

# Mechanical Properties and Lattice Parameters of $\text{Lu}_{2x}\text{Gd}_{2(1-x)}\text{SiO}_5\text{:Ce}$ Scintillation Crystals

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Structural and mechanical characteristics of complex oxide compounds  $\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5\text{:Ce}$  (LGSO) crystals were studied at different cation ratio in the host. For this purpose, a series of LGSO crystals with Lu concentration 5–70 at.% has been grown by the Czochralski method. Anisotropy of mechanical properties for these materials has been studied. The obtained results can be useful at choice of optimal growth direction for crystals and at mechanical processing of scintillation elements.

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## 1. Introduction

Rare-earth oxyorthosilicates with common formulae  $\text{Ln}_2(\text{SiO}_4)$ , where Ln are lanthanides, Y, and Sc, are well known scintillators used in medical diagnostics, high-energy physics, well logging. Crystals of rare-earth orthosilicates belong to the monoclinic syngony. Symmetry space groups of monoclinic  $C2/c$  or  $P2_1/c$  types are observed in them depending on  $\text{Ln}^{3+}$  ionic radii [1]. Perfect cleavage planes in some of them, for example, in  $\text{Gd}_2\text{SiO}_5$  (GSO) [2], hamper mechanical processing of ingots and decrease yield of crystal elements. Monoclinic syngony is characterized by high lattice movement, that is, shear deformation can occur in it in four independent directions, including wedge angle, without crystal destruction. At the constant lattice movement in the monoclinic syngony, lowering of the symmetry leads to decrease of populated position multiplicity in lattice from 8 in the base-centered space group  $C2/c$  to 4 in the space group  $P2_1/c$ . In accordance with the 5th Pauling rule [3], this leads to disturbance of the close-packed lattice rule. Such a lattice loosening (lower multiplicity of the occupied positions) results in weakening of bond energy and in increase of free energy in the crystal.

$\text{Si}^{4+}$  ions in GSO lattice have the rigid crystallographic coordination [4]. Such coordination polyhedra are very durable in a wide range of thermodynamic conditions.  $\text{Gd}^{3+}$  ions have the "non-classic" crystallographic coordination numbers 7 and 9. These polyhedra are easy deformable in dependence on shape and relative position of "rigid" polyhedra and Ln ionic radius. Therefore,

changes in GSO:Ce crystallophysical properties should be provided by substitution of "soft-coordinated"  $\text{Gd}^{3+}$  with isovalent Ln ions. For example, it was shown that  $P2_1/c$  space group in GSO matrix retains at 20% substitution of  $\text{Gd}^{3+}$  ions with radius (0.94 Å) by  $\text{Y}^{3+}$  with radius 0.9 Å [5]. Furthermore, crystal strength increases by mechanism of volume compensation in the lattice. It was determined in [6] and confirmed in [7] that polymorph transition  $P2_1/c-C2/c$  in LGSO crystals occurs with substitution of 10 to 20% of  $\text{Gd}^{3+}$  ions by  $\text{Lu}^{3+}$  ions (0.86 Å) (in dependence on the seed type used at growth). Change of type of lattice structure leads to modification of crystal properties; this effect was demonstrated on scintillation properties of LGSO:Ce crystals [7].

Real crystals are characterized by physical imperfections, such as atom deflection in the lattice. These factors diminish contribution of plastic deformation as compared to elastic deformation, and, as the result, it leads to destruction of the material at some threshold tensile stress. This factor is of special importance at production elements from grown crystal ingots. Thus, study of mechanical anisotropy in these crystals aimed at elaboration of practical recommendations concerning crystal element production is a topic of interest.

## 2. Experimental

Mechanical properties of solids may be determined by their response on mechanical load [8]. Studies of structure transformation in materials under mechanical action at microscopic area give information concerning physico-mechanical properties of their surface layer and relationships between deformation and destruction. Local strength action on microscopic areas is typical for

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all types of machining procedures utilizing an abrasive. Complex superposition of strengths is formed in the area of abrasive particles contact with machining material in dependence on applied load and physico-mechanical properties of contacting surfaces.

Search for easy and reliable criteria of material machinability results in formulation of a big quantity of relationships between this parameter and other characteristics of solids, foremost, the hardness [8, 9].

In general, machinability  $V$  and microhardness  $H$  are connected by the empirical formulae (1) (coefficient  $k$  and power index depend on conditions of  $H$  determination)

$$V = k/H^n. \quad (1)$$

In the present paper, microhardness was measured by a PMT-3 tester, with a diamond pyramid with a square base used as indenter. Microhardness was evaluated by the formula

$$H = 1.854P/d^2 \text{ [kg/mm}^2\text{]}, \quad (2)$$

where  $P$  — load on indenter,  $d$  — imprint diagonal. Error not exceeds 3–5%.

Anisotropy of mechanical properties of the crystal was evaluated by sclerometry method based on implying the scratch by the edge of diamond pyramid under the load [9, 10].

Microhardness  $H_S$  was evaluated as

$$H_S = 3.708P/d^2 \text{ [kg/mm}^2\text{]}, \quad (3)$$

where  $P$  — load on the indenter,  $d$  — fissure width. Error not exceeds 3–5%.

The measurements were conducted on polished elements cut from LGSO:Ce single crystals obtained by the Czochralski method from starting oxides  $\text{Gd}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{CeO}_2$  with purity not less than 99.99%. Concentrations of  $\text{Lu}_2\text{O}_3$  in melt were: 5%, 7%, 10%, 15%, 19%, 20%, 35%, 40%, 55%, 60%, and 70%. Crystals with diameter of 30 mm and of length 30–50 mm were grown in iridium crucibles of 60 mm diameter and 60 mm height. The growth atmosphere was Ar with addition of up to 1%  $\text{O}_2$ . The pulling rate was 1.2–3 mm/h, and rotation rate was 30–35 rot/min. Cerium concentration in the crystals was about 0.5 mol.%.

The main axis of symmetrical second order tensors have unrestricted orientation in crystals with monoclinic space symmetry, therefore, samples for measurements were cut as cubes with  $10 \times 10 \times 10$  mm dimensions (one of cube faces is perpendicular to the crystal growth axis  $[001]$ );  $\{101\}$ ,  $\{120\}$  and  $\{010\}$  planes were also studied. A typical view of destruction on polished surface under different loads is presented in Fig. 1 (20 g load forming a scratch without severe destruction was chosen for convenience).

### 3. Discussion

Measurements of microhardness at  $(001)$  plane under 20 g load show improvement of mechanical properties with  $\text{Lu}_2\text{O}_3$  content. In particular, microhardness ranges from 7.42 GPa ( $\text{Lu}_2\text{O}_3$  content 5 at.% to 18.84 GPa

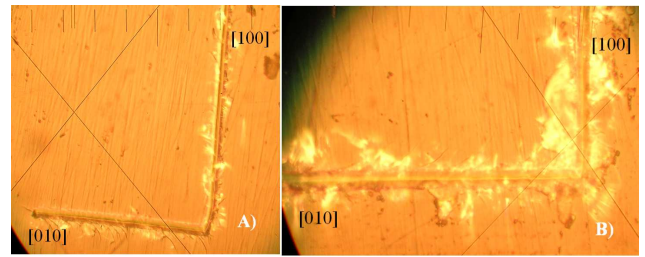


Fig. 1. Scratches on crystal surface at loads 20 g (A) and 50 g (B) in the  $(001)$  plane.

(70 at.% content). However,  $\text{Lu}_2\text{O}_3$  addition leads to bigger spread in hardness values along the sample surface certifying non-uniform distribution of dopants in the lattice. No large spread of microhardness was observed on the other planes.

LGSO samples with different space symmetry groups ( $P2_1/c$  or  $C2/c$ ) in polymorph transition range at about 20 at.% Lu were chosen to determine the influence of crystal space symmetry on its mechanical properties.

Both samples no. 1 and 2 were cut from crystals grown from melt with Lu content about 20 at.%. Different conditions of crystal growth allowed to obtain the sample no. 1 with  $P2_1/c$  symmetry type and lattice parameters:  $a = 9.11321$  nm,  $b = 6.9908$  nm,  $c = 6.7248$  nm,  $\beta = 107.423^\circ$  and lattice volume  $V = 408.773$  ( $Z = 4$ ); sample no. 2 has symmetry type  $C2/c$  with parameters:  $a = 14.490$  nm,  $b = 6.758$  nm,  $c = 10.524$  nm,  $\beta = 122.18^\circ$  and volume  $V = 872.233$  ( $Z = 8$ ), where  $Z$  is the number of formula units in the unit cell.

Lu content in obtained crystals was determined by the two independent methods — inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray diffraction (for details of methods, see [7]).

In accordance with X-ray studies, Lu content in both samples is the same (Table). This means the same quantity of Lu atoms in lattice sites. ICP-AES analysis demonstrates substantially larger quantity of Lu in the sample no. 2 ( $C2/c$  symmetry) certifying their presence at interstitial sites in the crystal lattice sites. As the result, the lattice loosens and plasticity increases.

The character of surface destruction for both samples in the  $(001)$  plane in different directions is demonstrated in Fig. 2. Sample no. 1 possesses higher brittleness, and the second sample is characterized by better plasticity confirming the conclusion made on the base of Table analysis.

Sclerometry profiles of microhardness anisotropy  $H_S$  for the samples no. 1 and 2 are shown in Fig. 3. The first crystal has clearly defined anisotropy of microhardness in  $[100]$  and  $[010]$  directions. The second crystal profile has elongated shape certifying the tension lattice deformation in the  $[100]$  direction and compression deformation in the  $[111]$  direction, inward the crystal center. In this case, anisotropy in a certain direction is connected with lattice own properties and presence of planes of easy slip.

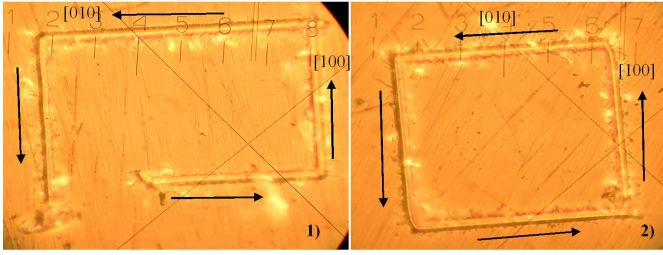


Fig. 2. Scratches on surfaces of the samples no. 1 (left) and 2 (right) in the (001) plane. Direction of indenter movement is shown by the arrows.

TABLE

Lu content in melt and in crystal host determined by different methods.

Sample no.	Lu content in melt [at.%]	Lu content in the crystal [at.%]	
		ICP-AES	X-ray analysis
1	20	13.4	14
2	20	20.5	14

Resistance is larger at scratching by the indenter in the direction across the rigid chains than along them (Fig. 4). Therefore, the observed anisotropy of brittle destruction in crystals is tightly connected with the Young modulus anisotropy. Anisotropy in crystals with plastic deformation is not connected with elastic characteristics, but provided by system of crystallographic planes and directions of shearing and twinning.

Determination of microstructure disturbance in different directions gives possibility to avoid propagation of fractures at crystal deformation in the process of crystal machining. It is shown that crystals with  $P2_1/c$  symmetry grown from melt with  $\text{Lu}_2\text{O}_3$  content from 2 at.% to 15 at.% possess high brittleness (Fig. 5). Crystals with  $C2/c$  symmetry grown from melt with  $\text{Lu}_2\text{O}_3$  content more than 20 at.% are more plastic. Substantial jump of microhardness from 9.12 to 18.84 GPa is observed at  $\text{Lu}_2\text{O}_3$  content increase up to 70 at.%.

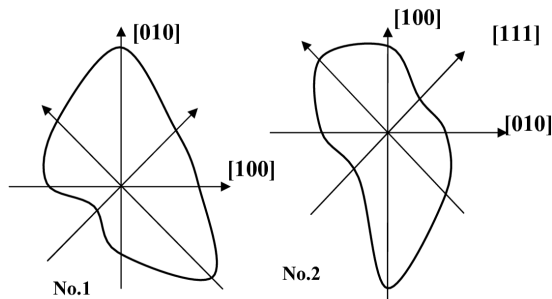


Fig. 3. Sclerometry profiles of microhardness anisotropy.

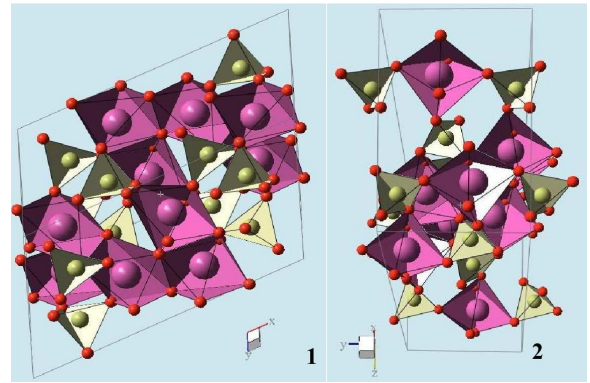


Fig. 4. Lattice structure of LGSO crystal: (1) — [001] plane,  $C2_1/c$  lattice; (2) — [100] plane,  $C2/c$  lattice (crystal packing is drawn with “Ball & Stick” program [10]).

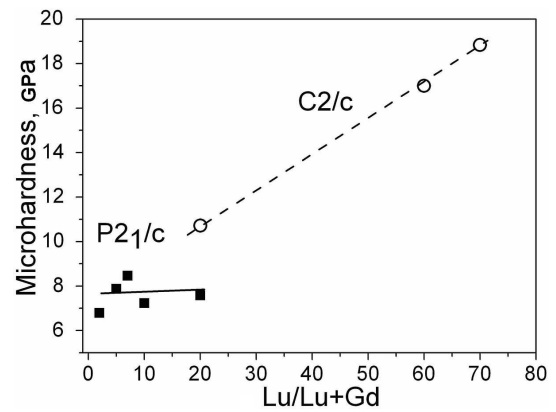


Fig. 5. Microhardness of LGSO crystals vs. Lu content in the host for different space symmetry types.

#### 4. Conclusions

Microhardness of LGSO crystals significantly depends on space symmetry type of crystal lattice. Crystals with monoclinic  $P2_1/c$  structure (2–15 at.% of Lu) possess high brittleness. Improvement of mechanical characteristics in crystals with space symmetry  $C2/c$  is observed at Lu content in the host more than 20 at.%. Substantial spread of microhardness in this symmetry type is, probably, connected with irregular distribution of Lu and Gd in lattice and with presence of these atoms at interstitial sites.

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