Functional Materials 11, No.3 (2004)

Anisotropy of mechanical properties of oxide single crystals for inorganic scintillators

I.P.Babiychuk, V.N.Baumer, V.G.Bondar, B.V.Grinyov, V.I.Krivoshein, L.L.Nagornaya, E.N.Pirogov, V.D.Ryzhikov

STC "Institute for Single Crystals", Institute for Scintillation Materials, National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

The microhardness anisotropy of single crystals $PbWO_4$, $CdWO_4$ and Gd_2SiO_5 by the method of sclerometry with the aim of determining possible character of destruction have been studied during mechanical processing in the course of preparation of scintillators.

Методом склерометрии исследована анизотропия микротвердости монокристаллов $PbWO_4$, $CdWO_4$ и Gd_2SiO_5 для определения возможного характера разрушения при механическом воздействии в процессе изготовления сцинтилляторов.

Single crystals of lead tungstate $PbWO_4$ (PWO), cadmium tungstate $CdWO_4$ (CWO) and gadolinium silicate (GSO) have recently again attracted attention due to their broad application in the high-energy physics and spectrometry [1]. Further expansion of the application field requires studies of mechanical properties of these materials. It is known that growth of single crystals of high mechanical strength and fabrication of manufactured articles thereof is hindered by their susceptibility to cleavages due to anisotropy of their properties [2]. Therefore, further studies of physico-mechanical properties, in particular, anisotropy of microhardness and microstresses of these crystals, are essential to know possible character of destruction of these crystals under deformation, which necessarily occurs during mechanical processing of crystals in the course of fabrication of scintillation elements. Data on anisotropy of these properties are important for evaluation of many parameters of abrasive processing. Under mechanical processing, these crystals behave as a rather brittle material, with cleavage planes (001) for PWO, (010) for CWO and (100) for GSO. In addition, PWO crystals are easily cleaved along planes (101) and (112) with expansion of fissures.

Single crystals used in the present work were grown by Czochralski method. It is known [3] that PWO crystals have tetragonal structure of scheelite type with spatial symmetry group $I4_1/a$ with lattice parameters $a = 5.50$ and $c = 12.12$ Å. The structure is based on a three-dimensional frame formed by infinite zigzag-shaped chains of Pb eight-vertex figures, which are connected by side edges into spirals around quaternary helical axes parallel to [001]. Between each pair of such chains, WO_4 tetrahedrons are located, which are not connected with each other. Inside the tetrahedrons, the bonds are covalent, and the bond between Pb and WO_4 is ionic.

Cadmium tungstate crystals have monoclinic structure of the wolframite type, which can be considered as a distortion of the scheelite structure spatial symmetry group P2, P2/c with lattice parameters $a = 5.02$, $b = 5.85$ and $c = 5.07$.

Gadolinium silicate crystals have monoclinic structure with spatial symmetry group $P2_1/c$ and grate (2–3 times) anisotropy [4] of thermal expansion coefficient to [010] and [100], [001] directions. Microhardness anisotropy studies were carried out by the method of sclerometry [5, 6]. PWO samples were oriented along the plane

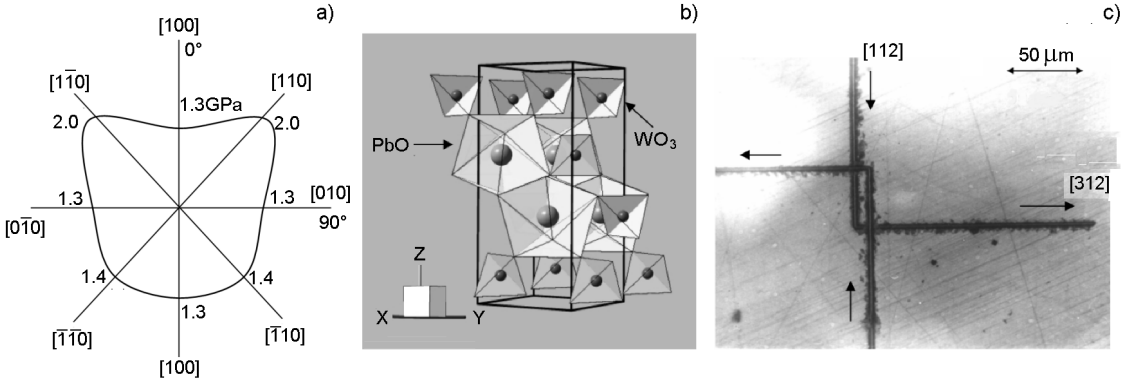

Fig. 1. a) Microhardness sclerometry rosettes on (001) plane. b) view on (001) plane of PWO. Alternation of cation and anion chains in direction OX. c) anisotropy of scratches on (001) plane at $P = 0.2$ N.

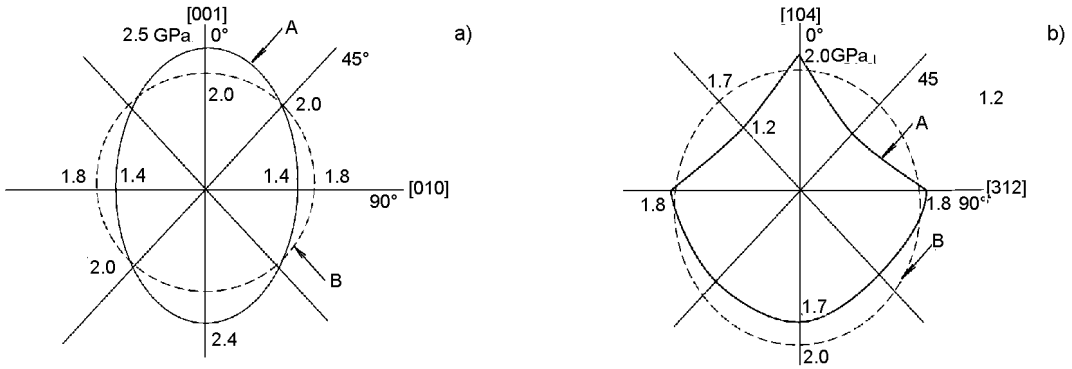

Fig. 2. a) Microhardness sclerometry rosettes on (100) plane. b) microhardness sclerometry rosettes on (112) plane.

(001), which is normal to the main crystallographic axis and is a cleavage plane, along the plane (100), and along the plane (112), which is parallel to the growth axis and is a cleavage plane in this crystal. CWO samples were oriented along the cleavage plane (010) and GSO samples were oriented along the cleavage plane (100). The microhardness was determined using a PMT-3 meter, with standard diamond tetrahedral pyramid as an arrowhead. Scratches were made by the rib of the pyramid in the radial direction after every 10°. The speed of scratching was constant; the load on the indentor was 0.1–0.5 N, with measurement errors not more than 5–10 %. From the width of the scratch obtained, microhardness was calculated, and sclerometric microhardness diagrams were constructed.

In Fig. 1,a, a hardness rosette obtained by scratching on the (001) side is shown. Maximum hardness is found in directions [110]. The maxima correspond to the directions of covalent bonds of the tungstate group WO_4 (Fig. 1,b). In directions [1$\bar{1}$0], [110] large maximums are observed, and in directions [110], [1$\bar{1}$0] — smaller ones. Anisotropy of the microhardness rosette is most possibly related to cleavage planes (101) and (112), forming acute angles with the plane under consideration. It is known that in those directions where cleavage planes are at acute angles to the indentor-affected plane, the hardness values are higher than in the opposite directions [7, 8]. The force applied to the indentor is decomposed into constituents. In the case when the cleavage plane is at an acute angle to the crystal side, the force P on the indentor is decomposed into a bending constituent, which is normal to the cleavage planes, and a stretching constituent, which is parallel to those [9]. This force ensures maximum microhardness. If the angle is obtuse, the constituent forces will be the bending force, identical to that of the previous case, and a compacting force directed downwards. The latter, following the cleavage direction, favors formation of fissures and ensures maximum microhardness (Fig. 1,c).

In Fig. 2,a one can see microhardness rosettes obtained on (100) side for samples cut from the top (A) or bottom (B) parts of

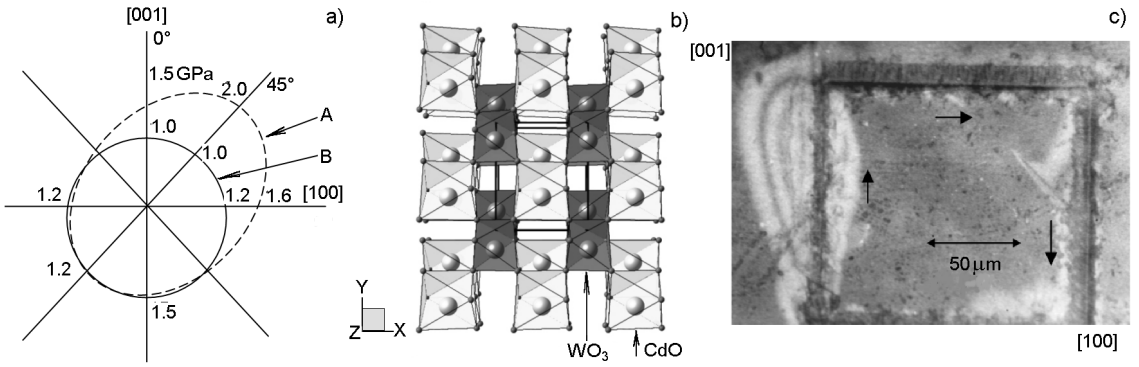

Fig. 3. a) CWO microhardness sclerometry rosettes on (010) plane: A — upper part of the crystal, B — bottom part of the crystals, b) anisotropy of scratches on (010) plane at $P = 0.2$ N.

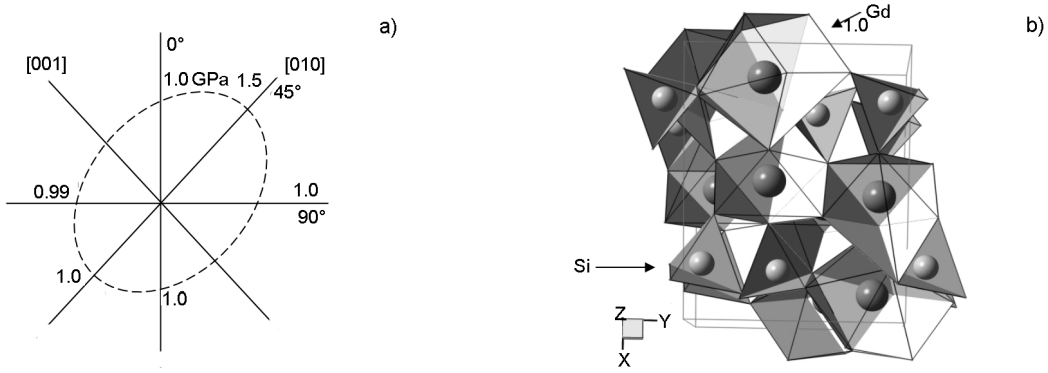

Fig. 4. a) GSO microhardness sclerometry rosettes on (100) plane, b) view on (100) plane of GSO.

the crystal. Maximums were observed with scratching in direction [001], corresponding to the intersection of the cleavage plane and the studied plane, and in the perpendicular direction [010]. The sclerometric hardness rosette has clearly expressed anisotropy. The microhardness anisotropy is related primarily to the cleavage planes at an angle to the given plane. The microhardness rosette on plane (112) is of similar shape (Fig. 2,b). A large maximum is observed in direction [104], and a smaller one — [312]. The shape of the microhardness rosette is determined by W–O bond chains coming onto the plane under consideration. In the direction normal to the bond chains, the microhardness is higher than along the chains, because, with movement of the indentor, higher number of bonds is severed in the first case than in the movement along the chains.

Microhardness rosettes for samples from the top (A) and bottom (B) part of the crystal (Fig. 2,b) have a distinction: the top part of the crystal has higher microhardness anisotropy, which is due to stoichiometry violations at the beginning of the growth process. During the growth process of CWO crystals [2], the component WO_3 is evaporated more rapidly, leading to increasing deviations from the stoichio-metry and to changes in the ratio of covalent and ionic bonds. To compensate for the volatile component, the raw charge contained some extra amount of WO_3. In the crystal, content of PbO was 49.1 %, WO_3 — 50.9 %.

With growth of cadmium tungstate single crystals, the most volatile component is CdO. In sample A, CdO content is 35.4 %, while in sample B it is 35.2 %. To maintain stoichiometry all over the crystal length, some amount of extra CdO is introduced, which leads to certain deviations from stoichiometry and increases the anisotropy of mechanical characteristics (microhardness, brittleness). In CWO crystals (Fig. 3), as distinct from PWO, microhardness anisotropy is not so clearly expressed (Fig. 3,a). However, the material brittleness is different in different directions (Fig. 3,c).

Fig. 4 shows the microhardness rosette on the (100) cleavage plane of a GSO crystal. In the (100) plane, Gd^{3+} cations are positioned layer by layer, localized in oxygen polyhedrons of two types with 7 and 9 coordination and direction of their translation in the sliding reflection plane (010)

along Z axis, i.e., the predominant GSO growth direction limited by (001) side. When a load to the crystal is applied normally to (100), plastic deformation occurs; the sclerometric rosette has the shape of an oval, with anisotropy in (010) direction.

In this work, we have specified the structure of PWO, CWO, GSO crystals and evaluated anisotropy of microstructure violations. The results obtained give a possibility to carry out mechanical treatment of the crystals in the optimum way, accounting for the crystal lattice defects, anisotropy of chemical bonds, as well as for position of the cleavage planes with respect to the direction of force application during mechanical treatment of the crystal. This work was supported by project STCU-48(j).

References

1. P.Lecoq, in: Proc. Conf. Inorganic Scintillators and Their Applications, Netherlands (1995), p.52.
2. M.E.Globus, B.V.Grinyov, Inorganic Scintillators, New and Traditional Materials, Kharkov, AKTA (2000) [in Russian].
3. G.F.Plakhov, E.A.Pobedinskaya, M.O.Simonov et al., *Kristallografiya*, **5**,1067 (1970).
4. T.Utsu, S.Akiyama, *J. Cryst. Growth*, **109**, 385 (1991).
5. V.K.Grigorovich, Hardness and Microhardness, Moscow, Nauka (1976) [in Russian].
6. Sclerometry, by ed. M.M.Khrushchev, Nauka Moscow (1968) [in Russian].
7. M.P.Shaskol'skaya, Crystallography, Vysshaya Shkola Moscow (1984) [in Russian].
8. LG.Tsinzerling, E.S.Berkovich, L.A.Sysoev et al., *Kristallografiya*, **14**, 1037 (1969).
9. Yu.S.Boyarskaya, M.I.Vasil'kovskaya, *Fiz. Tverd. Tela*, **5**, 2324 (1963).

Анізотропія механічних властивостей оксидних монокристалів для неорганічних сцинтиляторів

І.П.Бабійчук, В.М.Баумер, В.Г.Бондар, Б.В.Гриньов, В.І.Кривошеїн, Л.Л.Нагорна, Є.М.Пирогов, В.Д.Рижиков

Методом склерометрії досліджено анізотропію мікротвердості монокристалів $PbWO_4$, $CdWO_4$ и Gd_2SiO_5 для визначення характеру руйнування кристалів при механічному впливі в процесі виготовлення сцинтиляторів.