

UDC539.8:548.0

## Twinning Mechanism of Solid-State Reactions

M. SH. AKCHURIN, R. M. ZAKALYUKIN and A. A. KAMINSKIY

*Shubnikov Institute of Crystallography, Russian Academy of Sciences,  
Leninsky Pr. 59, Moscow 119333 (Russia)*

E-mail: akchurin@ns.crys.ras.ru

### Abstract

A new mechanism of solid-state reactions, based on a mass transfer process due to the plastic deformation is proposed. By the example of the nucleation in the course of the mechanosynthesis of complex oxides, there has been demonstrated a role of twinning processes in the nucleation of spinel ( $\text{MgAl}_2\text{O}_4$ ), lead titanate ( $\text{PbTiO}_3$ ) and yttrium-aluminum garnet ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) under grinding the powders of  $\text{MgO} + \text{Al}_2\text{O}_3$ ,  $\text{TiO}_2 + \text{PbO}$  and  $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$ , respectively. It has been proposed that the mechanical twinning is the main mechanism of mechanochemical solid-state reactions.

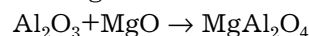
**Key words:** plastic deformation, twinning, mechanosynthesis, solid-state reactions

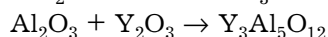
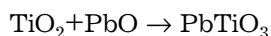
### INTRODUCTION

The influence of elastic and plastic deformations on the reactivity of solids has been studied for a long time [1–5]. The procedure of mechanosynthesis is usually carried out by means of deformation stirring the reagents in various types of mills, vibrators, disintegrators, *via* cold and hot pressing, by means of pressure with deformation shear in diamond anvils *etc.* The opportunity of synthesizing intermetallic compounds and refractory materials, inorganic and organic compounds, of making composite materials, of modifying polymers in the solid phase with no melting and dissolution of the reagents attracts a wide range of researchers, particularly from the standpoint of nanotechnology development. It should be emphasized that for the recent years one could observe a significant increase in the number of publications concerning the mechanical synthesis of complex oxides. At the same time the mechanisms of the mechanosynthesis processes themselves have not been established up to date, although the need for studying thereof is noted in many publications [4, 5]. The arguments concerning the mechanisms of mecha-

nosynthesis are mostly related to bringing the system to a pre-melting condition and to the use of well-known fluctuation mechanisms of nucleation with a diffusion mass transfer of individual atoms [3, 6, 7]. However, the mechanochemical syntheses can be carried out at a relatively low temperature. The main mechanism of heat transfer under these conditions is presented by plastic deformation, since the diffusion processes are inefficient at such temperature values, but they could facilitate the structural relaxation.

In this paper, we propose a new mechanism of nucleation based on the processes of mechanical twinning. Phase transformations in the course of twinning are well-known: for example, calcite  $R3c$  – aragonite  $Pcmn$ ; diamond  $Fd3m$  – lonsdaleite  $P63/mmc$ ; pyrite  $Pa3$  – marcasite  $Pmnn$  [8]. However, the mentioned transformations represent conventional phase transitions within the same structure, whereas in our case we consider complex phase transitions, as the result of those a third phase is formed from two different phases, *i. e.* a solid-state reaction occurs. By the example of occurring the reactions





we demonstrate the role of twinning processes in the formation of a new phase under the deformation stirring of corresponding components.

In the course of studying all the manifestations of plastic deformation, a question immediately arises concerning the participation of dislocations in these processes. However, the prevalent concepts of dislocations could not explain the occurring structural changes. Furthermore, the role of dislocations under the conditions of high strain level and relatively low temperature values is negligible. Earlier [9, 10], we studied the features of dislocation-free plasticity in ionic crystals (alkali-halide crystals, MgO, CaF<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> *etc.*) in the fields of a high mechanical stress and at  $T < 0.5T_{\text{melt}}$ . It was demonstrated that the basic mechanisms of plastic deformation, whereby there occur the fragmentation and turning the structure under the action of a concentrated load (an analogue of the deformation stirring) represent the processes of twinning, and the size of the nanocrystals under formation is inversely proportional to the hardness of the samples. The dislocation detected around prints and scratches only relax the strains at the border between a nanocrystalline area and the initial single crystal. Further studies demonstrated that the formation of grain boundaries in laser ceramics is also connected with the twinning processes, those lead to turning the crystal structure and grain interfacing [11, 12]. There were studied the structure and properties of the twin grain boundaries, and proposed the models of the formation thereof and “healing” the pores [13, 14], and so on. In general, these studies were focused on the processes of the formation of solid samples and almost do not concern any mechanisms of nucleation. It is natural to believe that the mechanical twinning could form also the basis of solid-state reactions taking place in the course of joint deformation of corresponding powders. Moreover, the formation of a new crystalline phase occurs in the system of contacting particles. In this paper, we demonstrate how the twinning can cause the nucleation of a new phase.

#### NUCLEATION OF MgAl<sub>2</sub>O<sub>4</sub>

In the course of the mechanosynthesis of spinel, the formation of new phase is carried out *via* a joint deformation of corresponding components [5, 7, 15]. The authors of [7] demonstrated that the deformation stirring of corundum and magnesium oxide single crystal powders in a ball mill could result in the yield of spinel amounting to about 80%. As mentioned above, the main mechanism of heat transfer under these conditions is presented by plastic deformation, whereas at high stress levels and relatively low temperature values, the single crystals under investigation are plastically deformed mainly *via* twinning [10]. The twinning represents a joining of two individual crystal symmetry elements that do not exist in the structure under consideration. Generally speaking, the twinning can occur in any plane and/or axis, those are not a plane or a symmetry axis of the mentioned structure, but with different probability values.

Let us consider structural features of single crystals participating in of the solid-state reaction from the standpoint of the ability thereof with respect to twinning, and investigate the possibility of forming structural elements of the spinel in the course of the plastic deformation of initial single crystals. The crystals of spinel exhibit a cubic structure, sp. gr.  $Fd\bar{3}m$ . The oxygen anions form the closest cubic packing, 1/2 of the octahedral voids and 1/8 of the tetrahedral voids wherein are filled with Al and Mg ions of, respectively. The magnesium oxide crystals have the structure of NaCl type; sp. gr.  $Fm\bar{3}m$ . Each magnesium ion is surrounded by six oxygen ions in the octahedral configuration. The aluminum oxide ( $\alpha$ -modification) has a trigonal structure and belongs to the class of symmetry operation  $3m$ . The oxygen ions form a hexagonal close packing. Two thirds of the octahedral voids between the oxygen layers are occupied by aluminum ions.

Thus, in the spinel structure aluminum ions are located in the octahedral environment of oxygen ions, as it is in corundum, whereas magnesium ions are located in a tetrahedral environment, although in MgO they are located in the octahedral environment. Let us inves-

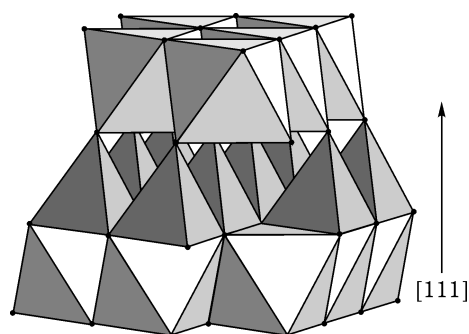


Fig. 1. Oxygen tetrahedra  $[\text{MgO}_4]^{-6}$  in the twinning plane of MgO. Oxygen octahedra are marked with light gray here tetrahedral are dark gray.

tigate the possibility of transferring the Mg ions into the tetrahedral position *via* twinning MgO. Non-metallic crystals belonging to the cubic system exhibit usually twinning in the plane (111), since the packing thereof remains close (the cubic close packing becomes the hexagonal close packing) [16]. The authors of [12] simulated the twins in cubic crystals *via* rotating a part of the structure around the third order axis through  $60^\circ$ , which corresponds to a shift of the closely packed layer in the (111) plane along the direction of [112] at a distance of  $a/\sqrt{6}$ , where  $a$  is the lattice parameter. As a result of the shift, the cations pass from the octahedral voids into the tetrahedral ones, *i. e.* within the structure of MgO there formed a fragment of the spinel structure such as an oxygen tetrahedron around the magnesium cation. Figure 1 demonstrates the structure of the twinning boundary.

Under the effect of sufficient stresses, shifting could occur within the subsequent layers, which should result in the displacement of twin boundaries according to the model of twinning the FCC structures [11]. The growth of twins is also observed in the course of annealing the deformed samples [16]. On the one hand, the twinning leads to increasing the symmetry level (appearing new symmetry elements), whereas, on the other hand, it results in appearing the defects (twinning boundaries). However, the twinning boundary exhibits a one feature: from neighbouring grains it attracts defects those cause the stresses of opposite sign and can annihilate at the boundary. As a consequence, the twinning boundary in the course of the movement thereof does not cause any significant stress.

It should be noted that in structures of NaCl type cations are located over the tetrahedral cavities, whereas on the twin boundary they are arranged over each other. As the result, there arise stresses those could relax at the expense of stoichiometry violation, and the harder the material, the greater is the deficiency of cations. For MgO, the deficiency of cations near the twinning boundary can reach several percent [10]. Therefore, one could believe that the mechanical activation, first of all, is associated with the plastic deformation of crystals *via* twinning, which leads to the fragmentation of the initial single crystals. The presence of twinning boundaries (increasing the surface area, appearing special sinks for defects, stoichiometry violation near the interface, and so on) determines the reactivity of the material.

Corundum crystals are characterized by the two main types of twins: in the basal (0001) plane and in the plain of morphological rhombohedron  $(10\bar{1}1)$  [17]. The aluminum ions in the spinel and corundum are located in the octahedral environment of oxygen ions, and there is no need for twinning the corundum in the basal plane of *via* rotating a part of the structure around the third order axis through  $60^\circ$ , whereby a part of the Al ions passes to the tetrahedral position. Twinning according to the system of  $(10\bar{1}1)$   $[\bar{1}012]$  discloses the surfaces of rhombohedron  $(\bar{1}\bar{1}01)$ , wherein there appear structural possibilities for embedding the magnesium tetrahedra (Fig. 2). It should be noted that the distance between the magnesium ions and oxygen ions in the twinned state (MgO $\perp$ ) exhibits a decrease from 2.11 Å in the original structure to 1.83 Å in MgO $\perp$  becoming close to the corresponding values inherent in the spinel (1.74 Å). The conversion level depends on the size of particles entering into the solid-state reaction which size, in turn, is determined by the ability of the particles to twinning. The aluminum oxide and magnesium oxide are very different with respect to hardness ( $H = 6$  and 18 GPa, respectively), so the preliminary activation of the starting components *via* deformation stirring, especially of the corundum, should lead to an increase in the yield of spinel phase, which is observed in the experiment [7].

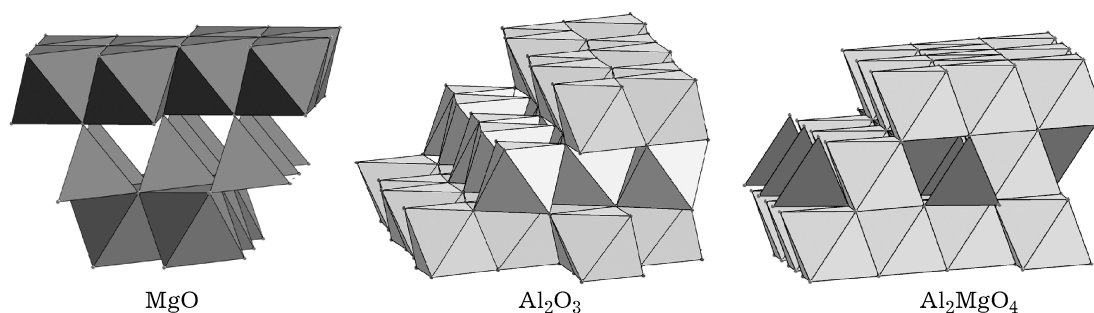


Fig. 2. Schematic diagram spinel formation from magnesium oxide and corundum in the course of mechanochemical synthesis. The magnesium oxide is presented by twin structure (111) [112]. The corundum is presented by twinning plane (1011).

It can be stated that in the course of the deformation stirring of MgO and Al<sub>2</sub>O<sub>3</sub> particles the mechanical twinning in the system contacting particles results in the formation of nuclei for a new phase of MgAl<sub>2</sub>O<sub>4</sub>. This also indicates the crystal formation is possible in this system not only due to the diffusion of individual atoms, but also due the structural fragments formed those exhibit appropriate angles and distances between atoms.

#### NUCLEATION OF PbTiO<sub>3</sub>

The synthesis of lead titanate (PbTiO<sub>3</sub>) also occurs as the result of a mechanochemical reaction in the course of simultaneously deforming the oxides of titanium and lead [2, 5]. In this case, the main mechanism of the mass transfer is presented by a plastic deformation *via* twinning. By the analogy with the nucleation of spinel, let us consider the mechanisms of the deformation of the initial components, which mechanisms result in the mechanosynthesis of perovskites. Lead titanate PbTiO<sub>3</sub> has a tetragonal structure (sp. gr. *P4mm*) at  $T < 490$  °C and the cubic structure at higher temperature values (up to  $T_{\text{melt}} = 1285$  °C). The titanium ions are located in the octahedral environment of oxygen ions; the oxygen polyhedron around the lead ion is presented by cuboctahedron.

The crystal structure of rutile TiO<sub>2</sub> (sp. gr. *P4/mnm*) belongs to a tetragonal crystal system and consists of octahedron (TiO<sub>6</sub>), linked between each other by two common edges. In this case, there are chains formed parallel to the axis of *c*; the latter lies in the plane corre-

sponding to the layers of the closest hexagonal packing. This explains the fact that there frequently occurs twinning in the plane of (011).

The tetragonal modification of lead oxide ( $\alpha$ -PbO, litharge, yellow lead) has a layered structure (sp. gr. *P4/nmm*), stable at a room temperature and at lower temperature values. The layers are arranged perpendicular to the *c* axis. Generally, the twinning thereof occurs according to the system of (001) [100].

As it was mentioned earlier, the plastic deformation of oxides mentioned occurs *via* mechanical twinning. In case of twinning the rutile on the system of (101)  $[\bar{1}01]$  and of twinning the litharge in the (001) plane, perpendicular to the optical axis, there are layers outcropping those under the interaction between each other form nuclei of a new phase of PbTiO<sub>3</sub>. Lead layers are embedded in the distorted rhombohedral voids of rutile wherein the oxygen environment of lead is completed to form cube octahedral shape inherent in lead titanate. As it was rightly noted the authors of [1], a fresh surface that appears in this case under twinning seems to be intended to participate in chemical reactions. The atoms forming the mentioned surface are coordinatively unsaturated, and the problem is presented only by the fact that it is required for choosing necessary reaction partners for them. Figure 3 demonstrates the formation of lead titanate in the course of interaction between the twin structures of PbO and TiO<sub>2</sub>. In the picture, the oxygen polyhedron around the lead ions are dark, whereas those around the titanium are light. The litharge is presented by the twinning plane (001) perpendicular to the *c* axis. Rutile is presented by the twinning plane according to the system of (101) $[\bar{1}01]$ .

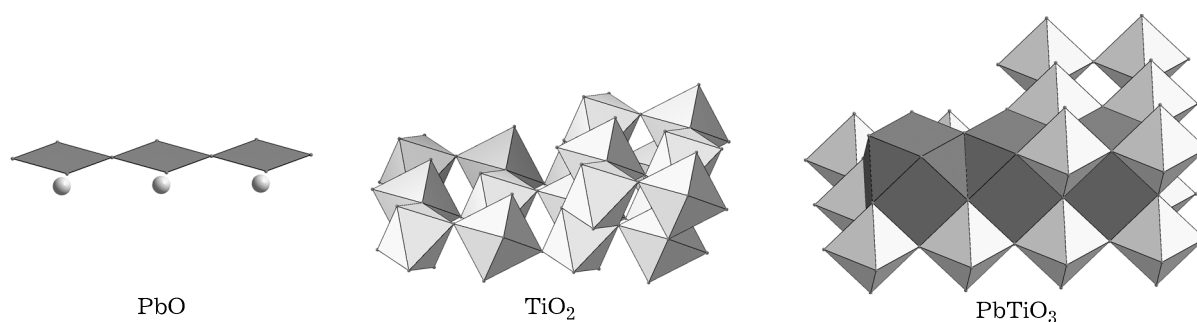


Fig. 3. Schematic diagram for lead titanate formation from yellow lead and rutile in the course of mechanochemical synthesis.

Thus, in the course of joint deforming the PbO and TiO<sub>2</sub> powders, the mechanical twinning results in the nucleation of a new phase that is PbTiO<sub>3</sub>.

#### NUCLEATION OF Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>

The interest in the nucleation mechanisms of yttrium-aluminum garnet is caused by a high practical significance of laser ceramics produced on the base thereof. The technology of obtaining the optical ceramics is determined the processes of grinding, drying, cold and hot pressing, vacuum annealing, *etc.* The nucleation of a new phase occurs mainly in the course of the deformation impact, whereas at the further stages there occurs the ceramics growing and compaction almost up to the density of a single crystal. By the analogy with the mechanisms of lead titanate and spinel formation, let us briefly consider the role of twinning in the nucleation of yttrium-aluminum garnet in the course of joint grinding the aluminum oxide ( $\alpha$ -modification) and yttrium oxide (for details see ref. [18]). The crystals of yttrium-aluminum garnet have a cubic structure. The aluminum ions occupy two types of nodes with different oxygen coordination: the 16 of them are located in the octahedral environment whereas the 24 of them are located in the tetrahedral environment of oxygen ions; 24 yttrium ions are surrounded by eight oxygen ions arranged at the vertices of a distorted cube. Yttrium oxide has a C-type cubic structure, similar to the structure of fluorite, but a quarter of the oxygen ions is shifted, and each metal atom therein is

surrounded by six rather than eight oxygen ions. The structure of the aluminum oxide ( $\alpha$ -modification) was considered above.

Thus, in the garnet structure the Al atoms are surrounded by four and six oxygen ions, whereas in the corundum structure they are only six; the yttrium atoms are surrounded by eight oxygen ions, whereas in the yttrium oxide structure they are six. Let us consider the possibility of forming the structural fragments of an of yttrium-aluminum garnet single crystal in the course of plastic deformation via twinning the initial components. The modelling of the structure was carried out using a Diamond software package, version 3 (Crystal Impact Co.). The twins were obtained rotating a part of the structure through 60° around the third order axis in the plane formed by the cations. In the course of shifting the cations lying in the twinning plane, pass into tetrahedral cavities, there-with all the tetrahedral are turned to the same side, *i. e.*, there is a fragment of garnet structure formed and aluminum ions are located both in the octahedral environment of oxygen ions, and in the tetrahedral environment thereof.

The single crystals of yttrium oxide have a distorted cubic structure wherein the yttrium atoms are surrounded by six oxygen atoms, whereas in the yttrium-aluminum garnet they are eight. Twinning the yttrium oxide occurs mainly in the planes of (111) and (110). Oxygen vacancies are located in the plane of a rhombic dodecahedron [18]. It should be noted that in the course of twinning the Al<sub>2</sub>O<sub>3</sub> the transition of aluminum from the octahedral position to the tetrahedral "releases" two bonds of oxygen atoms that in case of contacting with

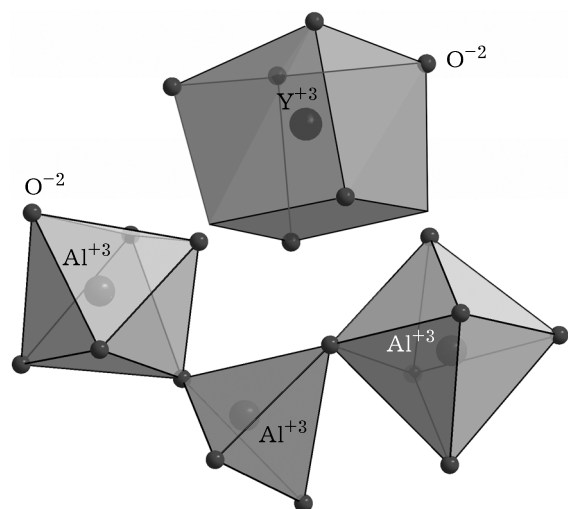


Fig. 4. Schematic diagram of the nucleation of  $Y_3Al_5O_{12}$  phase from the polyhedra of yttrium the twin structure of corundum in the course of mechanochemical synthesis.

$Y_2O_3$  in the twinning plane (110) cause finishing the structure thereof up to a complete environment of eight anions typical for  $Y_3Al_5O_{12}$ . Owing to this, a solid state reaction occurs to form the yttrium–aluminum garnet. The distances between the oxygen ions in the twin structure of corundum and those in the twinning plane of yttrium oxide are close to each other and equal to 3.76 and 3.82 Å, respectively. Figure 4 demonstrates the formation of the  $Y_3Al_5O_{12}$  structure from the twinning elements of  $Al_2O_3$  and  $Y_2O_3$ .

It can be noted that the joint deformation of  $Al_2O_3$  and  $Y_2O_3$  as the result of mechanical twinning in the system of contacting particles leads to forming the nuclei of a new phase of  $Y_3Al_5O_{12}$ . Further processing stages results in

their growth with obtaining continuous-solid samples.

The experimental data obtained and the simulation results require for the theoretical justification of the fact that the formation of twin structures in the single crystals under investigation is possible. The energy estimates are based on the comparison of the static lattice energy of the single crystal with twinning and that without twinning. The static energy can be estimated using semi-empirical pair potentials: the Coulomb potential, the Born–Mayer potential responsible for the short-range repulsion, the van der Waals potential and the Morse potential that simulates covalent interaction [19]. The calculations were performed using a MatLab software package. The calculations have demonstrated (Table 1) that appearing the twin significantly changes the lattice energy, and the FCC structure is characterized by a direct correlation with the hardness of the material. This indicates predominantly twinning thereof according to the system of (111) [112], whereas the other structures could be twinned according to other systems with a roughly equal probability. It should be noted that the energy of twin formation is to a considerable extent lower than the energy of the formation of dislocations. Even for alkali halide crystals the mentioned energy value about an order of magnitude lower. This could be explained by the fact that in the case of the dislocation plasticity the shift usually occurs by the lattice parameter, whereas in the case of twinning the shift occurs only by a part thereof (in this case by about 0.4a).

TABLE 1  
Energy of twin formation in cubic structures

Crystals	Hardness, GPa	Lattice energy, eV	Lattice energy with a twin, eV	Energy change, %	Energy of twinning, eV
$Lu_3Al_5O_{12}$	16.5	-625.65	-602.64	3.7	23.01
$Y_3Al_5O_{12}$	14.5	-620.11	-589.90	4.9	30.21
$Lu_2O_3$	9.5	-139.98	-135.82	3.0	4.16
$Y_2O_3$	7.6	-131.42	-122.67	6.7	8.75
MgO	6.0	-41.38	-41.13	0.6	0.25
LiF	1.0	-10.61	-10.46	1.4	0.15
NaF	0.65	-9.43	-9.35	0.9	0.08
NaCl	0.25	-7.94	-7.90	0.5	0.04

Thus, the plastic deformation *via* twinning results not only in the fragmentation of the crystals of the initial substances (mechanical activation), but also in the formation of new crystalline structures in the mixtures of solid reagents.

## CONCLUSION

The studies performed demonstrate that the mechanical activation of reagents and nucleation of a new phase in case of mechanochemical reactions in the system of contacting oxide particles could proceed through a new mechanism, wherein a crucial role is played by processes of twinning. One can hope that a new approach to the synthesis of complex oxides considering the ability of solid reagents to mechanical twinning will be developed in the future. Many, yet unknown properties of twins and twin boundaries will become helpful, as properties of single crystals do nowadays.

## REFERENCES

- 1 Butyagin P. Yu., *Usp. Khim.*, 63, 12 (1994) 1031.
- 2 Avvakumov E. G. (Ed.), *Mechanochemical Synthesis in Inorganic Chemistry (A Collection of Papers of the SO AN SSSR)*, Nauka, Novosibirsk, 1991.
- 3 Meyers M. A., Mishra A., Benson D., *J. Prog. Mater. Sci.*, 51 (2006) 247.
- 4 Boldyrev V. V., *J. Adv. Chem.*, 75, 3 (2006) 203.
- 5 Zyryanov V. V., *J. Adv. Chem.*, 77, 2 (2008) 107.
- 6 Vainshtein B. K. (Ed.), *Modern Crystallography*, vol. 3, Nauka, Moscow, 1980.
- 7 Kanevskiy V. M., *Crystallogr. Rep.*, 56, 4 (2011) 711.
- 8 Akchurin M. Sh., Kaminskiy A. A., *Dokl. AN*, 424, 4 (2009) 465.
- 9 Akchurin M. Sh., Galstyan V. G., *Fiz. Tv. Tela*, 37, 5 (1995) 845.
- 10 Akchurin M. Sh., Regel V. R., *Chem. Rev.*, 23 (1998) 59.
- 11 Akchurin M. Sh., Gainutdinov R. V., Zakalyukin Z. M., Kaminskiy A. A., *Dokl. AN*, 415, 3 (2007) 1.
- 12 Akchurin M. Sh., Zakalyukin R. M., *Crystallogr. Rep.*, 51, 6 (2006) 1059.
- 13 Kaminskiy A. A., Akchurin M. Sh., Gainutdinov R. V., Takaychi K., Shirakav A., Kaminskiy A. A., *Crystallogr. Rep.*, 50, 5 (2005) 935.
- 14 Akchurin M. Sh., Gainutdinov R. V., Kупenko I. I., Yagi Kh., Ueda K., Shirakav A., Kaminskiy A. A., *Dokl. AN*, 441, 6 (2011) 743.
- 15 Reichel U. and Kemnitz E., 8th Laser Ceram. Symp. (Abstracts), Nizhniy Novgorod, 2012, p. 44.
- 16 Klassen-Neklyudova M. V., *Mekhanicheskoye Dvoynikovaniye Kristallov*, Izd-vo AN SSSR, Moscow, 1960.
- 17 Belyaev L. M. (Ed.), *Rubin i Saffir*, Nauka, Moscow, 1974.
- 18 Akchurin M. Sh., Zakalyukin R. M., *Crystallogr. Rep.*, 58, 3 (2013) 439.
- 19 Akchurin M. Sh., Zakalyukin R. M., Kупenko I. I., *Surface*, 5 (2013) 92.