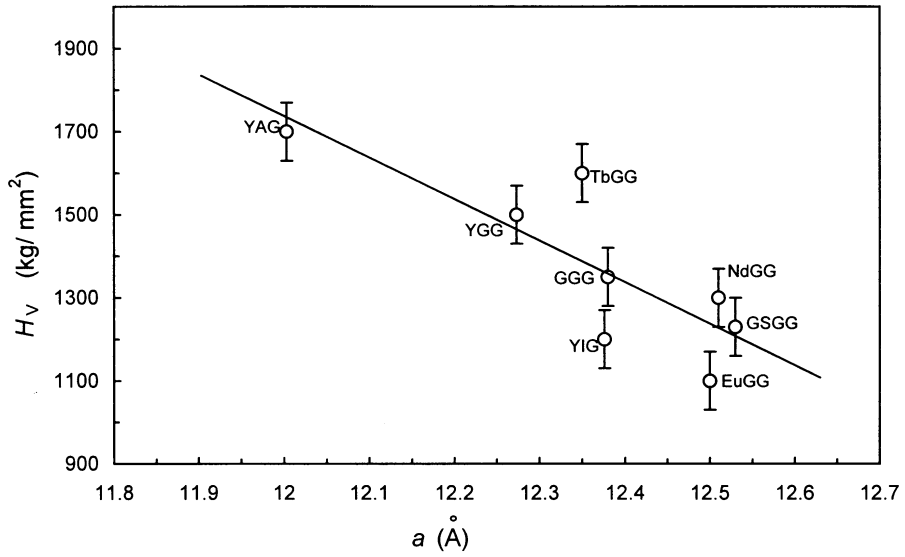

Figure 2. Plot of hardness (H_V) against lattice constant (a).

involves several parameters, some of which cannot be unambiguously chosen for compound crystals. Pillay (1982) overcame this difficulty by considering the hardness of several compounds with known ionicity and obtained the empirical relation

$$H_M = aI^2 + bI + c. \quad (4)$$

The constants a, b and c have values – 15·79, 11·33 and 7·63. These values are valid for a wide range of materials. Equation (4) may be used to estimate the ionicity from hardness values. The ionicities of rare earth garnets estimated using (4) are given in table 2. The ionicity values range from 0·71 for YAG to 0·78 for EuGG. These values are considerably less than the ideal value of 1 for purely ionic crystals and are indicative of a high degree of covalency. Further, these values are comparable with the values obtained by Pillay (1982) for several silicates, which are known to be highly covalent.

Some light can be thrown on what is responsible for the high degree of covalency in these garnets. There are three cation–anion bonds in the garnets corresponding to the tetrahedral (or d) sites, octahedral (or a) sites and dodecahedral (or c) sites. Most of the physical properties of garnets are essentially determined by these bonds, though some interaction between the cations in the d and c sites has been observed in charge distribution studies (Ching and Xu 1999; Xu *et al* 2000). Hofmeister and Campbell (1992) calculated the compressibility of rare earth garnets from Brout's (1959) formula which involves the infrared frequencies and the three afore mentioned bond lengths. Since the calculated values of the compressibility were found to be close to the experimental values, it may be inferred that the three cation–anion bonds play a role in determining the mechanical properties of the rare earth garnets. We should expect these bonds to play a role in determining the hardness also. Chin (1975b) has shown that covalently bonded crystals follow the empirical relation

$$C_{44} = 5{\cdot}28 \times 10^3\, r^{-5}, \quad (5)$$

where r is the length of the covalent bond involved. Since the Gilman–Chin parameter (H_V/C_{44}) has a value of 0·15 for YAG, (5) may be modified to

$$H_V = 0{\cdot}15 \times 5{\cdot}28 \times 10^3\, r^{-5}. \quad (6)$$

The average cation–anion distance in YAG is 0·18 Å (Euler and Bruce 1965). Substituting this value in (6), we get a value of 1500 kg/mm^2 for the hardness of YAG which may be compared with the experimental value of 1700 ± 120 kg/mm^2. This agreement is fair, considering the approximations involved. Thus the cation–anion bonds in the rare earth garnets appear to be responsible for the large hardness and, also, for the high degree of covalency in these crystals.

4. Conclusions

Vicker's microhardness measurements have been made on twelve samples of rare earth garnets. These include some pure, doped and mixed garnets. The hardness values range from 1100–1700 kg/mm^2. The hardness values correlate well with the values of the lattice constant. It is observed that the difference in hardness of pure and nominally Nd-doped crystals is within the experimental error of 5%. Calculations of the Gilman–Chin parameter and the ionicity from hardness data indicate that the bonding in the rare earth garnets is highly covalent.

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References

Chin G Y 1975a *Deformation of ceramic materials* (New York: Plenum)

Chin G Y 1975b *Trans. Am. Cryst. Assoc.* **11** 1

Ching W Y and Xu Y 1999 *Phys. Rev.* **B59** 12815

Euler F and Bruce J A 1965 *Acta Crystallogr.* **19** 971

Gilman J J 1973 *J. Appl. Phys.* **44** 982

Haussuhl S and Mateika D 1972 *Z. Naturforsch.* **27a** 1522

Haussuhl S, Mateika D and Tolksdorf W 1976 *Z. Naturforsch.* **31a** 1976

Hofmeister A M and Campbell K R 1992 *J. Appl. Phys.* **72** 638

Hua H, Mirov S and Vohra Y K 1996 *Phys. Rev.* **B54** 6200

Hussain K A and Sirdeshmukh D B 1993 *Cryst. Res. Technol.* **28** 1147

Julg A 1978 *Phys. Chem. Miner.* **3** 45

Khattak C P and Wang F F Y 1984 *Handbook on the physics and chemistry of rare earths* (New York: Holland) Vol. 3

Kishan Rao K and Sirdeshmukh D D 1983 *Bull. Mater. Sci.* **5** 449

Krishna Kumar K, Sathaiah G and Sirdeshmukh L 1994 *Ferroelectrics* **155** 213

Krishna Kumar K, Ramakrishna A, Sathaiah G and Sirdeshmukh L 1998 *J. Korean Phys. Soc.* **32** S321

Mott B W 1956 *Microindentation hardness testing* (London: Butterworths)

Nagaiah B, Ram Babu M and Sirdeshmukh D B 1979 *Indian J. Pure & Appl. Phys.* **17** 838

Nikogosyan D N 1997 *Properties of optical and laser-related materials – A handbook* (New York: John Wiley)

Pillay K S 1982 *Indian J. Pure & Appl. Phys.* **20** 46

Shannon R D, Subramanian M A, Allik T H, Kimura H, Kokta M R, Randles M H and Rossman G R 1990 *J. Appl. Phys.* **67** 3798

Sirdeshmukh D B, Subhadra K G, Kishan Rao K and Thirmal Rao T 1995 *Cryst. Res. Technol.* **30** 861

Sirdeshmukh L, Krishna Kumar K, Bal Laxman S, Ramakrishna A and Sathaiah G 1998 *Bull. Mater. Sci.* **21** 219

Subhadra K G, Kishan Rao K and Sirdeshmukh D B 2000 *Bull. Mater. Sci.* **23** 147

Thirmal Rao T and Sirdeshmukh D B 1991 *Cryst. Res. Technol.* **26** k53

Xu Y, Gu Z and Ching W Y 2000 *J. Appl. Phys.* **87** 4867