Systematic hardness measurements on single crystals and polycrystalline blanks of cesium halides

D B SIRDESHMUKH*, P GEETA KRISHNA and K G SUBHADRA

Department of Physics, Kakatiya University, Warangal 506 009, India

Abstract. Vickers and knoop hardness measurements were carried out on CsBr and CsI single crystals. Polycrystalline blanks of CsCl, CsBr and CsI were prepared by melting and characterized by X-ray diffraction. Vickers hardness measurements were carried out on these blanks. The hardness values were correlated with the lattice constant and the Schottky defect formation energy.

Keywords. Vickers hardness; knoop hardness; cesium halides.

1. Introduction

Among the alkali halides, cesium chloride, cesium bromide and cesium iodide crystallize in the well known CsCl structure (space group $Pm3m$). These crystals are useful as infrared optical materials (Harshaw Catalogue 1967), as radiation detectors (Optovac Catalogue 1993) and in nuclear fuel container technology (Fullam 1972).

While there is an enormous amount of work on the crystal growth of alkali halides with NaCl structure, work on cesium halide single crystals is limited. Single crystals are commercially supplied by Harshaw and Optovac at prohibitive cost. Single crystal growth in academic research centres is rare, perhaps, because among the alkali halides, the cesium halides are the most expensive. In the case of CsCl, single crystal growth is hampered by a structural transition just below the melting point (Harshaw Catalogue 1967).

For many applications and property measurements, polycrystalline blanks can be used in place of single crystals. The fabrication of aggregates is much simpler than growth of single crystals and, further, smaller quantities of raw material are required. Studies of polycrystalline aggregates of NaCl and KCl are reported by Dobson and Wilman (1962a), Subramanyam (1962), Armington *et al* (1973) and Leuenberger *et al* (1981). With the exception of an electron diffraction study of CsCl (Dobson and Wilman 1962b), there is no report of any study on the polycrystalline aggregates of the cesium halides.

Although there is considerable information on several physical properties of cesium halides, information on their hardness is sketchy. No report could be traced on the hardness of CsCl. Values of hardness of CsBr and CsI are quoted without any details in the Harshaw Catalogue (1967).

The purpose of the present communication is two-fold: (i) to report on the fabrication and characterization of polycrystalline blanks of cesium halides and (ii) to report results of systematic hardness measurements on single crystals as well as polycrystalline blanks of cesium halides.

2. Experimental

2.1 *Materials*

The single crystals used in these studies are shown in figure 1. The CsBr and CsI(H) crystals were grown and supplied by Harshaw. They are in the form of cubes bound by the (100) faces. The CsI(M) crystal was grown at the Institute of Crystallography, Moscow; it is a plate with (100) faces, cut out from a boule.

Polycrystalline blanks were prepared by melting about 2 g of the material in a minifurnace and cooling the melt slowly. The cooling rate was 10°C/h for the first 5 h and 50°C/h till the ingot reached ambient temperature. Further details are given in an earlier paper (Srinivas *et al* 1999). The resulting blanks were annealed at about 400°C for 8–10 h to minimize strains. The blanks fabricated by us (figure 2) are homogeneous and optically clear.

X-ray back reflection photographs of the blanks were recorded on a flat-plate camera using Cu radiation (figure 3). Although no measurements have been made on these photographs, a study of their appearance itself yields useful information. These photographs do not show Laue spots characteristic of single crystals. Instead they show powder lines with varying features. The photograph for CsCl shows spotty lines indicating presence of coarse grains. The highest angle (521) reflection is also spotty but is discontinuous indicating some preferred orientation. In the case of CsBr, the (521) reflection is a com-

*Author for correspondence
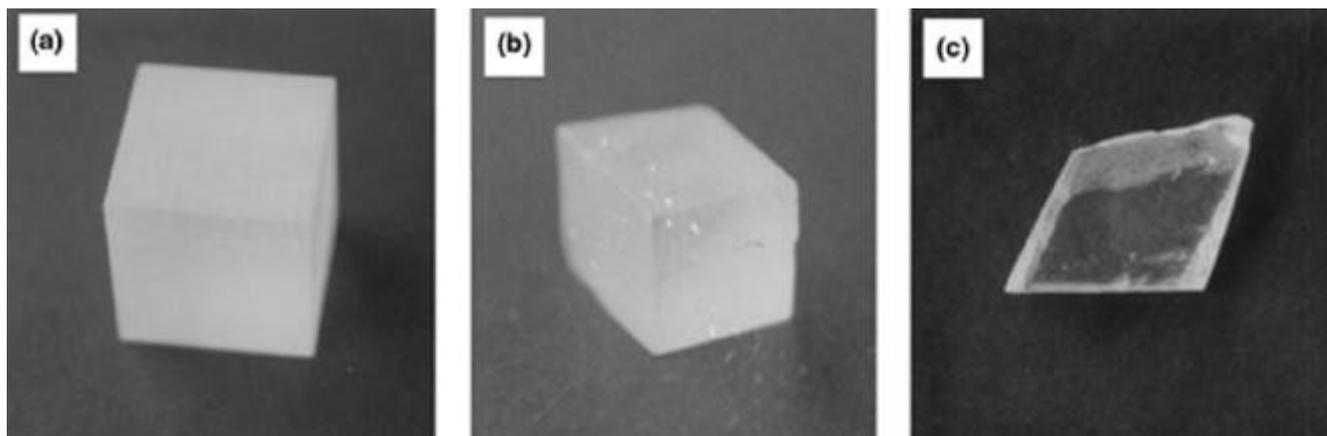
Figure 1. Photographs of single crystals of (**a**) CsBr, (**b**) CsI (H) and (**c**) CsI (M).

pletely continuous line indicating fine grains. Superposed over the (521) line are a few intense spots suggesting a slight degree of preferred orientation. In CsI, again, the (521) reflection is a continuous powder line suggesting existence of very fine grains. There are intense spots superposed over the line indicating preferred orientation.

From the optical clarity of the blanks and the features of the X-ray photographs, it may be concluded that the simple method of melting followed by slow cooling results in homogeneous and essentially polycrystalline blanks made up of fine or coarse grains with a slight degree of preferred orientation. The existence of preferred orientation was taken care of, while making hardness measurements (§ 2·2).

2.2 *Microhardness measurements*

Microhardness measurements were made with the help of a Leitz–Wetzlar Miniload Hardness Tester. Using a Vickers diamond pyramidal indenter, the Vickers hardness (H_V) was calculated from the relation

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

where P is the applied load and d the length of the diagonal of the indentation impression. With P in g and d in μm, H_V turns out to be in kg/mm^2. Hardness measurements were made at several loads in the range 5–100 g. The values of H_V calculated from (1) show a load dependence. The final values of H_V are corrected for this load dependence following a detailed discussion given in an earlier paper from this laboratory (Sirdeshmukh *et al* 2000). In the case of polycrystalline blanks, to take care of any preferred orientation, measurements were made for different orientations of the sample surface with respect to the indenter axis and the mean value was taken. For measurement of knoop hardness, the Vickers indenter was replaced with a knoop indenter and the knoop hardness, H_K, was calculated from the relation
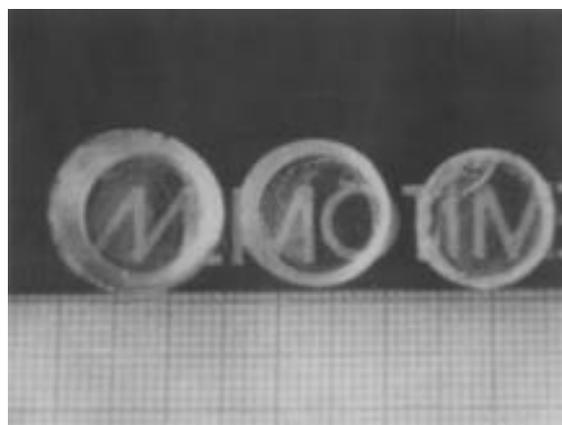
Figure 2. Photographs of polycrystalline blanks of (l to r) CsI, CsBr and CsCl.

$$H_K = 14500 \, P/l^2, \tag{2}$$

where P is the load and l the length of the long axis of elongated diamond-shaped indentation. Measurements were made by orienting the single crystals such that the <100> and <110> directions were parallel to the long axis of the indenter. This orientation was carried out by mounting the crystal on a circular stage.

By differentiating (1) and inserting the error Δd, the error in hardness (ΔH_V) can be estimated from the relation

$$\Delta H_V = -2H_V \, (\Delta d/d), \tag{3}$$

with a similar relation for ΔH_K.

3. Results and discussion

3.1 *Vickers hardness*

The results of Vickers hardness measurements are given in table 1. As mentioned in § 1, we could not trace any

earlier report on the microhardness of CsCl. For CsBr, our values for the single crystal and the polycrystalline blank agree within limits of experimental errors. Further, the
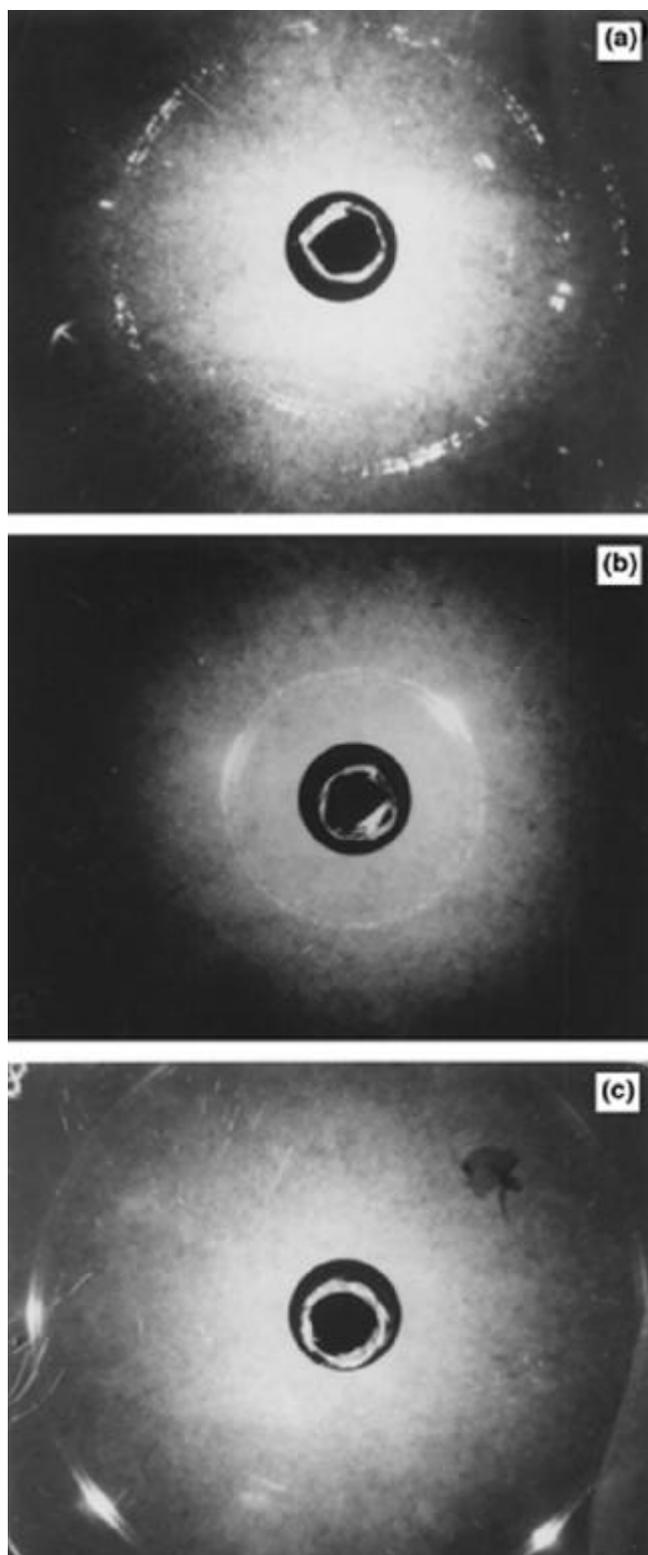
Figure 3. X-ray back reflection photographs of polycrystalline blanks of (**a**) CsCl, (**b**) CsBr and (**c**) CsI.

present values also agree with the value of 19·5 kg/mm^2 quoted in the Harshaw Catalogue (1967). For CsI, the Harshaw catalogue (1967) quotes a value of 20 kg/mm^2. In the present work a value of 12·8 kg/mm^2 has been obtained from measurements on the CsI(H) single crystal. This is much lower than (almost half) the Harshaw catalogue value. However, our hardness value for CsI(H) crystal agrees well with our values for CsI(M) and also for the polycrystalline blank. That CsI is much softer than CsBr was clear from the sizes of the indentations made on the two crystals at a given load.

Hardness and lattice constant are both related to the strength of the interatomic binding. The stronger the binding, shorter is the lattice constant and larger the hardness. Thus, we expect a correlation between the hardness and lattice constant in a family of related crystals. Smooth plots between hardness and lattice constants were obtained for the alkali halides with NaCl structure by Thirmal Rao and Sirdeshmukh (1991) and for divalent chalcogenides with NaCl structure by Sirdeshmukh *et al* (1995). Recently, Sirdeshmukh *et al* (2001) obtained a straight line plot between the hardness and lattice constant of rare earth garnets. The lattice constants of cesium halides are given in table 1. In figure 4a, the hardness values of the three cesium halides are plotted against their lattice constants. All data points lie on a straight line except the data point for the Harshaw Catalogue value for CsI.

Shukla and Bansigir (1976) proposed a model according to which the indentation made during a hardness measurement on an ionic crystal results in the creation of a certain number of Schottky defects. For a crystal with NaCl structure, they obtained the relation

$$H_V = 206\ E_f/r^3, \tag{4}$$

where E_f is the energy of formation of a Schottky pair and r the interionic distance. Here H_V is in kg/mm^2, E_f in eV and r in Å. The constant in the equation arises out of the work done by the indenter in displacing crystalline matter and the volume per vacancy pair, both of which are dependent on the structure of the crystal. Shukla and Bansigir (1976) obtained a linear plot between H_V and the parameter E_f/r^3 in accordance with (4). They did not include the cesium halides in their analysis. The model and the equation should be applicable to the alkali halides with CsCl structure with an appropriate change in the numerical value of the constant in (4). The values of E_f and r are given in table 1. In figure 4b, the values of E_f/r^3 for the cesium halides are plotted against the hardness values. Again, it is observed that all data points are close to a straight line, except the data point for the Harshaw catalogue value for CsI, and follow the equation

$$H_V = 537\ E_f/r^3, \tag{5}$$

which is similar to (4).

To conclude, the hardness values for CsI obtained from measurements on three samples agree amongst themselves. Further, our CsI hardness values satisfy two well-established empirical relations while the Harshaw value does not. These facts support the present hardness value of CsI as against the much higher value quoted in the Harshaw catalogue. Differences in the hardness values similar to that as observed by the authors for CsI in the present studies exist in the case of AgCl also, wherein the Harshaw catalogue value is 9·5 kg/mm^2 and two independent measurements (Chin *et al* 1973; author's unpublished results) yield a value of 5 kg/mm^2. However, these comparisons are limited by the fact that the details of measurements in the case of Harshaw Catalogue values are not available.

3.2 *Knoop hardness*

Knoop hardness measurements were made at the lowest possible load of 5 g. For larger loads, the knoop impression was going beyond the field of view. Due to possible load variation, the knoop hardness value at 5 g will not be comparable with the load-variation-corrected Vickers value. However, it has been pointed out by Armstrong and Raghuram (1973) and Thirmal Rao *et al* (1991) that while hardness is load-dependent, the hardness anisotropy is not. Hence only the knoop hardness anisotropy ratio $H_K(100)/H_K(110)$ is given in table 1. The ratio has values of ~1·4 for both CsBr and CsI. It has been observed (Sirdeshmukh and Kishan Rao 1988) that for alkali halides with NaCl structure, this ratio has a value

Table 1. Values of the Vickers hardness, H_V, knoop hardness anisotropy ratio [$H_K(100)/H_K(110)$], lattice constant (a), interionic distance (r) and the formation energy for Schottky defects (E_f).

Material		H_V (kg/mm^2) Single crystal	H_V (kg/mm^2) Polycrystalline blanks	$H_K(100)/H_K(110)$	a^b (Å)	r^b (Å)	E_f^c (eV)
CsCl		–	21·8 ± 2·0	–	4·123	3·571	1·860
CsBr		19·0 ± 2·0 19·5^a	18·5 ± 2·0	1·47	4·286	3·712	1·744
CsI	(H) (M)	12·8 ± 1·0 11·8 20·0^a	12·2 ± 1·0	1·44	4·567	3·955	1·407

[a]Harshaw catalogue (1967); [b]Wyckoff (1965); [c]Murthy and Murti (1971).
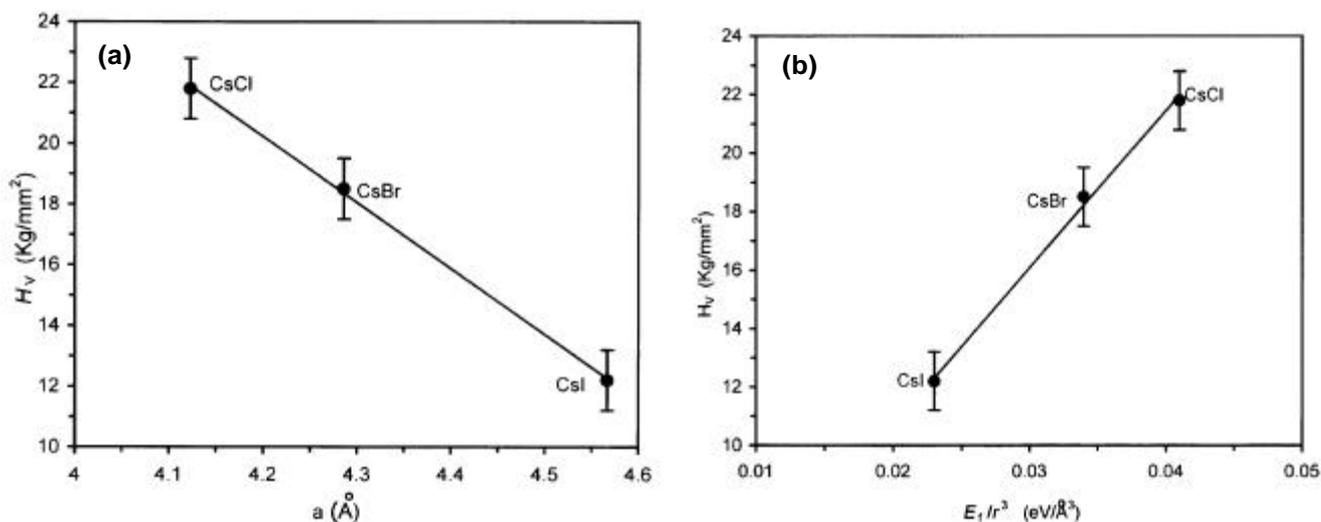
Figure 4. Plots of (**a**) microhardness (H_V) vs lattice constant (a) and (**b**) H_V vs the parameter E_f/r^3.

> 1. The alkali halides with CsCl structure also show the same trend.

4. Conclusions

Polycrystalline blanks of cesium halides have been prepared by melting followed by slow cooling. These blanks are optically clear. X-ray diffraction photographs show that they are homogeneous and nearly-fully polycrystalline. Vickers microhardness measurements on polycrystalline blanks and on single crystals show that the former have mechanical strength comparable with the latter. Vickers microhardness of the cesium halides correlates linearly with the lattice constant and the parameter E_f/r^3 where E_f is the formation energy of a Schottky pair and r the interionic distance. The knoop hardness anisotropy $H_K(100)/H_K(110)$ is about 1·4 for both CsBr and CsI.

Acknowledgements

References

Armington A F, Posen H and Lipson H 1973 *J. Electronic Mater.* **2** 127

Armstrong R and Raghuram A C 1973 in *The science of hardness testing and its research applications* (Ohio: American Society of Testing Metals)

Chin G Y, Van Uitert L G, Green M L and Zydzik K G 1973 *J. Mater. Sci.* **8** 1421

Dobson P S and Wilman H 1962a *Acta Crystallogr.* **14** 1275

Dobson P S and Wilman H 1962b *Acta Crystallogr.* **15** 556

Fullam H T 1972 *Mater. Res. Bull.* **7** 289

Harshaw Optical Crystals Catalogue 1967 (Cleveland, Ohio: Harshaw Chemical Co.)

Leuenberger H, Heisteni E N and Sucker H 1981 *Chem-Ing-Tech.* **53** 43

Murthy C S N and Murti Y V G S 1971 *J. Phys. C: Solid State Phys.* **4** 1108

Optovac Optical Crystal Handbook 1993 (Brookfield: Optovac)

Shukla M and Bansigir K G 1976 *J. Phys.* **D9** L49

Sirdeshmukh D B and Kishan Rao K 1988 *J. Mater. Sci. Lett.* **7** 567

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

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

Sirdeshmukh D B, Sirdeshmukh L, Subhadra K G, Kishan Rao K and Bal Laxman S 2001 *Bull. Mater. Sci.* **24** 469

Srinivas K, Thirmal Rao T, Subhadra K G and Sirdeshmukh D B 1999 *Phys. Edu.* **16** 273

Subramanyam S V 1962 *Acustica* **12** 37

Thirmal Rao T and Sirdeshmukh D B 1991 *Cryst. Res. Technol.* **26** K53

Thirmal Rao T, Kishan Rao K and Sirdeshmukh D B 1991 *Cryst. Res. Technol.* **26** K189

Wyckoff R W G 1965 *Crystal structures* (New York: Interscience Publishers) Vol. I