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Crystal Structure and Comparative Crystal Chemistry of $Al_2Mg_4(OH)_{12}(CO_3) \cdot 3H_2O$, a New Mineral from the Hydrotalcite–Manasseite Group

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Abstract—The crystal structure of a new mineral of the composition $Al_2Mg_4(OH)_{12}(CO_3) \cdot 3H_2O$ from the hydrotalcite–manasseite group has been determined by X-ray structure analysis. The parameters of the hexagonal unit cell are $a = 5.283(3)$, $c = 15.150(9)$ Å; sp. gr. $P\bar{6}2m$. The structure was refined over 52 crystallographically nonequivalent reflections up to $R = 0.039$. The hydrogen atoms of hydroxyl groups are localized. The new mineral differs from other representatives of this group by the complete order of all the atoms, which is reflected in a lower structure symmetry. The variety of minerals within the group is considered and interpreted in terms of polytypism, the atomic order in the structure of sublattices, and isomorphous substitutions.

INTRODUCTION

Depending on the composition of the octahedral brucite-type cationic layers composing the structures of a very large group of natural and synthetic compounds (the so-called dihydroxides), one can distinguish three subgroups in which the cations are (a) $Mg^{2+} + Al^{3+}$, (b) $Mg^{2+} + Fe^{3+}$, and (c) $Mg^{2+} + Cr^{3+}$. The octahedral environment of the cations is formed by hydroxyl $(OH)^-$ ions, whereas the interlayer voids are filled with $(CO_3)^{2-}$ anions and H_2O molecules. The two modifications characteristic of these compounds are considered as polytype $2H$ and $3R$ modifications with different unit cell parameters a and c (in the hexagonal setting): 3.1 and 15.6 Å for the former and 3.1 and 23.4 Å for the latter polytype.

In the subgroup of (Mg, Al)-hydroxides of the compositions $Mg_6Al_2(OH)_{16}(CO_3) \cdot 4H_2O$ (**I**), the $2H$ polytype is manasseite and the $3R$ polytype is hydrotalcite; in the subgroup of the (Mg, Fe) hydroxides having similar compositions, the $2H$ polytype is sjögrenite and the $3R$ polytype is pyroaurite. The corresponding minerals in the subgroup of (Mg, Cr)-hydroxides are stichtite and barbertonite. The above compositions of natural and synthetic hydrotalcite [1–3] differ from the composition established in the X-ray structure determination of this mineral—$Mg_4Al_2(OH)_{12}(CO_3) \cdot 3H_2O$ (**II**) [4]. Hydrotalcite formulas **I** and **II** have different numbers of CO_3 groups, the same numbers of (Mg + Al) cations, and different values of the Mg : Al ratio (3 : 1 for **I** and 2 : 1 for **II**).

Later on, one more mineral—chlormagaluminite $(Mg, Fe)_4Al_2(OH)_{12}(Cl, (CO_3)_{0.5})_2 \cdot 2H_2O$—was included into the hydrotalcite–manasseite subgroup. The hypothetical structure model of this mineral admits the ordered arrangement of Al atoms in the (Mg, Fe, Al)-octahedra of a brucite layer [5]. The mineral of composition **II**, recently approved by the Comission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (no. 92-028 [6]), should also be related to this subgroup, although the detailed mineralogical and structural data for this mineral have not been published. In relation to this, the mineral from the Jacupiranga alkaline-ultrabasic carbonatite massif (São Paulo, Brazil), first described as manasseite [7] but, in fact, having a composition consistent with the data for a new representative of the subgroup of the dihydroxides under consideration, is of great interest, and the determination of its structure was the main purpose of this study.

EXPERIMENTAL

The mineral under consideration was discovered in the form of bright orange–red 2–6-mm large grains in dolomites [6]. The crystals had hexagonal trapezoidal faceting, with prismatic faces and basal pinacoidal faces, parallel to which perfect cleavage was observed. X-ray single-crystal studies (a SYNTEX automatic diffractometer, sp. gr. $P\bar{1}$, MoK_α radiation) were performed on a 0.025-mm-thick crystalline platelet with a

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Table 1. Characteristics of the minerals of the hydrotalcite–manasseite subgroup according to different sources

Mineral	Chemical formula	Sp. gr. or lattice type	Unit cell parameters, Å	References
Hydrotalcite	$Al_2Mg_6(OH)_{16}CO_3 \cdot 4H_2O$ (I)	$R\bar{3}m$	$a = 3.102, c = 23.404$	[2]
	$Al_2Mg_6(OH)_{16}CO_3 \cdot 4H_2O$ (I)	R	$a = 6.142, c = 46.24$	[8]
	$Al_2Mg_4(OH)_{12}CO_3 \cdot 3H_2O$ (II)	$R\bar{3}m$	$a = 3.054, c = 22.81$	[4]
Manasseite	$Al_2Mg_6(OH)_{16}CO_3 \cdot 4H_2O$ (I)	$P6_3/mmc$	$a = 3.1, c = 15.5$	[1]
	$Al_2Mg_6(OH)_{16}CO_3 \cdot 4H_2O$ (I)	H	$a = 6.13, c = 15.37$	[9]
Chlormagaluminite	$Al_2(Mg, Fe)_4(OH)_{12} \cdot (Cl, (CO_3)_{0.5})_2 \cdot 2H_2O$	$P6_3/mcm$	$a = 5.29, c = 15.46$	[5]

maximum dimension in the plane of 0.625 mm. The twelve most intense reference reflections provided the establishment of a hexagonal unit cell with the lattice parameters $a' = 3.050(1)$ and $c = 15.150(9)$ Å, which, together with the data on the chemical composition, indicated that the crystal belonged to the hydrotalcite–manasseite subgroup (Table 1). As is seen from Table 1, the basis parameters of the hexagonal unit cells can be chosen differently depending on the presence or absence of a small number of weak reflections indicating an increase in the minimum translation vector a': (*i*) $a = a' = 3.05$ Å, (*ii*) $a = 2a' = 6.1$ Å, or (*iii*) $a = a'\sqrt{3} = 5.28$ Å. There is another, fourth, possible variant of the translation, (*iv*) $a = 2a'\sqrt{3} = 10.56$ Å (Fig. 1). To avoid any possible loss of experimental data, the basic set of X-ray reflections was obtained for the unit cell with the maximum parameter, $a = 2a'\sqrt{3} = 10.566$ Å, within half of the Ewald sphere ($\sin\theta/\lambda = 0.81$ Å^{-1}). Altogether, 262 reflections with $I > 2\sigma(I)$ were recorded. The analysis of their intensities indicated the diffraction class $6/mmm$. Upon averaging, the experimental set contained 52 crystallographically independent reflections; the reliability factor for the equivalent reflections was $R = 0.059$ (over 39 groups of reflections). The absence of reflections with odd h and k indices indicated a parameter half as large, $a = 5.283$ Å. The attempt to pass to the unit cell with the parameter $a = 2a' = 6.01$ Å with the aid the matrix (2/3 1/3 0, –1/3 1/3 0, 001) resulted in the loss of seven reflections; the remaining reflections had either even h or even k indices. This indicated the presence of a pseudotranslation $a' = 3.05$ Å along the [210] direction in the unit cell with the parameters $a = 5.283(3)$ and $c = 15.150(9)$ Å. We performed a complete structure determination within this unit cell. All of the calculations were performed using the AREN program complex [10] taking into account anomalous atomic scattering. Structure amplitudes were calculated from the intensities with due regard for the polarization and Lorentz factors.

The regular extinctions in the intensities of the ($000l$) reflections with $l = 2n + 1$ within the diffraction class $6/mmm$ indicated the space group $P6_322$. A structure model was determined by direct methods within this space group up to the reliability factor $R = 0.12$. The model structure consisted of two brucite-type layers perpendicular to the 6_3 axes, each of them being built by three (Mg, Al)-octahedra (layer *1'* in Fig. 2a). The O and C atoms are located between the layers at the same height z (the O net in Fig. 2a). In addition to the 6_3-axis, the brucite layers were also related by the plane m normal to this axis and passing through the (C, O) nets and by the coordinate plane c absent in the initial symmetry group. The interlayer nets related by the 6_3-axis and the c plane also had half-filled positions of C and O atoms of the CO_3 groups and H_2O molecules. The 50% occupancy of the C-position lying at the intersection of the 2 and 6_3 axes with the three O atoms bound to it and also at the intersection of three O atoms from the H_2O molecules followed from the chemical composition of compound **II** and was confirmed by the electron-density values on the F-synthesis for the model obtained. The identical interlayer nets allowed us to describe the model within the sp. gr. $P6_3/mcm$, which was inconsistent with the presence of weak reflections not obeying the extinction rule imposed by

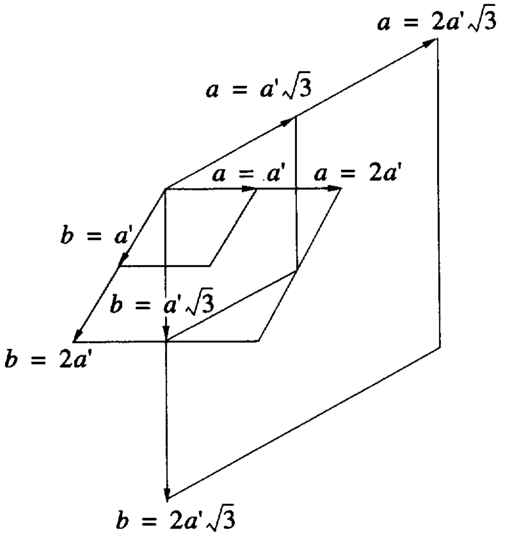


Fig. 1. Relationship between the a vectors of the hexagonal unit cells in the structures of various minerals of the dihydroxide group.

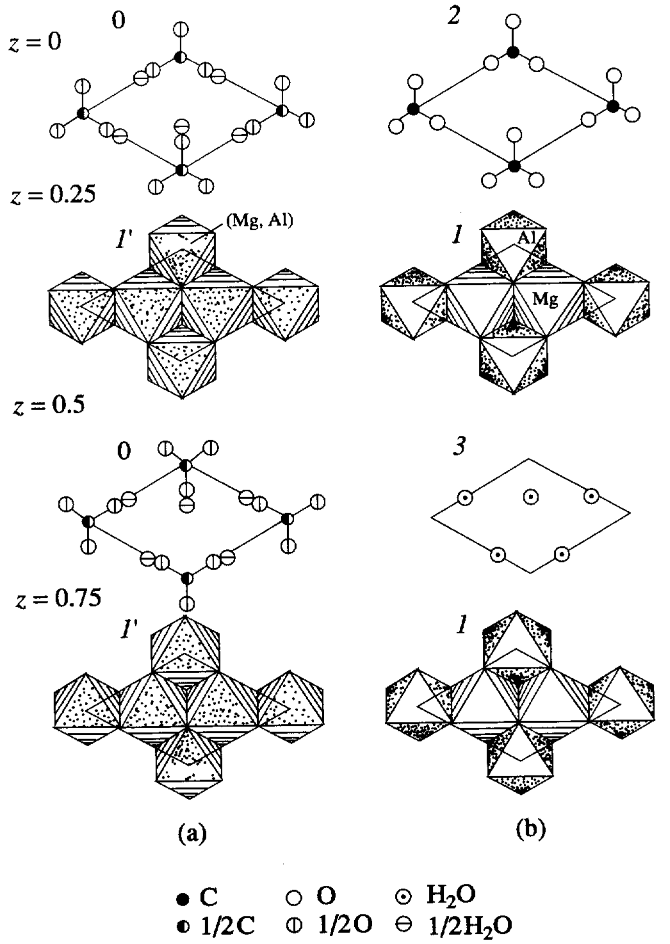


Fig. 2. The scheme of (a) disordered (–*0*–*1'*–*0*–*1'*–*0*–) and (b) ordered (–*2*–*1*–*3*–*1*–*2*–) arrangement of atoms in the layer structural elements in the hexagonal unit cell with the parameter $a = a'\sqrt{3} \approx 5.28$ Å. Notation: a brucite layer is denoted by *1* and *1'* for the ordered and disordered variants of octahedra filling, respectively; the interlayer net with the statistical distribution of O atoms is denoted by the number 0; the carbonate-containing net and the H_2O-net are denoted by the numbers *2* and *3*, respectively.

the plane *c*. The inconsistency of the symmetry elements of the model obtained and the experimentally observed regular extinctions and also the ambiguous structure of the interlayer nets containing the CO_3-group and three H_2O molecules led to the sp. gr. $P\bar{6}2m$ in which the two nearest nets in the planes *m* could be independent and could contain CO_3-groups (the first one) and triads of H_2O molecules (the second one) (Fig. 2b). This assumption was confirmed in the course of the structure determination and refinement. The (000*l*) extinctions are explained by the equal scattering power of the (CO_3) and ($3H_2O$) nets spaced by a half-translation along the *z*-axis.

Then, the structure model (Fig. 2b) was refined within the group $P\bar{6}2m$ up to $R = 0.06$ in the isotropic approximation. The Al and Mg atoms were located on two threefold axes, in accordance with chemical formula **II**. A high value of the thermal parameter of the C atom (> 10 Å^2) indicated possible splitting of its position. The *F*-synthesis provided the localization of the peak lying at a distance of 0.3 Å from the initial position of the C atom (and from the *m* plane) along the *z*-axis. Thus, we placed this atom into this position with 50% occupancy. The refinement of the split C-position reduced the reliability factor down to $R = 0.055$ and the thermal parameter down to 6.0 Å^2. The H atoms of the hydroxyl groups were localized from the difference synthesis. We failed to localize the H atoms of the H_2O molecules, probably because of the high mobility characteristic of free water molecules (which was seen from the high values of their thermal parameters). The refinement of the positional parameters of H atoms reduced the *R*-factor down to 0.047, whereas the allowance for the anisotropy of thermal vibrations of Al and Mg atoms and the anisotropic extinction ($E = 0.0000222$) reduced it even more—down to $R = 0.039$. The difference electron-density maps showed no valuable peaks.

The positional and thermal parameters of the atoms are listed in Table 2, and the interatomic distances are given in Table 3.

It should be emphasized that the crystal was characterized by a weak scattering power, the number of experimental reflections was rather small, and, therefore, the accuracy of the coordinate and interatomic distance determination was relatively low.

STRUCTURE DESCRIPTION

The crystal structure determined is built by three types of layer elements (*1*, *2*, and *3* in Figs. 2b and 3) perpendicular to the $\bar{6}$-axis and bonded to one another by hydrogen bonds (Fig. 3). Layer *1* is of a brucite type and has the composition [$AlMg_2(OH)_6$], it consists of Al- and Mg-octahedra, and the O(1) and O(2) atoms of hydroxyl groups form a close-packing motif in two O-nets (with three atoms per unit cell in each net) and are spaced 2.91 and 3.19 Å from one another. Layer *2* is a carbonate net of the composition [CO_3] consisting of three O(3) atoms displaced from the close-packing positions toward the C atom located on one of the three threefold axes in a way such that four O(3)–O(3) distances between the CO^{2-} anions are 3.53 Å and two O(3)–O(3) distances inside these anions are 2.23 Å. Layer *3* is a net of three H_2O molecules whose O atoms are also arranged by the motif of a close packed layer with four H_2O–H_2O distances equal to 2.79 Å and two distances equal to 3.68 Å. The common feature of all three structural elements is oxygen nets built by the same number of atoms arranged by the close-packing motif.

Three layer structural elements along the hexagonal axis form the sequence –*1*–*2*–*1*–*3*–*1*–. The two closest layers *1* are related by the symmetry planes *m* passing

Table 2. Positional and thermal ($Å^2$) parameters of atoms in the $Al_2Mg_4(OH)_{12}CO_3 \cdot 3H_2O$ structure

Atom	x/a	y/b	z/c	B_{eq} or B_{iso} (*)
Mg	1/3	2/3	0.243(3)	1.8(1)
Al	0	0	0.259(3)	2.6(1)
C	0	0	0.021(8)	6.3(9)*
O(1)	0	0.651(2)	0.325(8)	2.9(2)
O(2)	0.318(2)	0	0.190(1)	2.7(2)*
O(3)	0.244(3)	0	0	4.3(6)*
H_2O	0.598(5)	0	1/2	6.5(8)*
H(1)	0.35(3)	0.35(3)	0.398(9)	3.0*
H(2)	0	0.36(3)	0.125(9)	3.0*

through the nets of layers *2* and *3*. Each O atom of the interlayer net is located between two OH groups of the neighboring brucite layers and forms hydrogen O–H···O···H–O bonds providing layer interactions. If one uses the notation of close-packed layers and neglects the small deviations from close packing, the sequence of O-nets in the structure can be written as $A_1A_2A_1B_1B_3B_1$ (Fig. 3), where the numerical subscript corresponds to the structural element of the layer. The position of O atoms in nets *2* and *3* is uniquely determined by the position of the corresponding hydroxyl groups from layer *2*. The neighboring interlayer O-nets *2* and *3* are displaced with respect to one another, in accordance with the close-packing law, as are the O(H) nets of layer *1*. It should be emphasized that each O atom of the interlayer nets between *2* and *3* is an acceptor for two hydrogen bonds with two OH-groups, which gives a ratio of 2 : 1 between the number of OH-groups and the number of O atoms in the interlayer nets irrespectively of the net compositions. It seems that there are no other interactions between the structure layers, which is confirmed by a large distance between nets *2* and *3* and the O atoms from layer *1*: 2.88 and 2.65 Å, in comparison with the distance 2.04 Å between the O-nets in layer *1*. The positions of H_2O molecules with respect to Al and Mg atoms are equivalent, whereas the C atoms are located on the same threefold axis with Al atoms, which, we believe, is an essential characteristic not only of this structure but also of other structures of the compounds of this group.

RESULTS AND DISCUSSION

We established a new, rather interesting ordered arrangement of the interlayer CO^{2-} and H_2O-nets in the structure, which was never observed earlier in any related minerals of the dihydroxide group. According to the known structure data for the compounds of this group calculated only for the hexagonal unit cell with the parameter $a = 3.054$ Å [4], the interlayer nets are characterized by a statistic distribution of H_2O molecules and CO_3 groups, which is, in fact, the superposition of nets *2* and *3* observed in this study (the O layer in Fig. 2a) projected onto the unit cell with the parameter $a = 3.054$ Å (the O layer in Fig. 4a). For the chlorine-containing variety of manasseite, chlormagaluminite (Table 1), it was possible (with due regard for weak reflections) to choose a unit cell with the parameter $a = 5.29$ Å, but the structure of the interatomic layers was not established. By analogy with the minerals of the pyroaurite–sjögrenite subgroup, which, according to [1], are almost identical (their structures differ only in the cationic composition), it was always assumed that, in the minerals of the manasseite–hydrotalcite subgroup, the H_2O molecules and CO_3 groups are randomly distributed over the interlayer nets. Moreover, the structures of the minerals of this group (considered in detail elsewhere [1]) were always described within the unit cell with the parameter $a = 3.1$ Å, despite the fact that in some cases weak reflections corresponding to the parameters $a = 5.37$ and $a = 6.2$ Å [11–13] were observed. It was noted [1] that the chemical analysis yields an $M^{3+} : M^{2+}$ ratio of either 1 : 3 or 1 : 2 and only sometimes 1 : 5 for the statistical distribution of these cations in brucite layers.

The crystallochemical analysis of the dioxide crystal structures based on our results and the data reported in [1–9, 11–15] allowed us to draw some new conclusions about possible variations in their composition, structures, and the unit-cell parameters. The analysis

Table 3. Interatomic distances (Å) and angles (deg) in H-bonds in the $Al_2Mg_4(OH)_{12}CO_3 \cdot 4H_2O$ structure

Mg-octahedron	Al-octahedron	CO_3-group
Mg–O(2) 1.97(2) × 3 –O(1) 2.12(3) × 3 ⟨2.05⟩	Al–O(2) 1.98(3) × 3 –O(1) 2.09(2) × 3 ⟨2.04⟩	C–O(3) 1.32 × 3 –C 0.6(1)
	H-bonds	
H_2O–H_2O 2.79(1)	H(1)–O(1) 1.0(1) H_2O 1.6(1)	H(2)–O(2) 1.0(1) O(32) 1.99(1)
∠O(1)–H(1) ··· H_2O 168(7)		∠O(1)–H(2) ··· O(3) 149(7)

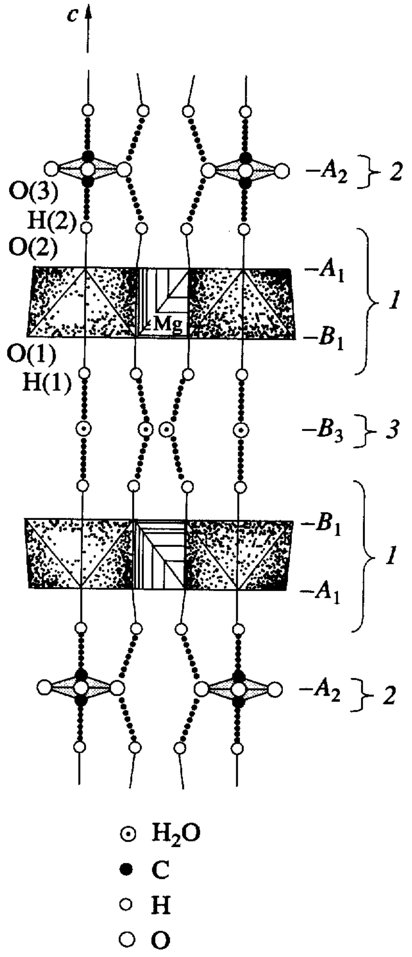


Fig. 3. The (100) projection of the $Al_2Mg_4(OH)_{12}(CO_3) \cdot 3H_2O$ structure. One can see the alternation of the structural elements (–*2*–*1*–*3*–*1*–*2*–) and close packed layers ($A_2A_1B_1B_3B_1A_1A_2$) along the *c*-axis. The dashed lines indicate hydrogen bonds.

was performed under the assumptions that

(1) The compounds under consideration belong to the hexagonal system.

(2) The brucite layers in all the structures alternate with the interlayer nets along the hexagonal axis.

(3) Each interlayer net (both H_2O- and CO_3-containing) has the ordered structure. There are two factors explaining the distribution of partly occupied O positions in one net prior to the localization of C and H atoms observed earlier in the structural studies: (1) random alternation of nets of two equally probable different compositions along the *c*-axis and (2) the calculation of models within the highly symmetric space group and the neglect of weak reflections reducing this symmetry. The possible effect of the second factor is also confirmed by this study.

(4) The structural unit reflecting the composition and the structure of the compound is chosen to be a layer slab of a thickness of about $c' = 7.6$ Å consisting of one brucite layer and two adjacent interlayer nets each of which belongs to this structural unit for only 50%. One of these interlayer nets contains only CO_3 groups, whereas the other consists of H_2O molecules.

(5) The brucite layer has the composition $[(Al, Mg)_y(OH)_{2y}]$, where the values $y = 1, 3, 4$, and 12 correspond to the composition of the hexagonal unit cell with the parameters $a \approx 3.05, 5.3, 6.1$, and 10.6 Å, respectively (Fig. 5a).

(6) Both brucite layers and interlayer nets are bound by hydrogen O–H···O(*A*)···H–O bonds in which the accepters are the atoms of the interlayer nets: either O or additional *A* anions (e.g., Cl in chlormagaluminite). Therefore, the ratio of the total number of acceptor (O, *A*) atoms to the number of OH groups is 1 : 2 and with due regard for assumption (5), the number of (O, *A*) atoms equals the number of (Al, Mg) cations in the brucite layer. Since OH groups form layers by the close-packing motif, the interlayer (O, *A*) nets are also arranged by a motif close to the close-packing motif.

CHEMICAL COMPOSITION AND THE VARIATIONS IN THE *a* PARAMETER OF THE HEXAGONAL UNIT CELL

As has been noted above, the dihydroxide group is often described by chemical formula I with the ratio of the number of atoms from the interlayer nets to the number of OH groups being 7 : 16 instead of 1 : 2. This difference can be explained by three factors: (1) some hydroxyl groups do not participate in hydrogen bonding because there is no acceptor atom in the interlayer net, (2) there are possibly experimental errors in the determination of H_2O positions, and (3) there is a small number of additional *A* anions (e.g., Cl) which are not taken into account. The possible effect of the third factor is indicated by the following estimates. In the structure without additional *A* anions, the thickness of the chosen structural unit is 7.58 Å, which is consistent with the value of 7.60 Å established for the compound not containing additional anions [4]. At the same time, in chlorine-containing chlormagaluminite [5], the corresponding average value is substantially larger, 7.8 Å, in accordance with the larger radius of Cl^- in comparison with that of O^{2-}. No structure determinations were made for other compounds, but the average thickness of the structural unit ranged within 7.69–7.8 Å (Table 1), thus indicating the possible presence of additional anions with radii exceeding that of O^{2-}. A similar dependence was also observed in [3] for the Cl^-, F^-, Br^-, I^-, NO_3^-, and SO_4^{2-}-containing synthetic analogues of manasseite and hydrotalcite. It should be noted that an increase in the structural-unit thickness could also be caused by an insufficient number of acceptor atoms in the interlayer net providing bonding between the brucite-type layers. The experimental confirmation of the simultaneous presence of two types of grains with the pseudoparameters 7.6 and 7.8–7.9 Å in polycrystalline specimens can be found in [1, 11].

Proceeding from electrical neutrality of the compounds under consideration, hydrogen bonding, and the possible presence of additional monovalent A^- anions, one can write the chemical formula of minerals of the hydrotalcite–manasseite series in the form

$$Al_xMg_{(y-x)}(OH)_{2y}(CO_3)_{(x-d)/2}A^-_d \cdot H_2O_{(y-3x/2+d/2)}. \quad \textbf{(III)}$$

In the general case, the A^- anions can be located in any interlayer nets. Let us analyze formula **III** for the composition of the chosen structural unit in hexagonal unit cells with the above-mentioned four different values of the parameter a (Figs. 1, 5).

(i) $a = a' \approx 3.05$ Å (Fig. 4). The composition of minerals of the hydrotalcite–manasseite series admits the presence of defect-free brucite layers (with the statistical filling of octahedra) and interlayer nets with H_2O molecules in the structure with the minimum parameter. In the nets containing CO_3 groups in the absence of oxygen defects, the positions of C atoms on one of the threefold axes should be filled with C-atoms only partly. For the case under consideration, the number of atoms in formula **III** is (Al + Mg) = y = 1, because there is only one cation position in a brucite layer. The nonnegativity condition for the stoichiometric coefficients in the transformed formula **III**, $Al_xMg_{(1-x)}(OH)_2(CO_3)_{(x-d)/2}A_d \cdot H_2O_{(1-3x/2+d/2)}$, yields the inequality $0 \le d \le x \le 1$. The total number of acceptor atoms in the interlayer nets and the number of cations in a brucite layer are equal to unity; therefore, the distribution of additional A anions and the filling of octahedra with the cations of different valences can only be statistical.

A multiple increase in the parameter a can be explained by the ordering of the Al and Mg cations in a brucite layer or by the ordered arrangement of atoms in a CO_3-containing interlayer net. Below, we consider in detail the effect of both these factors on the variations of the parameter a. For the sake of simplicity, Fig. 5 shows an idealized arrangement of O atoms fully occupying their positions according to the close-packing motif (Fig. 5b).

(ii) $a = 2a' \approx 6.1$ Å (Fig. 6). The sum of the cations in **III** is $(Al^{3+} + Mg^{2+}) = y = 4$. The number of acceptor atoms in each interlayer net is (O + A) = 4. Therefore, the carbonate net should contain one CO_3 group complemented with one (H_2O) or A acceptor, or else it should be completely substituted by four such additional atoms. Therefore, there is either 0.5 (CO_3) per structural unit or else there are no such groups at all, and formula **III** takes one of two forms:

$$Al_{(1+d)}Mg_{(3-d)}(OH)_8(CO_3)_{0.5}A_d \cdot H_2O_{(2.5-d)} \quad \textbf{(IV)}$$

or

$$Al_dMg_{(4-d)}(OH)_8A_d \cdot H_2O_{(4-d)} \quad \textbf{(V)}.$$

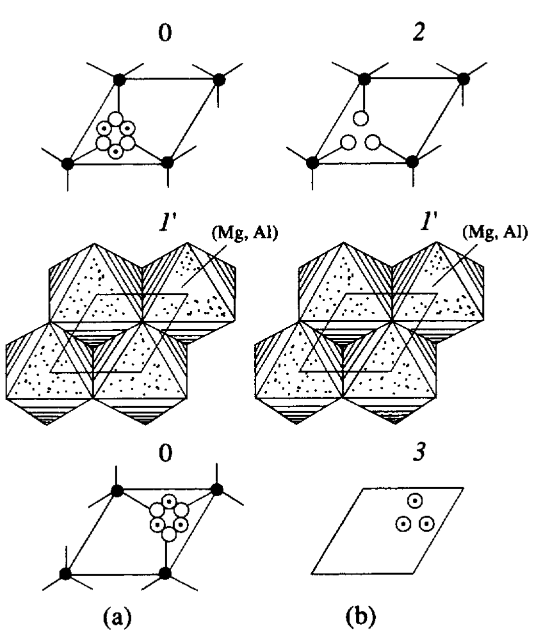


Fig. 4. A structural unit in the hexagonal unit cell with the parameter $a = a' \approx 3.01$ Å. For notation, see Fig. 2. (a) Totally disordered variant (–0–$1'$–0–); all the atoms in the interlayer O-type nets have the occupancy coefficient 1/6; (b) ordered alternation of interlayer CO_3- and H_2O-nets by the law (–2–$1'$–3–); the occupancies of all the positions of the interlayer nets are 1/3.

If a compounds has a carbonate group but has no A anions (d = 0 in **IV**), then Al : Mg = 1 : 3, which is quite consistent with possible cation ordering in the brucite layer for the unit cell under consideration (layer 1 in Fig. 6) and coincides with the common value of this ratio for these cations. Nevertheless, in this case, it follows from **IV** that the number of H_2O molecules differs by 0.5 from the given values in each structural unit. A small number of additional monovalent A^- anions makes this discrepancy less obvious, but, upon increasing the number of trivalent cations, one can also obtain instead of the Al : Mg = 1 : 3 ratio the ratio $(1 + d) : (3 - d)$. To the compositions **I** often given for hydrotalcite and manasseite (Table 1) there corresponds a vacancy instead of an acceptor atom in the interlayer net ($A_d = \square_{0.5}$), and formula **III** takes the form $AlMg_3(OH)_8(CO_3)_{0.5}\square_{0.5} \cdot 2H_2O = 1/2(Al_2Mg_6(OH)_{16}(CO_3) \cdot 4H_2O) = 1/2$ (**I**). The vacant position in the carbonate net (□ in Fig. 6) admits the entrance of additional atoms into the structure. This was also confirmed in [3].

We have found no reliable data on the compounds described by formula **V**. At the same time, a somewhat simplified compound without A anions and with a minimum unit cell with $a = a'$ was mentioned as a possible composition elsewhere [1, 14].

(iii) $a = a'\sqrt{3} \approx 5.3$ Å. For this case, formula **III** has $(Al^{3+} + Mg^{2+}) = y = 3$ with the number of acceptor atoms in each interlayer net (O + A) also equal to 3. The

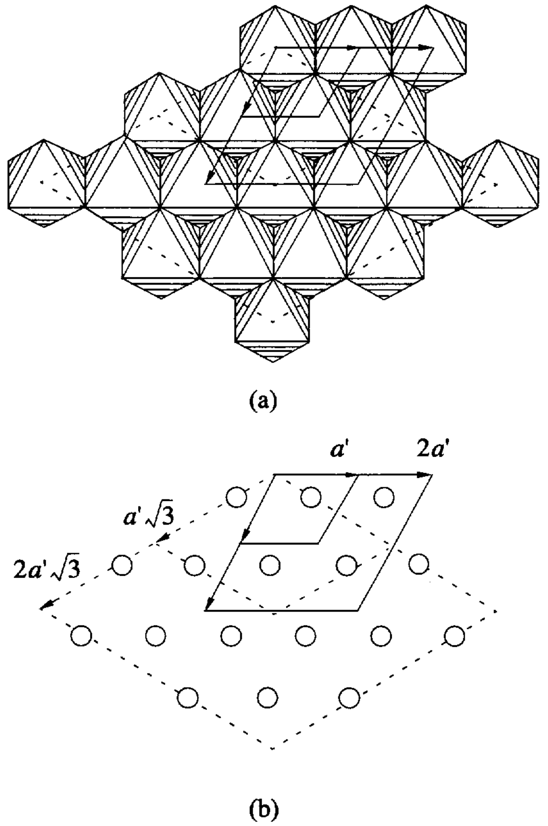


Fig. 5. Showing (a) the orientation of the reference basis vectors of possible hexagonal unit cells with respect to the brucite layer with disordered cations, and (b) an idealized close-packed interlayer net.

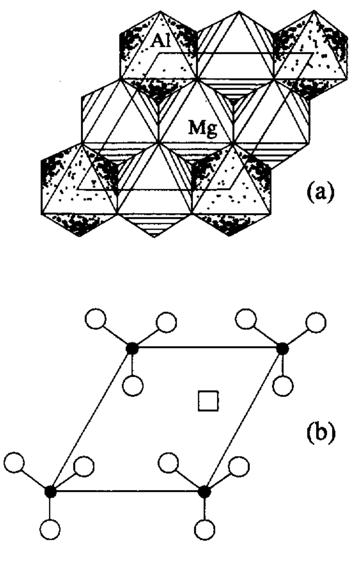


Fig. 6. Schematic of (a) possible order of cations in the brucite-type layer and (b) the carbonate-containing nets in the hexagonal unit cell with the parameter $a = 2a' \approx 6.1$ Å; Al : Mg = 1 : 3. A small square denotes a position containing either H_2O-molecules or vacancies.

carbonate net can contain only one CO_3 group. It is this variant of the composition that is described in this structural study (Fig. 2b). Formula **III** takes the form $Al_{(1+d)}Mg_{(2-d)}(OH)_6(CO_3)_{0.5}A_d \cdot H_2O_{(1.5-d)}$. Without additional A atoms (at $d = 0$), **III** = (1/2) (**II**). The Al : Mg = 1 : 2 ratio corresponds to a possible cationic ordering in the brucite layer and ordering of C atoms in the carbonate net (Fig. 2b). At this value of the ratio of the number of differently charged cations observed by different authors, the thickness of one structural unit is minimal (≈7.6 Å) and indicates the absence of additional acceptor atoms or vacancies.

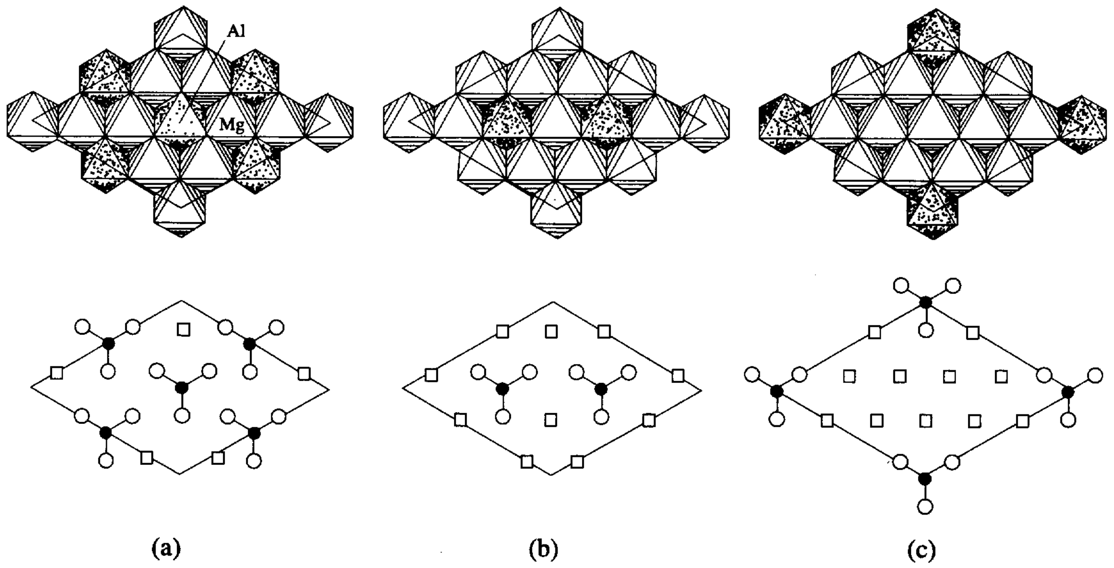
In principle, A atoms can enter the structure only if they substitute water molecules, which should be accompanied by an increase in the number of trivalent cations in comparison with their number at an Al : Mg = 1 : 2 ratio and a simultaneous reduction of the number of H_2O molecules. If one takes this into account, the formula of chlormagaluminite [5] with the proper number of water molecules and the parameter $a = 5.29$ Å should be written as $Mg_3Fe^{3+}Al_2(OH)_{12}CO_3Cl \cdot 2H_2O$ and not as $(Mg, Fe^{2+})_4Al_2(OH)_{12}((CO_3)_{0.5}, Cl)_2 \cdot 2H_2O$ (Table 1). The main difference reduces to the degree of iron-ion oxidation and the separation of some additional Cl-ions from the CO_3 group.

(*iv*) $a = 2a'\sqrt{3} \approx 10.6$ Å (Fig. 7). In this case, the number of cations in the brucite layer in formula **III** is $(Al^{3+} + Mg^{2+}) = y = 12$, i.e., equal to the number of acceptor atoms $(O + A)$ in each interlayer net. If the carbonate net contains only four CO_3 groups, then the structural unit reduces to the unit cell with the parameter $a \approx 5.3$ Å considered in (*iii*).

Formally, another possible composition of the structural unit $2CO_3 + 3(H_2O, A)$ (2 in Fig. 7a) described by formula **III** = $Al_{(3+d)}Mg_{(9-d)}(OH)_{24}(CO_3)_{1.5}A_d \cdot H_2O_{(7.5-d)}$ for a carbonate-containing net can be reduced to formula **IV** considered in (*ii*), although at the given a parameter the order of cations with different valences and C atoms can be different (cf. Figs. 6 and 7a). All the other remarks about the composition coincide with those given in (*ii*).

To the composition of the carbonate-containing net $2CO_3 + 6(H_2O, A)$ (Fig. 7b) there corresponds the structural-unit formula **III** = $Al_{(2+d)}Mg_{(10-d)}(OH)_{24}CO_3A_d \cdot H_2O_{(9-d)}$. Without allowance for additional anions in the interatomic nets, the ratio of the numbers of cations of different valences is 1 : 5. The possible formation of similar structures is confirmed by the data given in [1, 11]. Figure 7b illustrates possible cation ordering in a brucite layer for this case.

And, finally, one more possible composition of the interlayer net containing CO_3 groups is $CO_3 + 7(H_2O, A)$. The structural unit here is described by the chemical formula **III** = $Al_{(1+d)}Mg_{(11-d)}(OH)_{24}(CO_3)_{0.5}A_d \cdot H_2O_{(10.5-d)}$. Figure 7c illustrates the structure of the carbonate-containing net and possible ordering of cat-



(a) (b) (c)

Fig. 7. The scheme of possible ordering of cations in a brucite layer and a carbonate-containing net in the hexagonal cell with the parameter $a = 2a'\sqrt{3}$ 10.56 Å for the ratio of cations of different valences (a) Al : Mg = 1 : 3, (b) 1 : 5, and (c) 1 : 11. For notation, see Fig. 6.

ions in a brucite layer. In this case, the Al : Mg ratio becomes Al : Mg = 1 : 11. We have not found any indications of such a ratio in any publications, but a close ratio (1 : 12) was reported in [1].

A similar analysis can also be performed for larger hexagonal cells. It is possible to substantiate other ratios of cations with different valences. It should be noted that any of the above considered (and not considered) unit cells can readily be projected onto the minimum unit cell with the statistical distribution of cations in a brucite layer and the statistical filling of the interlayer nets (Fig. 4a). In fact, this is confirmed by some structural studies.

POLYTYPE MODIFICATIONS AND VARIATIONS IN THE PARAMETER *c* OF THE HEXAGONAL UNIT CELL

The chosen layer structural unit of the thickness $c' \approx$ 7.6 Å can be described in terms of close packed O-nets as $A_2A_1B_1B_3$ (see, e.g., Fig. 3), where the subscripts indicate which structural elements these nets belong to. The combination of these structural units sharing the boundary interlayer nets *2* and *3* along the *c*-axis can be described as either $A_2A_1B_1B_3B_1A_1A_2$ or $A_2A_1B_1B_3B_1C_1C_2$.

In the former case, the nearest brucite layers along the direction of their alternation (A_1B_1 and B_1A_1) are related by the symmetry plane *m* passing though the interlayer net B_3. In the latter case, they are rotated with respect to one another (A_1B_1 and B_1C_1) by 180° about the axis *2* passing through the O atoms of the interlayer net (B_3) normal to its plane. These two ways of layer combination predetermine the existence of various polytype modifications, each of which can uniquely be described by a sequence of the symmetry operations indicated above (*m* and *2*). The simplest variants *mm*... and 22... correspond to the well-known dihydrate modifications 2*H* and 3*R* [1]. The symbols *H* and *R* indicate hexagonal and rhombohedral unit cells, whereas the numbers indicate the number of layer structural units. As follows from the previous consideration, for the statistical distribution of the interlayer nets *2* and *3* (i.e., their complete identity), the polytype modification 3*R* should have the parameter $c = 3c'$ ($\approx$23 Å) reported in [1, 2, 4]. To this case there corresponds the sequence $A_0A_1B_1B_0B_1C_1C_0C_1A_1A_0$ of close-packed O-nets, where 0 denotes the statistically filled interlayer net. If nets *2* and *3* alternate, then the parameter *c* of the modification is doubled in accordance with the sequence $A_2A_1B_1B_3B_1C_1C_2C_1A_1A_3A_1B_1B_2B_1C_1C_3C_1A_1A_2$, and its symbol should be written as 6*R*. This parameter $c = 6c' = 46.24$ Å for the hydrotalcite structure is given in [8].

The generalized results of the theoretical crystallochemical analysis of some possible compounds of the dihydroxide group with due regard for possible variations in their composition, the parameters of the hexagonal unit cell, various polytype modifications, and the degrees of order are given in Table 4. These results can also be extended to other dihydroxide subgroups. Along with the well-known polytypes 2*H* and 3*R*, we also considered 4*H* polytypes with the parameter $c = 4c' \approx 31$ Å mentioned in [1, 14]. In the derivation of the space groups and possible degrees of order, it was taken into account that the above-described 180°-rotation of neighboring brucite layers in the unit cells with $a = a'\sqrt{3}$ and $a = 2a'\sqrt{3}$ lead to changes in the position

Table 4. Characteristics of hydrotalcite–manasseite-type compounds obtained from the theoretical crystallochemical analysis

Generalized chemical formula and its particular cases at $d = 0$ (a, b)	Symbol of the polytype modification	Unit cell parameters and space groups for different types of ordering in structures			
		fully disordered (–0–*1'*–0–*1'*)	fully ordered (–2–*1*–3–*1*–)	ordered alternation of interlayer nets (–2–*1'*–3–*1'*–)	ordering of cations in brucite-type layers (–0–*1*–0–*1*–)
$M^{3+}_{(1+d)}M^{2+}_{(3-d)}(OH)_8(CO_3)_{0.5}A_d \cdot H_2O_{(2.5-d)}$	*mm* ...	$a = a'$, $c = 2c'$ $P6_3/mmc$ (*)	1) $a = 2a'$, $c = 2c'$ $P\bar{6}m2$ 2) $a = 2a'\sqrt{3}$, $c = 2c'$ $P\bar{6}2m$	$a = a'$, $c = 2c'$ $P\bar{6}m2$	1) $a = 2a'$, $c = 2c'$ $P6_3/mmc$ (*) 2) $a = 2a'\sqrt{3}$, $c = 2c'$ $P6_3/mcm$
(a) $M^{3+}_2 M^{2+}_6 (OH)_{16}(CO_3) \cdot 5H_2O$,	22 ...	$a = a'$, $c = 3c'$ $R\bar{3}m$ (**)	$a = 2a'$, $c = 6c'$ $R3m$ (**)	$a = a'$, $c = 6c'$ $R3m$	$a = 2a'$, $c = 3c'$ $R\bar{3}m$
(b) $M^{3+}_2 M^{2+}_6 (OH)_{16}(CO_3)\eta \cdot 4H_2O$ (*, **)	*m*2 ...	$a = a'$, $c = 4c'$ $P6_3/mmc$	$a = 2a'$, $c = 4c'$ $P\bar{6}m2$	$a = a'$, $c = 4c'$ $P6_3/mmc$	$a = 2a'$, $c = 4c'$ $P6_3/mmc$
$M^{3+}_{(1+d)}M^{2+}_{(2-d)}(OH)_6(CO_3)_{0.5}A_d H_2O_{(1.5-d)}$(***)	*mm* ...	$a = a'$, $c = 2c'$ $P6_3/mmc$	$a = a'\sqrt{3}$, $c = 2c'$ $P\bar{6}2m$	$a = a'$, $c = 2c'$ $P\bar{6}m2$	$a = a'\sqrt{3}$, $c = 2c'$ $P6_3/mcm$ (***)
(a) $M^{3+}_2 M^{2+}_4 (OH)_{12}(CO_3) \cdot 3H_2O$(**, @)	22 ...	$a = a'$, $c = 3c'$ $R\bar{3}m$ (**)	–	$a = a'$, $c = 6c'$ $R3m$	–
	*m*2 ...	$a = a'$, $c = 4c'$ $P6_3/mmc$	–	$a = a'$, $c = 4c'$ $P6_3/mmc$	–
$M^{3+}_{(2+d)}M^{2+}_{(10-d)}(OH)_{24}(CO_3)A_d \cdot H_2O_{(9-d)}$	*mm* ...	$a = a'$, $c = 2c'$ $P6_3/mmc$	$a = 2a'\sqrt{3}$, $c = 2c$ $P\bar{6}2m$	$a = a'$, $c = 2c'$ $P\bar{6}m2$	$a = 2a'\sqrt{3}$, $c = 2c'$ $P6_3/mcm$
(a) $M^{3+}_2 M^{2+}_{10} (OH)_{24}(CO_3) \cdot 9H_2O$ (b) $M^{3+}_2 M^{2+}_{10} (OH)_{24}(CO_3)\square_3 \cdot 6H_2O$	22 ...	$a = a'$, $c = 3c'$ $R\bar{3}m$	–	$a = a'$, $c = 6c'$ $R3m$	–
	*m*2 ...	$a = a'$, $c = 4c'$ $P6_3/mmc$	–	$a = a'$, $c = 4c'$ $P6_3/mmc$	–
$M^{3+}_{(1+d)}M^{2+}_{(11-d)}(OH)_{24}(CO_3)_{0.5}A_d \cdot H_2O_{(10.5-d)}$ (a) $M^{3+}_2 M^{2+}_{22} (OH)_{48}(CO_3) \cdot 21H_2O$ (b) $M^{3+}_2 M^{2+}_{22} (OH)_{48}(CO_3)\square_9 \cdot 12H_2O$					

Note: For minerals of the hydrotalcite–manasseite subgroup, $a' = 3.05$–3.10 and $c' = 7.6$–7.8 Å; *, **, and *** are the characteristics for manasseite, hydrotalcite, and chlormagaluminite, respectively, according to various sources; @ is the new mineral considered in this study; (–*1*–) and (–*1'*) denote the ordered and disordered variants of the arrangement of cations of different valences in a brucite layer; (–0–), (–2–), and (–3–) are the interlayer nets statistically filled with O atoms without the localization of C atoms, carbonate-containing nets, and H_2O nets, respectively.

multiplicities for differently charged cations. Therefore, in this case no variants of the structure with the ordered arrangement of cations can exist.

CONCLUSION

The study of a new mineral with the ordered structure from the hydrotalcite–manasseite subgroup allowed us to revise and systematize the known structural characteristics of various representatives of this subgroup. As a result of the analysis performed, we substantiated theoretically, for the first time, the experimentally observed integer ratios for di- and trivalent cations and established the reasons for the variations in the parameters of their hexagonal lattice associated with changes in the chemical composition. The main conclusions drawn reduce to the following.

(1) The unit cell with the parameter $a \approx 3.05$ Å describes only a fully disordered variant of the struc-

ture, both with respect to the anion and cation positions. Within this unit cell, one cannot explain the experimentally obtained ratios of the constituent elements in the chemical formulas of the minerals of the dihydroxide group.

(2) The compound of the $M_2^{3+}M_6^{2+}$ $(OH)_{16}CO_3 \cdot 4H_2O$ type with the ratio $M^{3+} : M^{2+} = 1 : 3$ can be described within the hexagonal unit cell with the parameter $a \approx 6.1$ Å. The structures of these minerals have vacancies in the interlayer nets, which provides the possibility for some additional ions to enter into these nets with the simultaneous substitution of some divalent cations by cations of higher valence. The $M^{3+} : M^{2+} = 1 : 3$ ratio follows from the composition and structure of the carbonate-containing interlayer net in this unit cell and can be attained as a result of filling of octahedra in a layer.

(3) The compounds of the $M_2^{3+}M_4^{2+}$ $(OH)_{12}CO_3 \cdot 3H_2O$ type with the $M^{3+} : M^{2+} = 1 : 2$ ratio can have a hexagonal unit cell with $a \approx 5.3$ Å. Some additional anions can enter these structures only due to the substitution of water molecules under the condition of an increasing number of trivalent cations. The $M^{3+} : M^{2+} = 1 : 2$ ratio follows from the composition and structure of the interlayer CO_3 net and admits the ordered distribution of cations of different valences over the octahedra of a brucite layer.

(4) The compounds with the cation ratio $M^{3+} : M^{2+} = 1 : 5$ and their ordered arrangement can crystallize in the hexagonal unit cell with $a \approx 10.56$ Å. The same unit cell can also be formed in the structures with the ratio of cations of different valences $M^{3+} : M^{2+} = 1 : 3$, but with a somewhat different scheme of their ordering in comparison with the unit cell characterized by the parameter $a \approx 6.1$ Å. The same unit cell allows the ordered cation arrangement at the $M^{3+} : M^{2+} = 1 : 11$ ratio.

(5) The integer ratio of M^{3+} and M^{2+} follows from the ordered structure of the carbonate-containing interlayer net and manifests itself in a regular increase of the parameter a of the hexagonal unit cell. The most often encountered ratios of the cations of different valences, $M^{3+} : M^{2+} = 1 : 3$ or $1 : 2$, correspond to the minimum increment in periodicity.

(6) The constant value of the above ratios in different specimens indirectly indicates that the equally probable interlayer carbonate-containing nets and H_2O-nets in the dihydroxide structures are independent. An increase of this ratio towards higher M^{2+} contents should be accompanied by an increase in the H_2O content and the approach of the composition to $Mg(OH)_2 \cdot H_2O$. Compounds with a higher number of water molecules were reported in [15].

As is seen from Table 4, the formation of the mineral modifications or varieties in the group of compounds under consideration is directly related to the most important crystallochemical phenomena such as isomorphism, polytypism, and structural ordering. As a result of these processes, the chemical composition of the compounds changes both qualitatively and quantitatively; the space groups and the unit-cell metrics also change. The minerals of this group have different names either because of their different chemical compositions (chlormagaluminite) or because they are described by the R or P lattices (hydrotalcite and manasseite, respectively). Both of these features make the mineral studied above very close to manasseite. At the same time, the mineral differs from manasseite by the value of the parameter a of the hexagonal unit cell and by the space group, which determine the maximum possible order of its structure.

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