

ORIENTATION STATES IN RHOMBIC NdGaO₃D.I. SAVYTSKII, S.B. UBIZSKII, L.O. VASYLECHKO, I.M. SYVOROTKA
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The ferroelastic domain structure of NdGaO₃ is analyzed by three theories: group symmetry, tensor method and twinning by pseudosymmetry. The theories provide a coherent description of domain pairs and a determination of the position of *W* and *S* walls.

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Wide use of the rare-earth orthogallate and orthoaluminate single crystals as the substrate materials for HTSC films attracts considerable interest to the study of their crystal and twinning structure. Ability to twinning is due to result of small lattice deviation of ideal cubic structure. Usually one notes a negative influence of this fact on critical parameters of synthesized HTSC films [1]. Majority of works [2-7] dealing with twinning problem in these substrate materials is focused on experimental determination of the twin states' orientation only. This work is devoted to theoretical investigation of twinning in NdGaO₃ that has a rhombic structure and is one of the most perspective substrate materials.

Neodymium gallate has a rhombic cell (space group *Pbnm*) with parameters $a = 0.54276$ nm, $b = 0.54979$ nm, $c = 0.77078$ nm [6] at the room temperature. Its crystal structure as that of most stoichiometric compounds of the ABX₃ composition can be also considered as a small deformation of an ideal cubic (prototypic) perovskite cell (point group $G = m3m$) which transforms into monoclinic one with parameters $a = b = 0.3863$ nm, $c = 0.3854$ nm and $\alpha = 89.26^\circ$. This pseudo-perovskite monoclinic cell with $a = b$ has a symmetry of point group $F = mmm$. Relation between parameters of rhombic and pseudo-perovskite monoclinic cells (see Fig. 1) can be written in the form

$$a_0 = a_m - b_m, \quad b_0 = a_m + b_m, \quad c_0 = 2c_m. \quad (1)$$

According to the paper [8] the symmetry reducing of point group from $G = m3m$ (order $n = 48$) to $F = mmm$ (order $n = 8$) can cause the appearing of a low-symmetric (ferroelastic) phase of the $n_G/n_F = 6$ different twin orientation states (ferroelastic domains) with the same crystal structures but of another lattice space orientation.

Let us assume that the axes orientation of ferroelastic domain D_1 is the same as shown in Fig. 1. Further calculations will be carried out in chosen geometry. The point group of the NdGaO₃ rhombic phase for monodomain D_1 is $F = mmm$

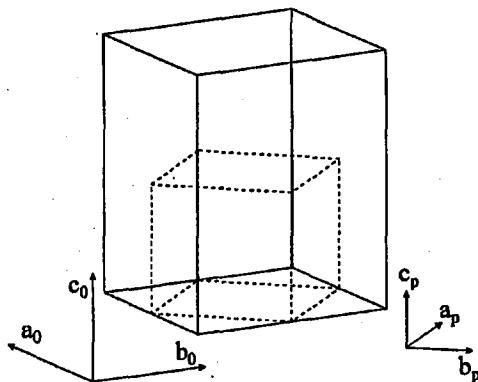


Fig. 1. The general view of the NdGaO_3 unit cell and selection of pseudo-cubic (perovskite) one.

with elements of symmetry $1, 2_z, 2_{-xy}, 2_{xy}, -1, m_x, m_{-xy}, m_{xy}$, where elements are presented in orientation of the perovskite cell. The rest five twin states can be generated from domain D_1 by performing of manipulations $g \in G = m3m$ which do not belong to F . Each of six domains complies with one of the left cosets of $F(H_j)$ subgroups which are the result of the G group expansion [8]. One of possible decompositions for $G = m3m$ and $F = mmm$ can be

$$G = m3m = F + m_x F + m_{-yz} F + m_{yz} F + m_{-xz} F + m_{xz} F. \quad (2)$$

These six classes, their symmetry elements and appropriate domains as well as possible domain walls between D_1 and D_j are presented in Table. It should be pointed out that the symmetry elements which fall in j -row are those which can link domain D_1 with D_j . That is, performing this symmetry operation the D_j -domain could be derived from domain D_1 . As it can be seen from Table, domains D_1 and D_2 can be connected by the 2nd-order symmetry operations $(m_x, m_y, 2_x, 2_y)$ and the 4th ones $(\bar{4}_z, \bar{4}_z^3, 4_x, 4_x^3)$. Additionally, the $D_3 \dots D_6$ -domains can be connected with D_1 by the 3rd-order turns too.

From the above decomposition on classes, one can derive an orientation of possible domain walls between D_1 and D_j . If domains are connected with some symmetry plane then this plane can be a compositional plane W_{1j} between adjacent domains. Besides, if there is the 2nd-order axis among symmetry elements H_j which is perpendicular to this plane, the existence of another compositional plane S_{1j} which would be also perpendicular to W_{1j} [9], is possible, but it has no rational indices. In the general case the symmetry considerations do not allow to get all conceivable orientations of domain walls.

A full set of possible domain walls between D_1 and D_j could be obtained taking into account that the compositional plane (domain wall) should contain all directions for which the change in length of an infinitesimal vector of the prototypic phase, due to the spontaneous strain, takes the same value in the two adjacent orientation states of prototypic phase [10]. To ensure a compatibility of deformation

TABLE

Results of theoretical consideration of twinning in NdGaO₃ (the conventional symbols denote: D — domain type; $e = 2d/3b$; $\gamma = 2d/3b-1$; $\varphi = 2d/3b+1$; $\lambda = 5.6$; $\sigma = 2.3$; $\delta = 3.3$).

Left cosets	Symmetry elements	D	Spontaneous strain tensor [11]	Domain wall orientation by	
				spontaneous strain method	twinning theory
$\{mmm\}$	$12_x2_{-xy}\bar{1}$ $m_xm_{-xy}m_{xy}$	D_2	$b \quad d \quad 0$ $d \quad b \quad 0$ $0 \quad 0 \quad -2b$		
m_x $\{mmm\}$	$m_xm_y\bar{4}_z\bar{4}_z^32_x$ $2_y4_x4_z^2$	D_2	$b \quad -d \quad 0$ $-d \quad b \quad 0$ $0 \quad 0 \quad -2b$	$W'_{12} \quad (100) \quad (110)$ $W''_{12} \quad (010) \quad (1\bar{1}0)$	$(100) \quad (110)$ $(010) \quad (1\bar{1}0)$
m_{xz} $\{mmm\}$	$m_{xz}\bar{4}_y\bar{3}_{-x-yz}$ $\bar{3}_{x-y-z}2_{xz}4_y$ 3_{x-yz} 3_{x-y-z}	D_3	$-2b \quad 0 \quad 0$ $0 \quad b \quad -d$ $0 \quad -d \quad b$	$W_{13} \quad (101) \quad (224)$ $S_{13} \quad (1e\bar{1}) \quad (\bar{\gamma}\varphi\bar{2})$	$(101) \quad (224)$ $(1\lambda\bar{1}) \quad (\bar{\sigma}\delta\bar{1})$
m_{-xz} $\{mmm\}$	$m_{-xz}\bar{4}_y^3$ $\bar{3}_{xyz}\bar{3}_{-xy-z}$ $2_{-xz}\bar{4}_y^3$ $3_{xyz}3_{-xy-z}$	D_4	$-2b \quad 0 \quad 0$ $0 \quad b \quad d$ $0 \quad d \quad b$	$W_{14} \quad (10\bar{1}) \quad (2\bar{2}4)$ $S_{14} \quad (1e1) \quad (\bar{\gamma}\varphi\bar{2})$	$(10\bar{1}) \quad (2\bar{2}4)$ $(1\lambda 1) \quad (\bar{\sigma}\delta 1)$
m_{yz} $\{mmm\}$	$m_{yz}\bar{4}_x^3\bar{3}_x^2$ $\bar{3}_x^2_{-xy-z}2_{yz}\bar{4}_x^3$ 3^2_{-xy-z} 3^2_{-xy-z}	D_5	$b \quad 0 \quad -d$ $0 \quad -2b \quad 0$ $-d \quad 0 \quad b$	$W_{15} \quad (011) \quad (\bar{2}24)$ $S_{15} \quad (e1\bar{1}) \quad (\gamma\varphi\bar{2})$	$(011) \quad (\bar{2}24)$ $(\lambda 1\bar{1}) \quad (\sigma\delta\bar{1})$
m_{-yz} $\{mmm\}$	$m_{-yz}\bar{4}_x\bar{3}_{xyz}^2$ $\bar{3}_{x-y-z}^2_{-yz}$ $4_x\bar{3}_{yz}^2\bar{3}_{x-y-z}^2$	D_6	$b \quad 0 \quad d$ $0 \quad -2b \quad 0$ $d \quad 0 \quad b$	$W_{16} \quad (01\bar{1}) \quad (2\bar{2}4)$ $S_{16} \quad (e11) \quad (\gamma\varphi\bar{2})$	$(01\bar{1}) \quad (2\bar{2}4)$ $(\lambda 11) \quad (\sigma\delta 1)$

in adjacent domains the following relationship should be satisfied:

$$\sum (T_{ij} - T'_{ij})x_i x_j = 0, \quad (3)$$

where T_{ij} and T'_{ij} are the components of the spontaneous strain tensors; x_i and x_j are coordinates in prototypic phase [9].

The spontaneous strain tensors for all six possible orientation states of the $m3mFmmm(ss)$ transformation are presented in [11]. If we take into account that rhombic axis of domain D_1 (D_5 in [11]) in chosen coordinate system is parallel to OZ axis of the perovskite cell then according to the condition (3) one can obtain five equations

$$4dxy = 0, \quad (4a)$$

$$(x+z)(x+2dy/3b-z) = 0, \quad (4b)$$

$$(x-z)(x+2dy/3b+z) = 0, \quad (4c)$$

$$(y+z)(2dx/3b+y-z) = 0, \quad (4d)$$

$$(y-z)(2dx/3b+y+z) = 0. \quad (4e)$$

The equations' solutions are corresponding pairs of mutually perpendicular planes. The spontaneous strain tensors for each of six domains as well as Miller indices for possible domain walls between D_1 and D_j both, in perovskite and in rhombic presentations are indicated in Table. In virtue of the fact that NdGaO_3 crystallizes in rhombic ferroelastic phase there is no possibility to find extrapolated values of the ideal cubic (prototype) cell parameters which are required to calculate the b and d components in the spontaneous strain tensors and to obtain the Miller indices numerical values for the S_{1j} -type walls. Nevertheless, the twin states with reticular compositional walls of the $\{110\}_0$ and $\{224\}_0$ families having fixed Miller indices can be expected in NdGaO_3 from obtained results as well as the domain walls of the $\{1-e \ 1+e \ 2\}$ -type being perpendicular to $\{224\}_0$. The S_{1j} walls have a temperature-dependent orientation caused by dependence of the $3b/2d$ constituent vs. temperature during thermal expansion of the cell.

Just obtained results are correlated with those which were get previously for isostructural rhombic LaGaO_3 [12]. At formal consideration of the process as a simple uniform shift it was derived that there is a possibility for existing of two systems of the conjugate domains (twins) in rhombic crystals of the ABX_3 type.

The first of them is a degenerated system with compositional planes $K_1 = \{110\}$ and shift directions $\mu_1 = \{1\bar{1}0\}$. That is responsible for orientation state D_2 , which can be connected with D_1 ground state (matrix) by mirror reflection about K_1 (m_x and m_y in perovskite presentation) and rotation through 180° around μ_1 (2_x and 2_y for perovskite cell). Domain walls are m_x and m_y planes, respectively.

The second non-degenerated system consists of reflection twins with $K_1 = \{224\}_0$ (m_{xz} ; m_{-xz} ; m_{yz} ; m_{-yz}) and axial twins with shift directions $\mu_1 = \langle 111 \rangle_0$ (2_{xz} ; 2_{-xz} ; 2_{yz} ; 2_{-yz}). That is, the twin orientation states D_3 , D_4 , D_5 , D_6 appear in the matrix (D_1) under these twinning types where the same orientation state, for example D_3 , connected with D_1 via operation of reflection about (224) (m_{xz}) and rotation through 180° around the $[111]$ (2_{xz}) direction. For the case of reflection twins the interface boundary between D_1 and D_j will be a reticular plane $K_1 = (224)$ (m_{xz}), whereas for the axial twins the domain wall has irrational indices. For example, domain walls in LaGaO_3 is close to $(\bar{1}21)_0$ (or $(3\bar{1}1)$ in perovskite presentation [12]).

The twin boundary orientation between D_1 and D_j ($j > 2$) being jointly connected through the 2nd-order turn was determined in [12] for LaGaO_3 on the base of the twin conjugation using calculated twinning elements of reflection about the $\{224\}_0$ planes (m_{xz} ; m_{-xz} ; m_{yz} ; m_{-yz}). It means that the second circular section plane K_2 for reflection twin $K_1 = \{224\}_0$ is a compositional plane K_1 (domain wall) between D_1 and D_j when they are connected by the turn around the 2nd-order axis.

Under the same twinning elements calculation procedure [12] the following results for $(224)_0$ reflection twin in NdGaO_3 were obtained: compositional plane $K_1 = (224)_0$; shift direction $\mu_2 \approx [4.8 \ \bar{6}.8 \ 1]_0$; shift plane $S \approx (2.1 \ 1 \ \bar{3}.1)_0$; axis of the main zone $\mu_2 = [111]_0$; the second circular section plane $K_2 \approx (\bar{2}.3 \ 3.3 \ \bar{1})_0$ ($(\bar{1} \ 5.6 \ \bar{1})$ in perovskite presentation). Orientations of all possible domain walls in

NdGaO₃ defined using twinning theory are listed in Table. It should be remarked in order to perform the same calculations that it is necessary to know the lattice parameters in ferroelastic phase only.

In accordance with analysis performed in [12] the mutual misorientation of the same domain pairs D_1 and D_j is different for the cases when they are connected by reflection and rotation. Thus, there is some deviation of D_j orientation from ideal case in ferroelastic phase. As this takes place, the small deviation depends on symmetry which connects domains (or, that is equivalent — on orientation of the domain wall dividing them). For example, in LaGaO₃ the (001) plane in the (224) reflection twins and in the [111] axial ones should be misoriented in reference to the (110) crystal matrix on different angles — 0.11° and 0.34° respectively. Unfortunately, a large density of the twin lamellae in LaGaO₃ did not allow to check this fact. The calculation shows that for NdGaO₃ the (110) plane misorientation in reflection twins and axial ones about the D_1 matrix plane should make an angle 0.13° and 0.75° correspondingly.

Experimental investigation of (001) oriented plates of NdGaO₃ using X-ray and microscopy techniques described in [7] has revealed all types of theoretically predicted twins. Moreover, the angles determining the spatial orientations of twin boundaries coincide with calculated values within accuracy of measurements.

Therefore, one may conclude: comparative analysis of the theoretical and experimental results showed that detected twinning in NdGaO₃ can be interpreted by means of the group theory, analysis of spontaneous strain tensors and twinning theory which complement each other in that case. Applying the group theory methods to the orientation states' quantity and enumeration of the symmetry elements which can link these states were obtained. The use of the spontaneous strain tensor method allowed to define all possible types of the domain walls in NdGaO₃, however a direct calculation of the S -walls is impossible due to the lack of needed information on the parameters of a hypothetical prototypic phase. The twinning analysis as a simple uniform shift has allowed to find the S -walls positions, but for this the before obtained information about possible planes of the mirror reflection $\{110\}_0$ and $\{224\}_0$ was additionally used. Theoretically derived results are in good agreement with experimentally observed twinning.

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