Synthesis and crystal structure of the new complex oxide $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$

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The complex oxide $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ was synthesized by the solid-state reaction in a sealed evacuated quartz tube at 1000 °C. Its crystal structure was determined by electron diffraction and X-ray powder diffraction. The structure can be represented as a tetrahedral framework, *viz.*, the polyanion $[(Mn_{0.285}Ga_{0.715})_{15}O_{29.86}]^{19-}$ stabilized by the incorporated cation $[Ca_{14}GaO_6]^{19+}$. The polycation consists of the GaO_6 octahedra surrounded by the Ca atoms, which are arranged to form a cube capped at all places. The tetrahedral framework is partially disordered due to the presence of tetrahedra with two possible orientations in the positions (0, 0, 0) and (x, x, x) with $x \approx 0.15$ and 0.17. The relationship between the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structures and related ordered phases with the symmetry $F23$, as well as the influence of the oxygen content on the ordering in the tetrahedral framework, are discussed.

Key words: complex manganese oxides, crystal structure, X-ray powder diffraction, electron diffraction.

In the literature, there are data on the structural type of complex oxides with the face-centered cubic lattice, which contain the calcium, trivalent metal (gallium and/or aluminum), and transition metal (Zn^{2+}, Co^{2+}, or Mn^{2+}) cations. $Ca_7Al_5Zn_3O_{17.5}$[1] crystallizing in the space group $F23$ is considered as the first example of the structures of this family. Its structure can be described as a framework consisting of the metal-oxygen tetrahedra, whose cavities contain octahedrally coordinated cations. The octahedrally and tetrahedrally coordinated positions are occupied by aluminum and zinc cations. The oxygen octahedra are surrounded by calcium cations that are in the positions with coordination numbers 6 and 9. The structure with the space group $F23$ is characterized by the completely ordered oxygen sublattice. Apart from compounds crystallizing in this space group ($Ca_7Al_5Zn_3O_{17.5}$,[1] $Ca_7Ga_5Zn_3O_{17.5}$ (see Ref. 2)), the related structures, such as $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$,[3] $Ca_7Co_3Ga_5O_{18}$,[4] and $Ca_7Zn_{2.75}Ga_{5.25}O_{17.63}$,[2] with the space group $F432$ are known. The increase in the symmetry from $F23$ to $F432$ is associated with the disorder in the anionic and cationic sublattices. For the $Ca_7Zn_{3-x}Ga_{5+x}O_{17.5+x/2}$ ($x = 0$, 0.25) solid solutions, there exists the structural phase transition: the compound with $x = 0$ has a structure with the space group $F23$, but the compound with $x = 0.25$ has a structure with the space group $F432$.[2] It was suggested[2] that the structural phase transition is related to the heterovalent substitution of gallium for zinc with the emergence of additional oxygen atoms.

In the present work, we report the synthesis and the crystal structure of the novel compound $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$, as well as the regularities of the transition from the phase with the space group $F23$ to the phase with the space group $F432$. For compounds having such structures, this transition is directly related to the oxygen content determining the structure and the number of different groups formed by tetrahedrally coordinated cations.

Experimental

The reagents MnO, Ga_2O_3 (Reakhim, analytical grade), and CaO, which was prepared by thermal decomposition of calcium carbonate at 900 °C for 12 h in a dynamic vacuum of $1.5 \cdot 10^{-2}$ Pa, were used as the starting materials. The synthesis was performed according to the previously described procedure.[5] The sample of the total composition $Ca_7Mn_{2.3}Ga_{5.7}O_{17.85}$ was prepared in a glove box filled with high-purity argon. The starting materials were weighed with the accuracy of ±0.001 g, ground in a jasper mortar, pressed into pellets, placed into alundum crucibles, and sealed into quartz tubes evacuated to residual pressure of 3 Pa. The samples were annealed at 1000 °C three times for a period of 50 h with intermediate grindings.

X-ray powder diffraction study was carried out at room temperature in a Huber G670 Guinier camera (Cu-Kα_1 radiation, curved Ge monochromator, transmission mode) equipped with

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an Imaging Plate detector. The sample was ground in an agate mortar in the presence of germanium as the internal standard and applied on a X-ray amorphous Lavsan film using an X-ray amorphous adhesive. The WinXpow (Stoe) software package was used for calculation of the X-ray diffraction (XRD) patterns and for the refinement of the unit cell parameters.

The XRD data for the structural study were collected on a Stoe STADI-P diffractometer (Cu-Kα_1 radiation, curved Ge monochromator, transmission mode, PSD linear detector) at ~20 °C. The full-profile refinement of the crystal structure according to the powder data was performed by the Rietveld method using the JANA2000 program package.[6] The positions and atomic displacement parameters were refined isotropically.

Energy-dispersive X-ray (EDX) analysis was performed on a JSM6490LV (Jeol) scanning electron microscope. The X-ray lines Ca(Kα), Mn(Kα), and Ga(Kα) were used for the analysis. The polycrystalline sample was stuck on a aluminum holder by means of a silver paste and coated by a thin carbon film.

The electron diffraction (ED) patterns were obtained on a Philips CM20 transmission electron microscope with an accelerating voltage of 200 kV. For the electron microscopic study, a small amount of the sample was crushed in an agate mortar under ethanol. The resulted suspension was applied on a holey carbon film deposited on a copper grid.

Unit cell and chemical composition. The total composition of the $Ca_7Mn_{2.3}Ga_{5.7}O_{17.85}$ sample was chosen by analogy with the composition of the compound $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$ on the assumption that the Ca(1) and Ca(2) positions in this structure are occupied exclusively by calcium. The data from the XRPA of the sample of the total composition $Ca_7Mn_{2.3}Ga_{5.7}O_{17.85}$ showed the presence of the basic phase, whose reflections were indexed on the assumption of a face-centered cubic unit cell with the cell parameter a = 15.1200(4) Å (determined with the use of germanium as the internal standard). The intensity distribution of the reflections of the cubic phase shows that it is isostructural to the compound $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$.[3] Besides the basic cubic phase, the impurity phases of the solid solution of $Ca_{1-x}Mn_xO$ (the space group $Fm\bar{3}m$, a = 4.57593(5) Å) and $Ca_5Ga_6O_{14}$ (the space group $Cmc2_1$, a = 11.501(2) Å, b = 11.266(2) Å, c = 10.488(2) Å)[7] are present in the sample in slight amounts. Taking into account the dependence of the unit cell parameter on the composition of the $Ca_{1-x}Mn_xO$ solid solution, which was built according to the data from Ref. 8, the composition of the solid solution was determined as $Ca_{0.359}Mn_{0.641}O$.

The unit cell of the basic cubic phase was confirmed by electron diffraction. The patterns of the basic sections of the reciprocal lattice are given in Fig. 1. The patterns were indexed in the face-centered cubic unit cell with the parameter $a \approx 15.1$ Å that agrees well with the XRD data. In the ED patterns, only systematic absences with the odd sums of indices $h + k$, $k + l$, $l + h$ were observed that is associated with the F-centered structure. Thus, one can assume the following set of the space groups: $F23$, $Fm\bar{3}$, $F432$, $F\bar{4}3m$, and $Fm\bar{3}m$. However, not all space groups are compatible with the symmetry of the tetrahedral metal-oxygen framework (see the oxygen atom distribution analysis over crystallographic positions in these space groups[3]). Thus, $F23$ and $F432$ are probable space groups.

The cationic composition of the basic cubic phase was analyzed by the EDX method and the Ca : Mn : Ga cation ratio was determined to be equal to 7.1(2) : 2.3(2) : 5.5(2) that agrees within standard deviation with the total composition of the starting sample. It should be noted that the sample is characterized by a small submicron particle size that makes it virtually impossible to analyze the individual particles of the target phase without the particles of the impurity phases being trapped by the probe. Therefore, the final chemical composition was established from the results of quantitative phase analysis by the Rietveld method and accorded with the crystal structure refinement data (see below) taking into account that, under the synthesis conditions, the oxidation state of manganese would be +2.0.

The evaluation of the oxygen content in the sealed quartz tube shows that no oxidation of a portion of Mn^{II} to Mn^{III} can be expected. The maximum amount of oxygen in the tube can be evaluated on the basis of the pressure, at which it was sealed (3 Pa). In the 10 mL tube, the amount of oxygen at ~20 °C may be ~10^{-8} mol and, when the sample weight is 0.5 g, the amount of the phase is ~$5 \cdot 10^{-4}$ mol. Thus, the oxygen present in the tube cannot appreciably alter the oxygen content of the phase.

The Rietveld crystal structure refinement showed that the sample contains 3.12(8) wt % of $Ca_{0.359}Mn_{0.641}O$ and 2.56(10) wt % of $Ca_5Ga_6O_{14}$. Using the $Ca_7Mn_{2.3}Ga_{5.7}O_{17.85}$ total composition of the starting sample and taking into account the fact that the synthesis was performed in the closed system, we calculated the composition of the cubic phase as

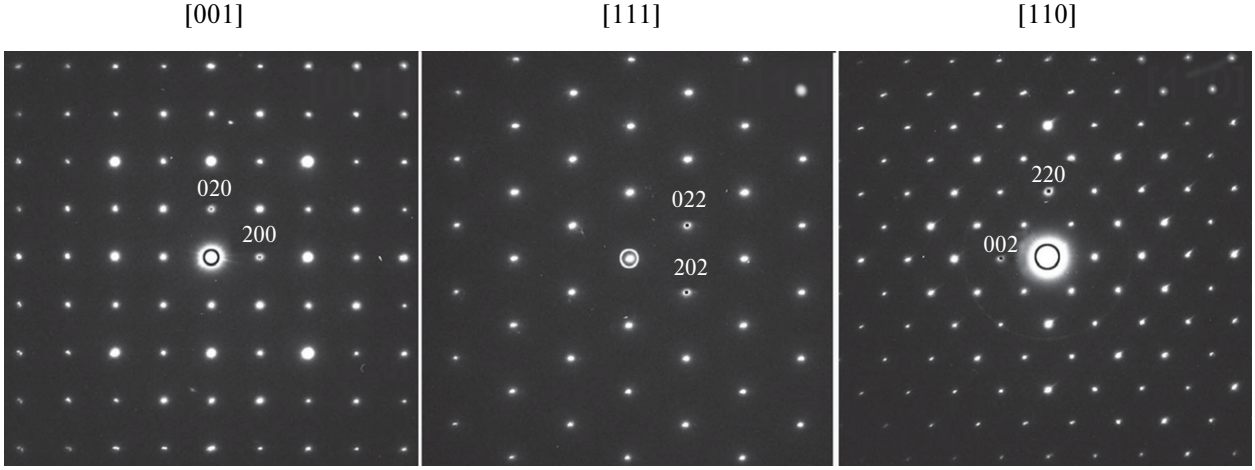

Fig. 1. The ED patterns for the compound $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ at the [001], [111], and [110] zones.

$Ca_{7.06(1)}Mn_{2.09(1)}Ga_{5.85(1)}O_{17.92(1)}$. The calculated composition agrees well with the composition $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ obtained upon the refinement of the occupancies of the cationic and anionic positions (see below).

The crystal structure refinement of $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$. The crystal structure of $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ was refined by the Rietveld method using the X-ray powder data. The reflections of the impurity phases $Ca_{0.359}Mn_{0.641}O$ and $Ca_5Ga_6O_1$ were also included in the refinement. The $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$ structure with the space group *F*432 was used as the initial model in the refinement.[3] In the crystal structure of $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$, there are the cationic positions 24e $(x, 0, 0)$ (Ca(1)) and 32*f* (x, x, x) (Ca(2)) occupied predominantly by the calcium atoms. The full occupancies of these positions correspond to seven calcium atoms per formula unit. We assumed that the positions Ca(1) and Ca(2) in the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structure are occupied exclusively by calcium. This assumption was confirmed by the calculation of the bond-valence sums (BVS) for these atoms (see the Results and Discussion). The distances between the oxygen atoms and the remaining cationic positions are very short (≤ 2.0 Å) and are not typical of the relatively large Ca^{2+} cations.

The gallium and manganese cations are arranged over the positions 4a (0, 0, 0) (Ga(1)), 24d (0, 1/4, 1/4) (Ga(2)), 32f (x, x, x) (Ga(3) and Ga(4)), and 4b (1/2, 1/2, 1/2) (Ga(5)). The scattering factor for the positions Ga(1), Ga(2), and Ga(5) was set to be equal to the scattering factor for the Ga atom and the refinement of the occupancies of these positions was performed with the fixed atomic displacement parameter U_{iso} = 0.01 Å^2. The obtained values g(Ga(1)) = 0.95(1), g(Ga(2)) = 0.97(1), and g(Ga(5)) = 1.00(1) suggest the full occupancies of these positions by Ga atoms. In addition, the metal—oxygen distances for the positions Ga(1) (1.856(4) Å) and Ga(2) (1.8818(18) Å) are not typical of the manganese cations in a tetrahedral environment (*e.g.*, in the structure of hausmannite Mn_3O_4, $d(Mn^{2+}—O)_{tetr}$ = 2.04 Å)[9] and the presence of Mn^{2+} cations in these positions is unlikely. The significantly larger metal—oxygen distances for the positions Ga(3) and Ga(4) ($<d(M—O)>$ = = 2.00 and 1.95 Å, respectively) suggest that these positions are simultaneously occupied by Mn^{2+} and Ga^{3+} cations. The scattering factor for the positions Ga(3) and Ga(4) was set to be equal to the scattering factor of the Ga atom and the occupancies of these positions were refined with the fixed atomic displacement parameter U_{iso} = 0.01 Å^2. The refined occupancies correspond to a scattering density of 18.0 e atom^{-1} for the position Ga(3) and 9.6 e atom^{-1} for the position Ga(4). Since it is impossible to determine occupancy factors for manganese and gallium in each position on the basis of the available data, we assumed that the occupancy factors for manganese in the positions Ga(3) and Ga(4) are equal. This correpsonds to the occupancy factors g(Ga(3)) = 0.303Ga + 0.349Mn and g(Ga(4)) = = 0.162Ga + 0.187Mn and results in the $Ca_7Mn_{2.14}Ga_{5.86}$ cationic composition of the compound.

Two 32-fold cationic positions (x, x, x) with $x \approx 0.17$ (Ga(3)) and 0.15 (Ga(4)) are in close proximity to each other (0.746 Å). It is obvious that these positions can not be occupied simultaneously, therefore g(Ga(3)) + g(Ga(4)) is equal to 1. The attempt to place one fully occupied position with $x \approx 0.16$ instead of these two positions with partial occupancies leads to an increase in the R_1 factor to 0.105. In addition, the difference Fourier map displays the negative residual elecron density maximum

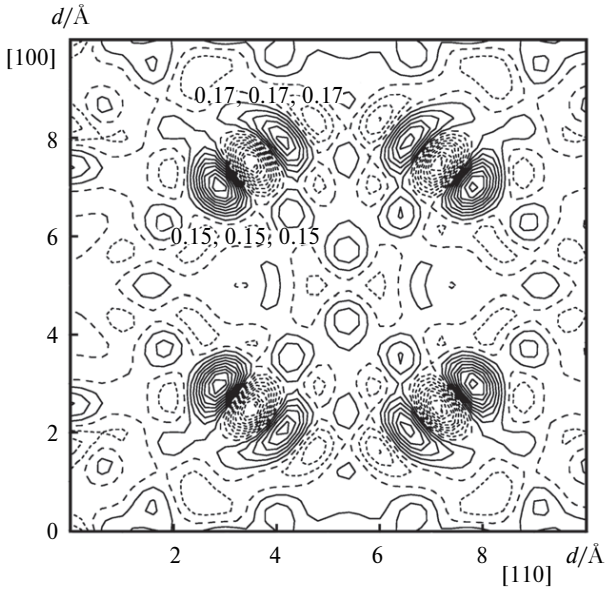

Fig. 2. The difference Fourier map near to the positions Ga(3) and Ga(4). The positive contours are depicted by solid lines and the negative contours are depicted by dashed lines. The countours are drawn at 0.5 e Å^{-3} intervals.

at $x \approx 0.16$, which is surrounded by two positive maximums in the positions Ga(3) and Ga(4) (Fig. 2). This evidences that the positions Ga(3) and Ga(4) with the partial occupancies are really present in the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structure. It is possible to achieve an ordered arrangement of the cations in the positions Ga(3) and Ga(4) passing from the space group *F*432 to its subgroup *F*23. Each 32-fold position is split into two 16-fold positions. However, any cationic distribution over the 16-fold positions (x, x, x) of the group *F*23 differing from that of the group *F*432 leads to an increase in the *R* factors. For this reason, the group *F*23 was excluded from the consideration.

As it follows from the calculated cationic composition and from the +2 formal oxidation state of Mn, there is a little of the oxygen vacancy sites that corresponds to the formula $Ca_7Mn_{2.14}Ga_{5.86}O_{18-\delta}$ (δ = 0.07). Based on the crystal structure analysis (see below), one can expect that the vacancy sites will be in the position O(2). Since there is no point in the refinement of the occupancy of the light atom in the X-ray powder experiment, the occupancy of the position O(2) was fixed as g(O(2)) = 0.93 that corresponds to the composition $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$.

The final refinement of the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structure was performed in the isotropic approximation for the atomic displacement parameters and with the common atomic diplacement parameter for the oxygen atoms. The principal crystallographic parameters and *R* factors are given in Table 1, the atomic coordiantes and atomic displacement parameters are listed in Table 2, and selected interatomic distances are given in Table 3. The calculated, experimental, and difference XRD patterns are presented in Fig. 3.

Results and Discussion

The calculation of the bond-valence sums for those positions that are occupied exclusively by cations of one

Table 1. Rietveld refinement statistics for $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$

Parameter	Characteristics
Composition	$Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$
Crystal system	Cubic
Space group	*F*432
a/Å	15.12072(4)
V/Å^3	3457.142(9)
Z	8
d_{calc}/g cm^{-3}	4.201
Scanning region 2θ/deg	7.1—100 (0.01)
Radiation (λ/Å)	Cu-Kα_1 (1.54060)
Number of refined parameters	18
Number of reflections	122
R-Factors	
$R_I/R_p/R_{wp}$	0.024/0.013/0.016

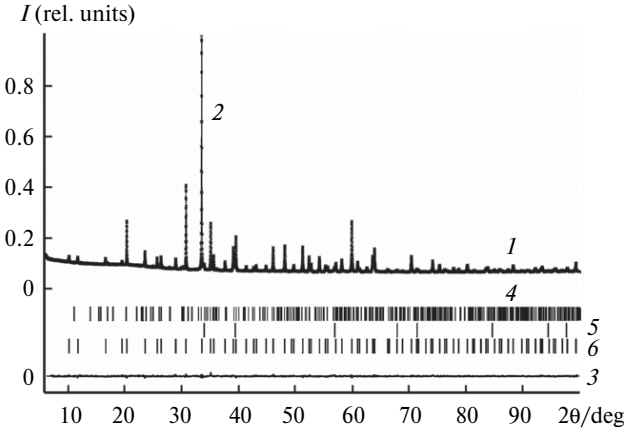

Fig. 3. The experimental (*1*), calculated (*2*, stars), and difference XRD patterns for $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ (*3*), as well as theoretical XRD patterns for $Ca_5Ga_6O_{14}$ (*4*), $Mn_{0.614}Ca_{0.356}O$ (*5*), and $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ (*6*).

type shows satisfactory agreement with the formal oxidations states. For Ca(1), Ca(2), Ga(1), and Ga(2), this sums are +1.99, +2.23, +2.82, and +2.66, respectively. The deviation of BVS from the value expected for the position Ga(2) can be due to the presence of manganese in this position; however, the similar scattering factors of manganese ($Z = 25$) and gallium ($Z = 31$) do not allow the unambiguous determination whether this position is occupied exclusively by gallium or by gallium together with manganese. Another possible reason for the deviation of BVS for the Ga(2) atom from the expected value is that the positions of the oxygen atoms were not precisely determined due to limitations of X-ray powder diffraction.

For gallium in the octahedrally coordinated position Ga(5), BVS is +2.86 (*cf.*: if this position is occupied by manganese, then BVS is equal to +3.35). Thus, the result of calculation of BVS indirectly supports the assumption that the octahedral position is occupied by gallium.

In the crystal structure of $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$, the Ca(1) and Ca(2) atoms are, respectively, in nine- or sixfold coordination environment formed by oxygen atoms. The coordination environment of the Ca(1) atom can be described as a heavily distorted monocapped cube and that of the Ca(2) atom can be described as a distorted octahedron. The Ga(2) and Ga(5) atoms have a regular tetrahedral and octahedral coordination, respectively.

It is reasonable to compare the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structure with the space group *F*432 and the ordered structure of the compound $Ca_7Al_5Zn_3O_{17.5}$ with the space group *F*23.[1] The tetrahedral frameworks of these structures consist of the vertex-sharing $M(1)O(4)_4$, $M(2)O(1)_4$, $M(3)O(1)_3O(2)$, and $M(4)O(1)_3O(4)$ tetrahedra. The orientation of all the $M(1)O(4)_4$ tetrahedra in the space group *F*23 is the same. In the space group *F*432, the M(1) atom is formally surrounded by eight O(4) oxygen atoms; however, the occupancy of the position O(4) is 0.5. Thus, only four of eight vertices of the cube are really present and the coordination environment of the M(1) atom is tetrahedral. There are two equiprobable orientations of the $Ga(1)O(4)_4$ tetrahedra in $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$, which are related by the fourfold symmetry axis.

Table 2. Atomic coordinates and atomic displacement parameters for $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$

Atom	Position	Occupancy	*x/a*	*y/b*	*z/c*	U_{iso}/Å^2
Ca(1)	24e	1	0.21159(7)	0	0	0.0110(5)
Ca(2)	32f	1	0.38891(4)	x	*x*	0.0029(4)
Ga(1)	4a	1	0	0	0	0.0136(8)
Ga(2)	24d	1	0	1/4	1/4	0.0099(3)
Ga(3)	32f	0.303Ga/0.348Mn	0.17422(5)	*x*	*x*	0.0103(6)
Ga(4)	32f	0.162Ga/0.187Mn	0.1457(1)	*x*	*x*	0.010(1)
Ga(5)	4b	1	1/2	1/2	1/2	0.0054(8)
O(1)	96j	1	0.2487(2)	0.1461(1)	0.0684(1)	0.0044(6)
O(2)	8c	0.93	1/4	1/4	1/4	0.0044(6)
O(3)	24e	1	0.3674(2)	0	0	0.0044(6)
O(4)	32f	0.5	0.0710(2)	*x*	*x*	0.0044(6)

Table 3. Selected interatomic distances (*d*) in the structure of $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$

Distance	*d*/Å	*N**	Distance	*d*/Å	*N**
Ca(1)—O(1)	2.503(2)	4	Ga(3)—O(1)	2.003(2)	3
Ca(1)—O(3)	2.356(3)	1	Ga(3)—O(2)	1.9847(8)	1
Ca(1)—O(4)	2.612(4)	4	Ga(4)—O(1)	1.948(3)	3
Ca(2)—O(1)	2.278(3)	3	Ga(4)—O(2)	2.733(2)	1
Ca(2)—O(3)	2.3978(8)	3	Ga(4)—O(4)	1.956(4)	1
Ga(1)—O(4)	1.859(4)	8	Ga(5)—O(3)	2.005(3)	6
Ga(2)—O(1)	1.881(2)	4			

* The number of the indicated distances.

In the structures of such cubic phases, groups of the tetrahedra with the M(3) and M(4) atoms at the center can be formally allocated. Group I consists of four $M(4)O(1)_3O(4)$ tetrahedra having no common vertices and contains the O(2) oxygen atom at the center, which is far spaced from the M(4) atoms (the distance in the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structure is 2.733(2) Å). Group II consists of four vertex-sharing $M(3)O(1)_3O(2)$ tetrahedra (the O(2) atom) (Fig. 4). In the space group *F*23, tetrahedral groups I and II are present in equal numbers and arranged in a chess order analogously to that of the cations in the structure of sodium chloride (Fig. 5), the O atom being absent at the center of group I. For the $Ca_7Al_5Zn_3O_{17.5}$ structure with the space group *F*23, the position M(3) corresponding to group II of four vertex-sharing tetrahedra is occupied exclusively by zinc atoms. This result is in agreement with the Pauling´s rules, according to which, the necessary condition for the stability of the group of four vertex-sharing tetrahedra is the presence of the divalent cations at the centers of tetrahedra.

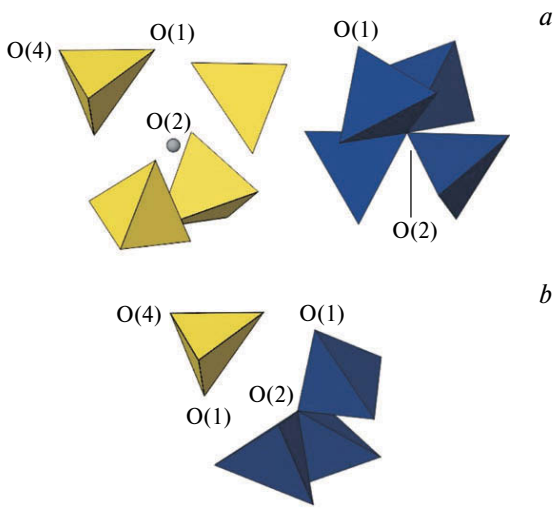

Fig. 4. The tetrahedral groups in the local structure of $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$; *a* is the structure of groups I (yellow tetrahedra) and II (blue tetrahedra); *b* is the possible structure of the mixed group. The tetrahedra with the Ga(3) and Ga(4) atoms are dark blue and yellow in color, respectively. The position O(2) at the center of group I is vacant.*

* Figures 4—6 are available in the full color in the on-line version of the journal (http://www.springerlink.com).

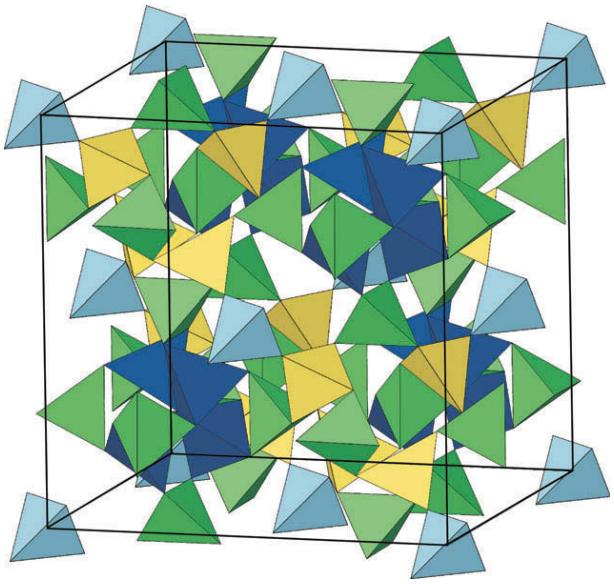

Fig. 5. The possible local structure of the tetrahedral framework in $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$. The tetrahedra with the Ga(1), Ga(2), Ga(3), and Ga(4) atoms at the center are blue, green, dark blue and yellow in color, respectively. The $Ga(5)O_6$ octahedra and the Ca atoms are not shown.

Let us consider how the occupancy of the atomic positions and the local structure are changed on passing to the space group *F*432. The positions Ga(3) and Ga(4) are statistically occupied and the sum of their occupancies is equal to one. It is convenient to consider the possible local variants of the coordination polyhedra and of their com-

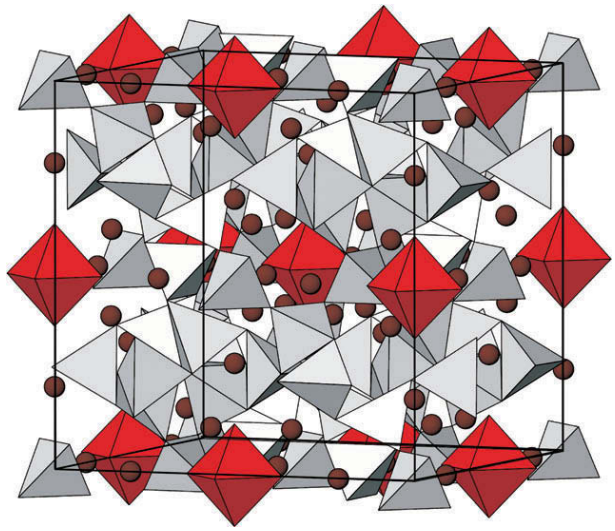

Fig. 6. The arrangement of the $Ga(5)O(3)_6$ octahedra (red color) in the tetrahedral framework. The Ca atoms are in brown.

pounds by transforming the disordered structure with the space group *F*432 to one of the possible ordered variants with the subgroup *F*23. One of the possible configurations of the structure is shown in Fig. 5. One of two orientations associated with the rotation by 90° is inherent to the $Ga(1)O(4)_4$ tetrahedra. A possibility of the existence of groups I and II in the real structure can be considered on the basis of the discussion of BVS at the O(2) oxygen atom. In group I, the O(2) atom is far spaced from the nearest Ga(4) cations and BVS at the O(2) atom will be considerably less than the formal oxidation state of the oxygen atom (0.31 if Ga(4) = Mn^{2+} and 0.26 if Ga(4) = = Ga^{3+}). It is therefore obvious that group I cannot exist in the structure as presented in Fig. 4: if such group of four tetrahedra existed, then the position O(2) at the center of the group should be vacant. Therefore, the portion of groups I in the structure should not exceed the portion of the oxygen vacancies in the position O(2), *i.e.*, 7%. In that case, a considerably higher occupancy of the position Ga(4) (~35%) should be assigned to the presence of the mixed groups comprising the $Ga(3)O(1)_3O(2)$ and $Ga(4)O(1)_3O(4)$ tetrahedra simultaneously. One of the possible variants of such mixed group consisting of three $Ga(3)O(1)_3O(2)$ tetrahedra and one $Ga(4)O(1)_3O(4)$ tetrahedron is shown in Fig. 4. If in such configuration Ga(3) is Mn^{2+} and Ga(4) is Ga^{3+}, BVS at the O(2) atom (1.82) is close to the formal oxidation state of the oxygen atom. The presence of the groups of type II in the structure is unlikely, since their presence is inconsistent with the sufficiently high occupancy of the position Ga(4). The simultaneous presence of the mixed groups in an amount of 93% and of group I in an amount of 7% is much more likely to give the 69 : 31 ratio of the occupancies of the positions Ga(3) and Ga(4) that is similar to an experimentally determined value of 65 : 35. The presence of the mixed groups was also noted in the $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$,[3] $Ca_7Co_3Ga_5O_{18}$ (see Ref. 4), and $Ca_{14}Zn_{5.5}Ga_{10.5}O_{35.25}$ structures.[2]

There are large emptinesses with a center in the position (1/2, 1/2, 1/2) in the tetrahedral framework of the $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ structure. This position is occupied by the Ga(5) cation having the octahedral environment formed by the O(3) oxygen atoms non-belonging to the tetrahedral framework (Fig. 6). The octahedron is surrounded by 14 calcium atoms arranged in the fashion of a cube with all capped faces. The structure can be described as the "guest-host" system, wherein the octahedra ("guests") are incorporated in the cavities of the tetrahedral framework ("host"). Thus, the structure can be represented as the polyanion $[(Mn_{0.285}Ga_{0.715})_{15}O_{29.86}]^{19-}$ stabillized by the incorporated polycation $[Ca_{14}GaO_6]^{19+}$.

According to the results of structure refinement of $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$ and of analysis of the structures of the related compounds, one can assume that the possibility of the formation of the disordered structure with the space group *F*432 and of the ordered structure with the space group *F*23 depends on the oxygen content, more exactly, on the occupancy of the position O(2). The O(2) atoms are in positions with the coordinates (0.25, 0.25, 0.25) and comprise the group of the tetrahedra with the Ga(3) and Ga(4) atoms. Up to eight O(2) atoms can be present in the unit cell. In the ordered $Ca_7Al_5Zn_3O_{17.5}$ (see Ref. 1) and $Ca_7Ga_5Zn_3O_{17.5}$ (see Ref. 2) structures, there are four O(2) atoms per unit cell. This offers an opportunity of the ordered alternation of the tetrahedral groups of type I (without the O(2) atom at the center) and type II (with the O(2) atom at the center) in a ratio of 50 : 50, which occurs within the space group *F*23, the occupancy of the fourfold position O(2) in the space group *F*23 (g(O(2))) being equal to 1. If more than four O(2) atoms fall within one cell, this leads to the appearance of the mixed groups and to the transformation to the space group *F*432. In that case, the position O(2) will be eightfold with the occupancy g(O(2)) > 0.5. The portion of the group of type I will be decreased proportionally to $1 - g$(O(2)). All the compounds of this family, for that g(O(2)) is more than 1/2 and the index at the O atom is more than 17.5, such as $Ca_{6.3}Mn_3Ga_{4.4}Al_{1.3}O_{18}$,[3] $Ca_7Co_3Ga_5O_{18}$,[4] $Ca_7Zn_{2.75}Ga_{5.25}O_{17.63}$ (see Ref. 2), and $Ca_7Mn_{2.14}Ga_{5.86}O_{17.93}$, have a disordered structure with the said symmetry.

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