Bulgarian Chemical Communications, Volume 45, Number 4 (pp. 418–426) 2013

Crystal chemistry of “glaserite” type compounds

R. Nikolova, V. Kostov-Kytin

Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences,
“Acad. G. Bonchev” Str., bl. 107,1113, Sofia, Bulgaria

Received February, 2013; Revised May, 2013

Crystal chemical data for more than 100 compounds with “glaserite” type structure are summarized and evaluated. A revised general formula for “glaserite” type compounds (GTC) is deduced – $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$. It gives information for two important structural characteristics of GTC. The first one is that main structural unit is the ${}^{2}_{\infty}[M(TO_4)_2]$ layer where all the atomic positions are fully occupied. The second one is that the occupancy of X and Y positions depends on the layer charge and these positions can either be both unoccupied, one can be entirely occupied whereas the other is totally unoccupied, or both can be entirely occupied. Precise criteria for “glaserite” type topology (GTT) are proposed distinguishing GTT from other topologies built by similar or identical layers. The range of structural stability of the “glaserite” type compounds is outlined in terms of the established up to now cation composition and site occupancy. The topological flexibility is evaluated through geometrical criteria based on the lattice parameters or certain dimensional and angular correlations. The established compositional diversity, topological versatility and wide range of formation conditions are good prerequisite for preparation of new materials adopting the “glaserite” topology and estimation of certain physical phenomena such as temperature induced phase transitions.

Key words: glaserite, “glaserite” type topology, “glaserite” type compounds.

INTRODUCTION

The structure of the mineral glaserite was originally determined by Gossner (1928) [1] and confirmed later by Bellanca (1943) [2] and Pontonnier et al. (1972) [3]. The structure of its synthetic analogue was solved by Okada and Ossaka in 1980 [4]. Later on, it has been established that there are many substances which are isostructural with glaserite. In the course of gathering information for new compounds with such topology different approaches have been applied to describe this structural type. Moore (1981) [5] reported that in glaserite, the cations and anions form two types of columns in a hexagonal arrangement: type I containing only, Na^+ and K^+ cations and type II, containing both cations and anions (K^+ and SO_4^{2-}). Since the ions in each column are tightly bound along its length, the structure has been considered as a hexagonal packing of rods. Such an approach was applied by Takagy *et al.* (1983) [6] for the structure of $CaK_3H(PO_4)_2$ and used also by other authors, e.g. Lazoryak (1996) [7]. Later on, the results from investigations of various physical phenomena (phase transitions without topological changes, luminescence properties, etc.) occurring in certain “glaserite” type compounds (GTC) suggested that their structures can be considered as alternating layers composed by corner-sharing octahedra and tetrahedra with or without additional charge compensating cations [8–17]. An interesting approach for presentation of the “glaserite” type compound $Ba_3MgSi_2O_8$ was reported by Park *et al.* [18]. The authors have derived its structure from the perovskite one by considering variations on the stacking of layers of the type AX_3 and AX_2.

Upon accumulation of crystal chemical data many authors have tried to classify the GTC and clarify their structural features. Based on approximately 10 compounds known at that time Moor (1973) and Eysel (1973) independently from each other found out that “The glaserite structure and its deformed derivatives can be predicted for $(A,C)_yBX_4$ solid solution” [19, 20]. Later on, Lazoryak (1996) defined criteria for stability of the “glaserite” type topology and postulated that “Glaserite structural type $X^{[6+6]}Y_2^{[4+6]}M^{[6]}(EO_4)_2$ is stable for compounds where $0.59 < \Delta r < 0.89$

---

* To whom all correspondence should be sent:
E-mail: rosica.pn@clmc.bas.bg

(Δr = rX(Y) – rM; Shanon ionic radii)" [7]. The superscripts denote the coordination number expressed in terms of the bond lengths between the central cation and the ligand oxygen atoms.

Recently, it has been established that a synthetic sodium zirconosilicate material – $Na_{3-x}H_{1+x}Zr(SiO)_4 \cdot yH_2O$ ($0<x<3$, $0<y<1$) exhibits a "glaserite" type topology [21, 22]. Two features of this compound attract attention. The first one is the presence of water molecules in a structural topology known as an anhydrous one. The second feature is related with the possibility for protonation of this compound. Sodium ions could be leached out upon treatment with hydrochloric acid without destroying the structural topology. Such behavior is indicative of a "microporous" or a "layered" structure rather than of a dense-packed one. To better understand the crystal-chemical relation of this zirconosilicate to other materials adopting "glaserite" topology a search of such compounds in the available structural databases has been undertaken [23, 24]. Detailed analysis of the crystal-chemical characteristics of the collected compounds has revealed the amazing chemical diversity and structural versatility of the "glaserite" materials.

This work summarizes data from the crystal-chemical characterization of over 100 compounds with "glaserite" type topology. All of them are oxides. In fact, only one compound with "glaserite" type structure and fluorine instead of oxygen was found [3]. Precise criteria for GTT definition are introduced. The general formula previously reported for these materials [7] is reconsidered and new features and limitations are added to it. The topological flexibility is evaluated through introduced here geometrical criteria. Based on the gathered crystal-chemical information the range of structural stability of the "glaserite" type compounds is outlined in terms of the established up to now cation composition and site occupancy. This work is not an attempt to classify the "glaserite" type compounds but rather to comprise, to describe, and to evaluate the chemical diversity and structural versatility of the "glaserite" type topology.

RESULTS AND DISCUSSION

Crystal-chemical characterization of the "glaserite" type topology

In this paper the layer model for description of GTT is adopted as presented in Figure 1.

The TO_4 tetrahedron can be defined as a primary building unit of the "glaserite" structure type. Three of the oxygen atoms of a TO_4 tetrahedron are shared with the adjacent MO_6 octahedra, whereas one oxygen atom is non-bridging. Each of the M atoms is linked to six different TO_4 groups. Repetition of such connectivity results in the formation of a secondary building unit – a ${}^{2}_{\infty}[M(TO_4)_2]$ layer of corner-sharing MO_6 octahedra and TO_4 tetrahedra (see Fig. 1a). The resulting construction upon "glaserite" type stacking of the layers allows the appearance of two additional cationic positions (Fig. 1b and Fig. 2). For the highest symmetry case they can be defined as follows: a twelve coordinated position located between the layers and surrounded by six oxygen atoms from one of the layers and six more oxygens from the other layer ($X^{[6+6]}$) (Fig. 2a) and a ten coordinated position which is layer embedded and surrounded by nine oxygen atoms from the same layer and one oxygen from the adjacent layer ($Y^{[9+1]}$) (Fig. 2b). Such presentation of the X

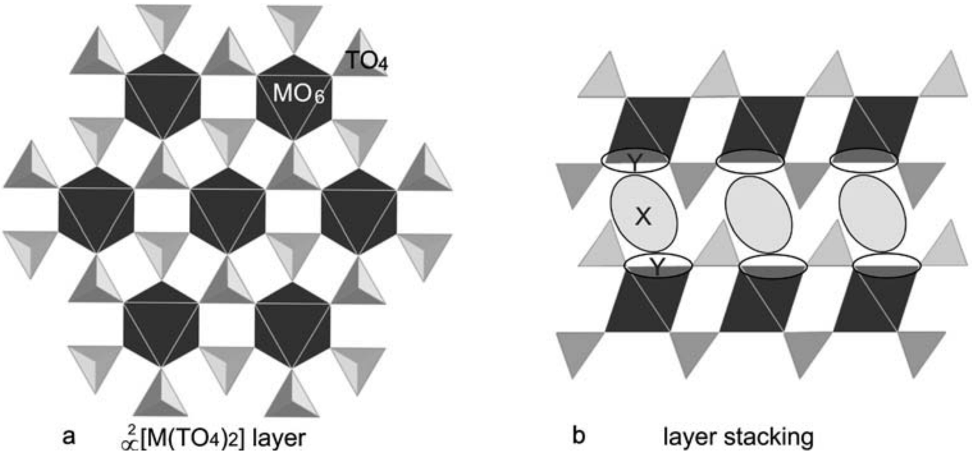

Fig. 1. Schematic presentation of the "glaserite" type topology: a) ${}^{2}_{\infty}[M(TO_4)_2]$ layer– top view; b) layers stacking – side view and possible interlayer cations positions (X, Y)

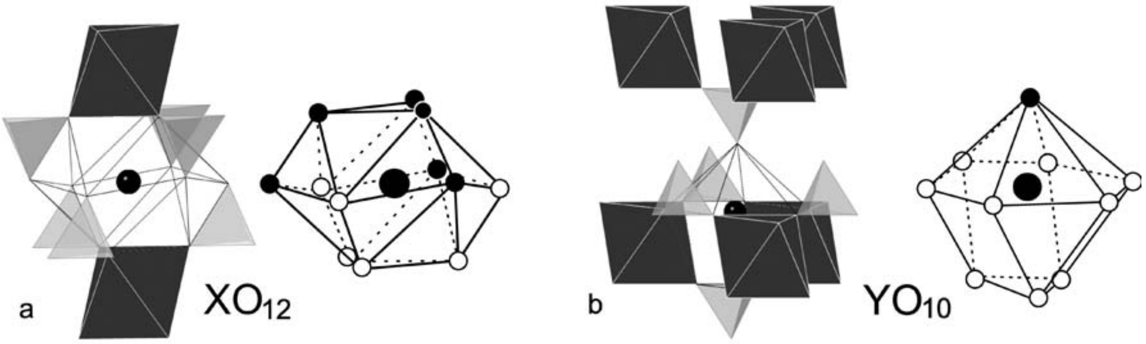

Fig. 2. Interlayer cations environment in the highest symmetry GTT case expressed in terms of the oxygen ligands from the “upper” (filled circles) and the “lower” (empty circles) layer

and Y atoms coordination does not match the one proposed by Lazoryak in his general formula – $X^{[6+6]}Y_2^{[4+6]}M^{[6]}(EO_4)_2$ [7]. It is because this author applies the columnar model for description of the glaserite construction. It is worth noting that the multiplicity of the Y position in GTT is always twice that one of X (X:Y=1:2).

The ${}^{2}_{\infty}[M(TO_4)_2]$ layer is common for a large number of compounds e.g. $Zr(HPO_4)_2.2H_2O$ (αZrP) [25], palmierite [26], $A_{2(3)}MT_2O_7$ [27] and references therein (Fig. 3).

In this work three essential structural characteristics are introduced to strictly define the “glaserite” type topology and distinguish it from other topologies with ${}^{2}_{\infty}[M(TO_4)_2]$ layers. The first one is that GTT does not contain additional atomic positions except the described M, T, X, and Y ones. For example, the structure of $Zr(HPO_4)_2.2H_2O$ (αZrP) provides opportunity for appearance of different interlayer positions due to its well-known capability for intercalation interrelated with the presence of OH^- group at the free apexes of the TO_4 tetrahedra (Fig. 3a). Another essential structural feature of GTT is that the free tetrahedral apexes point outside the layer towards the interlayer space. Up to now, the authors applying the layer model in the description of GTT point out only that the unshared corners of the tertahedra are oriented alternatively up and down in direction perpendicular to the layer [4, 7–9, 16, 19]. In the “palmierite” type structures this rule is observed however the free apexes point inside the layer (Fig. 3b) and the consequences of this is a different configuration of the charge compensating cations (see the stacking sequence of palmierite in [19]). The third one is that the layer stacking in GTT is realized without bridging oxygen atoms as shown in Fig. 1b. In contrast, in the $A_{2(3)}MT_2O_7$ compounds (Fig. 3c) the ${}^{2}_{\infty}[M(TO_4)_2]$ layers are linked by a bridging oxygen atoms leading to less pronounced characteristics of layeredness as compared with the GTT.

Quite obviously the ${}^{2}_{\infty}[M(TO_4)_2]$ layer charge depends on the type and valence of the M and T positioned cations. On its side, the layer charge is predetermining the occupancy, type, and valence of the

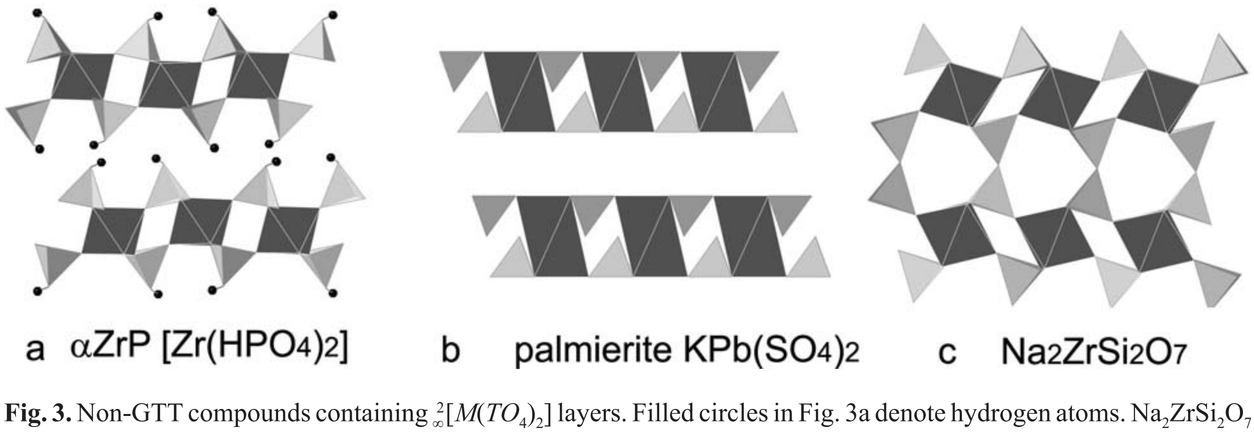

Fig. 3. Non-GTT compounds containing ${}^{2}_{\infty}[M(TO_4)_2]$ layers. Filled circles in Fig. 3a denote hydrogen atoms. $Na_2ZrSi_2O_7$ is a representative of the group of compounds with general formula $A_{2(3)}MT_2O_7$

X and Y positioned cations. Thus, when the layer is electroneutral both charge compensation cation positions will be unoccupied. In all other cases either X, or Y, or both X and Y positions will be occupied by appropriate in charge cations. Lazoryak's general formula, however, does not provide information about the cationic positions occupancy and their actual coordination in case of structural deviations from the highest symmetry.

Thus, a reconsideration of the general formula of GTC has been undertaken in terms of the postulated above essential structural features for GTT. A check-up in the available structural data bases has been performed and some of the results are summarized below.

- among the compounds adopting GTT there are 5 minerals and more than 100 synthetic compounds;
- altogether 47 elements from the periodic table can occupy the established four cationic positions (X, Y, M, and T) in the studied group;
- the T position (always fully occupied) includes the following elements: transition metals (V, Cr, Mo, W, Re, Fe, Ru) and non-metals (Si, P, S, Se). Altogether – 11;
- the M position (always fully occupied) is taken by: alkali metals (Na), alkali earth metals (Mg, Ca), transition metals (Sc, Y, Ti, Zr, Hf, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Zn, Cd) including lanthanides (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), and poor metals (Al, In, Tl, Ge, Sn, Sb). Altogether – 32;
- if occupied the X and Y positions are taken by alkali metals (Na, K, Rb, Cs), alkali earth metals (Ca, Sr, Ba), transition metals (Ag), and poor metals (Tl, Pb). All of them – 10;
- the ${}^{2}_{\infty}[M(TO_4)_2]$ layer charge can take up the following values: 0, –1, –2, –3, –4, –6;

Based on the performed crystal chemical review a precise general formula (GF) for "glaserite" type compounds can be deduced and presented as follows: $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$ (X+Y = 0; 1; 2; 3; M = 1; T = 2). Additional limitations and variety ranges for the general formula are presented in Table 1.

The amazing compositional diversity, the possibility for some chemical elements to occupy more than one cationic position (sometimes even in a single compound), the availability of mixed cationic positions, and the opportunity for X and Y to be both either free (unoccupied) or entirely occupied bring to a great variety of records for the general formula. Table 2 presents derivatives of the as introduced GTC general formula in accordance with the specificity (see third column) and occupancy of the cationic positions X, Y, M, and T ("conditions"). Each one is illustrated with the long and short formula of a particular "glaserite" compound in order to clarify the way the empirical chemical formulas for certain GTC can be derived. The last column shows the number of compounds found in the available structural data bases.

The distribution of GTC in groups according to the specificity of the cationic positions reveal that the conditions indicated in lines 2 and 4 of Table 2 are most favorable for the formation of such materials. According to the X and Y positions occupancy three groups of GTC can be differentiated. There are only 8 compounds with electroneutral layers and free X and Y positions. In 45 compounds only the X position is occupied (always completely) and 55 other phases contain both X and Y cations (full occupancy). Up to now only one compound – $K_2Zr(PO_4)_2$ (line 7 in Table 2) is established in which the Y position is occupied whereas the X one is free. This is indicative that the X position is more occupationally preferred than the Y one.

The proposed crystal-chemical formula does not contain information about the coordination numbers of the charge compensating cations since these values are not constant (Table 1, last column). These are strongly influenced by the structural deviations from the highest symmetry case for GTT occurring upon variations of the cationic positions specificity (Table 2). In some GTC H atoms are added to the chemical formula to overwhelm the spatial limitations affecting the charge compensating cations.

Table 1. Limitations and variety ranges of the GTC general formula $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$ (X+Y = 0; 1; 2; 3;)

Cation position	number of elements occupying the position	valence of elements occupying the position	CN (BVS)*
X	0; 1; 2	1+, 2+	6, 7, 8, 9, 10, 12
Y	0; 1; 2	1+, 2+	4, 5, 7, 8, 9, 10, 12
M	1; 2	1+, 2+, 3+, 4+	6
T	1; 2	4+, 5+, 6+, 7+	4

* The coordination number CN is determined on the basis of the bond valence sums (BVS) after testing each CIF file with the ***soft BV 0.96*** software [28]

Table 2. Derivatives of the general formula $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$ in accordance with the specificity and occupancy of the cationic positions (X, Y, M, and T)

No	General formula	Conditions	Examples		Ref.	Number of GTC
			Long formula	Short formula		
1	$XY_2[M(TO_4)_2]$	$X \neq Y \neq M \neq T$	$BaNa_2[Mg(PO_4)_2]$	$BaNa_2Mg(PO_4)_2$	[12]	12
2	$XY_2[M(TO_4)_2]$	$X = Y \neq M \neq T$	$AgAg_2[Fe(VO_4)_2]$	$Ag_3Fe(VO_4)_2$	[29]	31
3	$XY_2[M(TO_4)_2]$	$X \neq Y$; $X = M$; $Y \neq M \neq T$	$NaK_2[Na(SO_4)_2] = K_2Na_2(SO_4)_2$	$KNaSO_4$	[2]	1
4	$XY_{\square}[M(TO_4)_2]$	$X \neq M \neq T$; $Y = 0$	$Rb\square[Fe(MoO_4)_2]$	$RbFe(MoO_4)_2$	[30]	41
5	$(X1,X2)Y_{\square}[M(TO_4)_2]$	$X1 \neq X2 \neq M \neq T$; $Y = 0$	$(Ba_{0.3}Sr_{0.7})[Zr(PO_4)_2]$	$Ba_{0.3}Sr_{0.7}Zr(PO_4)_2$	[31]	1
6	$X(Y1,Y2)_2[M(TO_4)_2]$	$X = Y1 \neq Y2; Y2 = M \neq T$	$Ba(Ba_{0.5},Na_{0.5})_2[Na(PO_4)_2] = Ba_2Na_2(PO_4)_2$	$BaNaPO_4$	[32]	4
7	$X_{\square}Y_2[M(TO_4)_2]$	$Y \neq M \neq T$; $X = 0$	$\square K_2[Zr(PO_4)_2]$	$K_2Zr(PO_4)_2$	[33]	1
8	$X_{\square}Y_{\square}[M(TO_4)_2]$	$M \neq T$; $X = 0$, $Y = 0$	$\square\square[Ni(ReO_4)_2]$	$Ni(ReO_4)_2$	[34]	7
9	$X_{\square}Y_{\square}[M(T1,T2O_4)_2]$	$M \neq T1$; $T1 \neq T2$; $X = 0$, $Y = 0$	$\square\square[Zr(Mo,WO_4)_2]$	$Zr(Mo,WO_4)_2$	[35]	1
10	$XY_{\square}[(M1,M2)(TO_4)_2]$	$X \neq M1 \neq M2 \neq T$; $Y = 0$	$K\square[(Mg_{0.5}Zr_{0.5})(MoO_4)_2]$	$K(Mg_{0.5}Zr_{0.5})(MoO_4)_2$	[36]	1
11	$XY_2[M(TO_4)_2]$	$X = Y = M \neq T$	$TlTl_2[Tl(WO_4)_2] = Tl_4(WO_4)_2$	Tl_2WO_4	[37]	2
12	$XY_2H[M(TO_4)_2]$	$X = Y \neq M \neq T$	$NaNa_2H[Mg(PO_4)_2]$	$Na_3HMg(PO_4)_2$	[38]	5
13	$XY_{\square}H[M(TO_4)_2]$	$X \neq M \neq T$; $Y = 0$	$K\square H[Zr(PO_4)_2]$	$KHZr(PO_4)_2$	[39]	2

For example, in $Na_3HZr(GeO_4)_2$, $K_3HCa(PO_4)_2$ and $Na_3HMg(PO_4)_2$ this occurs on the account of a randomly attached to the framework hydrogen [40–42]. The $Na_{3-x}H_{1+x}Zr(SiO)_4.yH_2O$ material also accommodates charge compensating H^+ as well as water molecules in its structure [21, 22]. Interestingly, the water is trapped between the charge compensating Na atoms and not positioned in the interlayer space, the way this occurs in the αZrP. Since the $Na_{3-x}H_{1+x}Zr(SiO)_4.yH_2O$ material does not exhibit rehydration or intercalation properties we are prone to classify this zirconosilicate as a GTC.

No doubt, the cations radiuses play a key role for the structural versatility and range of stability of GTC. As reported in the Introduction section in 1996 Lazoryak defined criteria for stability of "glaserite" type topology and postulated that "Glaserite structural type is stable for compounds where $0.59 < \Delta r < 0.89$ Å ($\Delta r = r\ X(Y) - rM$; Shanon ionic radii). When this difference decreases, metastable or β-K_2SO_4–like structures are formed" [7]. Later on, Morozov *et al.* expanded the lower limit of the range to $0.375 \leq \Delta r \leq 0.89$ Å, reporting the structure of $Na_3Fe(PO_4)_2$ [43]. As a result of the performed here review of GTC this range is further expanded and can be written as $0 < \Delta r < 1.345$ Å. The lower value is obtained for the structure of Tl_2WO_4 [37] and the upper one – for $CsAl(MoO_4)_2$ [44].

The "glaserite" layer stability and structural flexibility

Inspection of the collected structures brought forward certain facts and observations and suggest that the main structural motif of the investigated materials is the ${}^2_\infty[M(TO_4)_2]$ layer. One example concerns compounds which undergo phase transitions upon thermal treatment without destroying their topology. It was noticed that this process affects noticeably only the environment of the charge compensating interlayer cations. The adjacent layers may mutually off-shift when a phase transition occurs but the layer structure itself remains almost intact and only slight deviation can be detected for the bond distances and angles of the atoms constituting them. The XO_n and YO_n polyhedra in the higher temperature phases (HTP) have higher symmetry and are larger in volume than the corresponding coordination polyhedral in the lower temperature phases (LTP). The latter ones exhibit noticeable non-equivalence in the bond lengths. In general, the thermal expansion of the XO_n and YO_n polyhedra is most pronounced in the direction perpendicular to the layers. An expected effect of the bond distances elongation occurring in the HTP is the lowering of the bond valence sums calculated for the charge compensating cations there as compared to those ones obtained in the LTP. $K_3Na(SeO_4)_2$,

$K_3Na(RuO_4)_2$, $BaZr(PO_4)_2$ are “glaserite” type materials which undergo phase transformation upon thermal treatment and the comparison of their high and low modifications characteristics is a pretty fair illustration of the above said [10, 45, 46]. The structural transformations that occur with the latter compound are such that the charge compensating Ba even changes its coordination number from 10 (LTP) to 12 (HTP) thus making its bonds with the layer weaker.

As mentioned above in some “glaserite” type compounds the layers are electroneutral and their structures do not contain charge compensating cations, i.e. X and Y are vacant: $Ni(ReO_4)_2$, $Co(ReO_4)_2$, $Zn(ReO_4)_2$, $Mn(ReO_4)_2$, $Zr(Mo,WO_4)_2$, $Zr(MoO_4)_2$, $Hf(MoO_4)_2$, [34, 35, 47, 48]. The lack of any bonds between the layers provide for their comparatively high mobility and various opportunities for mutual orientation. Thus, a remarkable number of different polymorphs of $Zr(MoO_4)_2$ with GTT have been reported in the literature ([47, 48] and references therein).

In general, GTC with compositionally identical layers and various in size charge compensating interlayer cations are interesting because they illustrate the “layer-splitting” role of the latter. The intralayer cations are, in fact, framework cations and hence, it is possible to calculate the framework density (FD) of such compounds the way this is made for microporous materials (FD = number of framework cations per 1000 Å^3). Best candidates for this procedure are GTT orthophosphates, orthovanadates and orthotungstates of rare earth elements (REE) and differing in size alkali elements (rK < rRb < rCs) with general formula $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$ (X,Y = K, Rb, Cs; M = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; T = P, V, W). These materials have been investigated in details by many authors and although not all theoretically possible structures have been experimentally observed or refined, there is sufficient amount GTC with refined lattice parameters and chemical formulas to perform such calculations [13–17]. As expected the FD values drop with the increase of the alkali cation radius. For example, in $K_2RbGd(VO)_4$ [16] this value is 12.8 whereas in $Rb_3Gd(VO)_4$ [14] FD = 12.5. Another examples are $KAl(MoO)_4$ [49] (FD = 15.94) *vs.* $CsAl(MoO)_4$ [44] (FD = 13.99); $NaCr(CrO)_4$ (FD = 18.98) – $KCr(CrO)_4$ (FD = 16.88) – $CsCr(CrO)_4$ [50] (FD = 16.11), *etc*. In practice, the “layer-splitting” role of the interlayer cation was noticed for $M_3Ln(PO_4)_2$ compounds (M = K, Rb, Cs) in terms of the correlation between their hygroscopicity and the alkali cation radius. Most hygroscopic are the Rb and Cs phosphates [13].

As a whole, the “glaserite” topology is quite flexible and able to endure deformations preserving however its main structural motif. This is manifested through a variety of symmetry related Space Groups in which the members of GTC crystalize, e.g. P–3m – C2/m – P2/m – P–1 or C2/c – P2/c *etc*.

The flexibility of GTT can be expressed by comparing unit cell parameters which actually describe the translational symmetry of each particular crystal structure. For many GTC two crystallographic unit-cell parameters lie within the plane of the layer and hence, the a and b parameters are assumed to describe the intralayer translational symmetry, whereas the c parameter describes the stacking sequence repetition. For structures with a and b inclined to the plane of layer appropriate coordinate-system transformations are performed as to meet the above assumption. Therefore, the a and b parameters are related with the layer dimensionality and the value of their ratio is indicative for the degree of intralayer deformation (Fig. 4a).

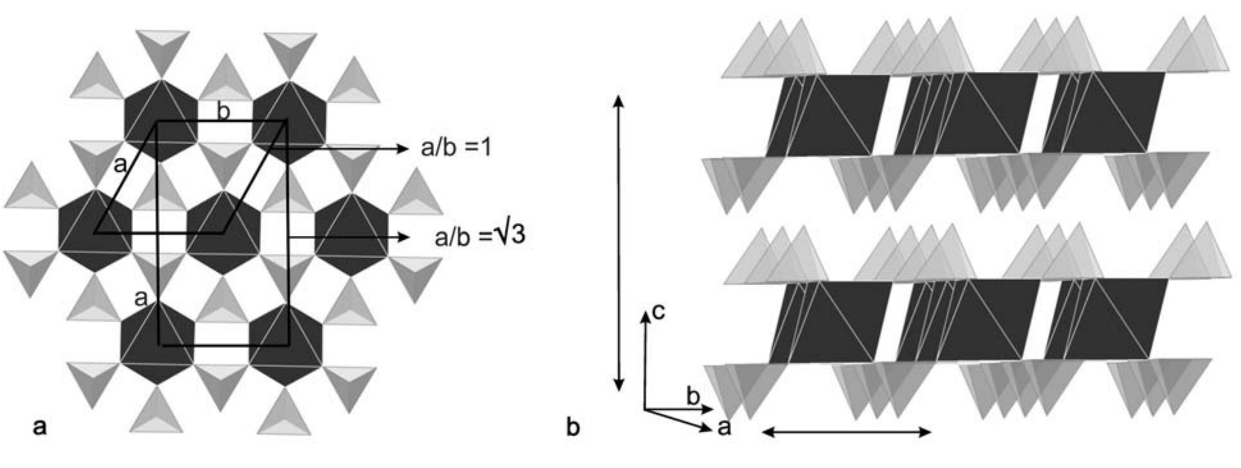

Fig. 4. GTT flexibility expressed in terms of lattice parameters ratios: a) two cell choices within the layer; b) schematic presentation of the magnitude of deformation within the layers and along their stacking

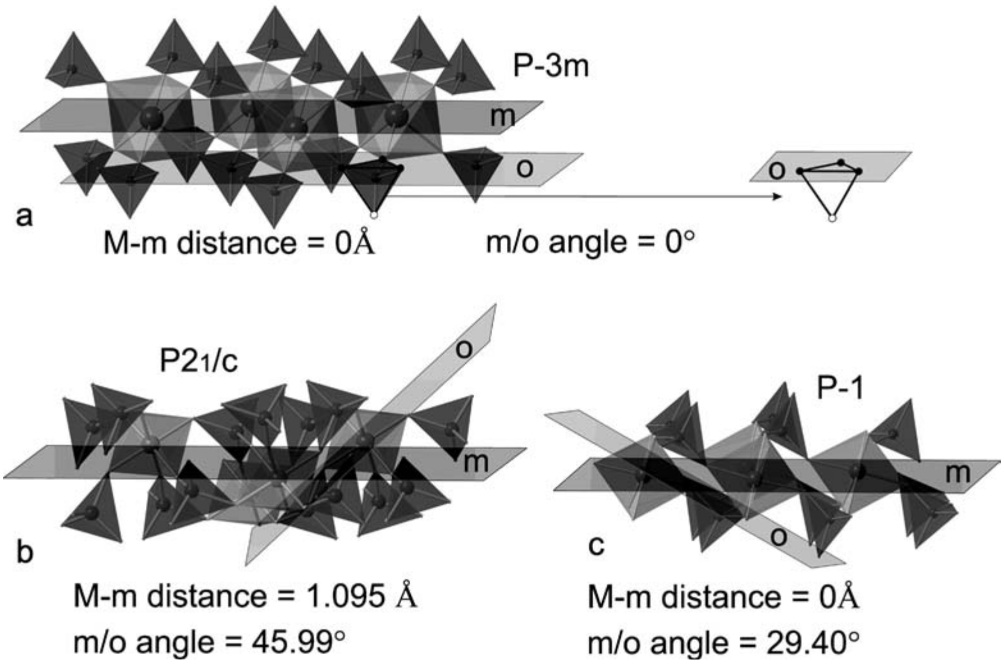

Fig. 5. Torsion of $^{2}_{\infty}[M(TO_4)_2]$ layer in terms of the relationship between atoms and planes. a) glaserite $K_3Na(SO_4)_2$; b) $CsSb(VO_4)_2$; c) $Na_3HZr(SiO_4)_2 \times 0.2H_2O$

On the other hand, the c value refers to the flexibility of the layer stacking. The highest possible symmetry of GTT is P–3*m*. In this “ideal” case of hexagonal setting $a_h = b_h$ or in the case of orthogonal choice the cell used is characterized with the ratio $a_o:b_o = \sqrt{3}$ (Fig. 4a). For the studied compounds the $a_0:b_0$ ratio deviates from the “ideal” value of $\sqrt{3}$ within the range 0.001 to 0.247 for $BaNa(PO_4)$ [51] and $KM(SeO_4)_2$ [52], respectively. On the other hand, the value of the *c* parameter varies between 5.285(1) Å in $\delta Zr(MoO_4)_2$ [47] to 25.409(4) Å in $KSb(PO_4)_2$ [53]. From these figures it can be concluded that similarly to other layered structures the deformation in GTT is anisotropic being more pronounced in direction of the layer stacking rather than within the layer (Fig. 4b).

Another set of parameters characterizing the topological flexibility is presented in Fig. 3 on the example of three particular GTC. By considering the $^{2}_{\infty}[M(TO_4)_2]$ layer two planes can be clearly defined: the mean plane defined by the M atoms – denoted here with **(m)** and the plane defined by the three bridged oxygen atoms from a given TO_4 tetrahedron is denoted here with (**o**). In the “ideal” case all M atoms lie in a single plane and both **m** and **o** planes are parallel to each other (Fig. 5a). However, deviations from these values are possible as the maximum measured distance of M atom from the mean *m* plane is 1.09 Å and the largest established angle between **o** and **m** planes is 45.99° for $CsSb(VO_4)_2$ [54] (Fig. 3b).

Obviously, the chemical diversity and structural versatility of GTC are closely related and depend also on the formation conditions which impress with the broadness of their range. Thus, three of the minerals are products of volcanic fumarolic activity e.g. glaserite (aphthitalite) – $K_3Na(SO_4)_2$ [1–3], yavapaiite – $KFe(SO_4)_2$ [55], eldfellite – $NaFe(SO_4)_2$ [56]. Merwinite – $Ca_3Mg(SiO_4)_2$ is of scarn origin (high temperature, low pressure contact metamorphic zones with marbles) [57]. Brianite – $Na_2CaMg(PO_4)_2$ is an exotic find established only in meteorite rocks [58]. The synthetic compounds can be prepared through a great variety of methods (from solution, hydrothermally, solid state reactions, electrosynthesis, *etc*.) and within temperature ranges from room temperature to 1800 °C.

The established compositional variety and wide range of formation conditions are good prerequisite for preparation of new materials adopting the “glaserite” topology.

CONCLUSIONS

Crystal chemical data for more than 100 compounds with “glaserite” type structure have been summarized, analyzed, and evaluated. A revised general formula for "glaserite" type compounds has been deduced – $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$ (X+Y = 0; 1; 2; 3;). It gives information for two important structural characteristics of GTC. The first one is that main structural unit is the ${}^{2}_{\infty}[M(TO_4)_2]$ layer in which all the atomic positions are fully occupied. The second one is that the occupancy of X and Y positions depends on the layer charge and these positions can either be both free, separately or both of them entirely occupied. Additional limitations and variety ranges of the general formula are presented with respect to the cationic characteristics most important of which is the great variety of coordination numbers for the X and Y positions.

Precise criteria for the "glaserite" type topology are proposed distinguishing it from other topologies constructed by similar or identical layers. One of them is that the free apexes of the layer constructing tetrahedral should point outside the layer towards the interlayer space and another one is that the layers stacking should be realized without bridging oxygen atoms.

The range of structural stability of the "glaserite" type compounds is outlined in terms of the established up to now cations composition and site occupancy. The topological flexibility is evaluated through purposely introduced here geometrical parameters based on the lattice parameters or certain dimensional and angular interrelations.

The established compositional diversity, topological versatility and wide range of formation conditions are good prerequisite for preparation of new materials adopting the "glaserite" topology and estimation of certain physical phenomena such as temperature induced phase transitions.

***Acknowledgments**: Financial support by the Bulgarian National Fund of Scientific Research (contract DRNF 02/1) is gratefully acknowledged.*

REFERENCES

1. B. Gossner, *Neues Jahrb, Mineral.*, B.-Band **57A**, 89 (1928).
2. A. Bellanca *Period. di mineral.*, **14**, 67 (1943).
3. L. Pontonnier, M. Caillet and S. Aleonard, *Mat. Res. Bull.*, **7**, 799 (1972).
4. K. Okada and J. Ossaka, *Acta Cryst. B*, **36**, 919 (1980).
5. P. B. Moore, *Bulletin de la societe Francaise de Mineralogie et de Cristsllographie*, **104**, 536 (1981).
6. S. Takagi, M. Mathew, W. E. Brown, *Acta Cryst. C*, **39**, 166 (1983).
7. B. I. Lazoryak, *Russ. Chem. Rev.*, **65(4)**, 287 (1996).
8. M. Auray, M. Quarton, P. Tarte, *Acta Cryst. C*, **42**, 257 (1986).
9. L. Rghioui, L. El Ammari, L. Benarafa, J. P. Wignacourt, *Acta Cryst. C*, **58**, i90 (2002).
10. J. Fabry, T. Breczewski, V. Petricek, *Acta Cryst. B*, **49**, 826 (1993).
11. J. Fabry, V. Petricek, P. Vanek, I. Cisarova, *Acta Cryst. B*, **53**, 596 (1997).
12. Y. Yonesaki, C. Matsuda, *Journal of Solid State Chemistry*, **184**, 3247 (2011).
13. P. P. Mel'nikov, L. N. Komissarova *Koord. Khim.*, **12(10)**, 1299 (1986).
14. P. P. Mel'nikov, G. Y. Pushkina, V. A. Efremov, V. B. Kalinin, L. N. Komissarova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **26**, 142 (1981).
15. V. A. Efremov, P. P. Mel'nikov, L. N. Komissarova, *Revue de Chimie Minerale*, **22**, 666 (1985).
16. V. A. Efremov, P. P. Mel'nikov, H. D. K. Eredero, V. K. Trunov, *Izvestiya Akademii Nauk SSSR, Neorganicheskie Materialy*, **27**, 88 (1991).
17. V. A. Efremov, P. P. Mel'nikov, L.N. Komissarova, *Koord. Khim.*, **7(3)**, 467 (1981).
18. C. Park, S. Hong, D. A. Keszler *Journal of Solid State Chemistry*, **182,** 496 (2009).
19. P. B. Moore, *Am. Mineral.*, **58**, 32 (1973).
20. W. Eysel, *Am. Mineral.*, **58**, 736 (1973).
21. V. Kostov-Kytin, R. Nikolova, D. Nihtianova, *Materials Research Bulletin*, **47,** 2324 (2012).
22. V. Kostov-Kytin**,** R. Nikolova, T. Kerestedjian, P. Bezdicka, *Materials Research Bulletin*, **48**, 2029 (2013).
23. International Centre for Diffraction Data ICDD DD view+ 4.10.0.4 using PDF-4+2010 RDB 4.1002.
24. Inorganic Crystal Structure Database (ICSD), Karlsruhe: Gmelin institute fur anorganische Chemie, (2005).
25. J. M. Toup, A. Clearfield, *Inorg. Chem.*, **16***,* 3311 (1977).
26. R. G. Tissot, M. A. Rodriguez, D. L. Sipola, J. A. Voigt, *Powder Diffraction*, **16(2)**, 92 (2001).
27. R. P. Nikolova, K. Fujiwara, N. Nakayama, V. Kostov-Kytin, *Solid State Sciences*, **11**, 382 (2009).
28. http://www.kristall.uni-mki.gwdg.de/softbv/
29. G. A. Becht, J. T, Vaughey, S. Hwu, *Chemistry of Materials*, **22(3)**, 1149 (2010).
30. T. Inami, *Journal of Solid State Chemistry*, **180**, 2075 (2007).
31. K. Fukuda, T. Iwata, A. Moriyama, S. Hashimoto, *Journal of Solid State Chemistry*, **179**, 3870 (2006).
32. C. Calvo, R. Faggiani, *Canadian Journal of Chemistry*, **53**, 1849 (1975).
33. M. Doerffel, J. Liebertz, *Zeitschrift fuer Kristallographie*, **193**, 155 (1990).
34. A. Butz, G. Miehe, H. Paulus, P. Strauss, H. Fuess, *Journal of Solid State Chemistry*, **138**, 232 (1998).
35. X. Deng, J. Tao, X. Yang, H. Ma, J. W. Richardson, Jr. X. Zhao, *Chemistry of Materials*, **20(5)**, 1733 (2008).
36. R. F. Klevtsova, Zh. G. Bazarova, L. A. Glinskaya, V. I. Alekseev, S. I. Arkhincheeva, B. G. Bazarov, P. V. Klevtsov, *Zhurnal Strukturnoi Khimii*, **36(5)**, 891 (1995).
37. K. Okada, J. Osaka, *Acta Cryst. B*, **35**, 2189 (1979).
38. Natl. Bur. Stand. (U.S.) Monogr. 25 21, 117 (1985).

39. A. Clearfield, L. B. McCusker, P. R. Rudolf, *Inorganic Chemistry*, **23**, 4679 (1984).
40. N. A. Nosyrev, E. N. Treushnikov, V. V. Ilyukhin, N. V. Belov, *Dokl. Akad. Nauk*, **218(4)**, 830 (1974).
41. J. C. Grenier, A. Durif, C. Martin, *Bulletin de la Societe Francaise de Mineralogie et de Cristallographie*, **92**, 30 (1969).
42. A. Kawahara, J. Yamakawa, T. Yamada, D. Kobashi, *Acta Cryst. C*, **51**, 2220 (1995).
43. V. A. Morozov, B. I. Lazoryak, A. P. Malakho, K. V. Pokholok, S. N. Polyakov, T. P. Terekhina, *Journal of Solid State Chemistry*, **160**, 377 (2001).
44. P. E. Tomaszewski, A. Pietraszko, M. Maczka, J. Hanuza, *Acta Cryst. E*, 58, i119 (2002).
45. K. Mogare, W. Klein, Eva-Maria Peters, M. Jansen, *Solid State Sciences*, **8,** 500 (2006).
46. D. Bregiroux, K. Popa, R. Jardin, P. E. Raison, G. Wallez, M. Quarton, M. Brunelli, C. Ferrero, R. Caciuffo, *Journal of Solid State Chemistry*, **182**(5), 1115 (2009).
47. A. M. K. Andersen, S. Carlson, *Acta Cryst. B*, **57**, 20 (2001).
48. S. Allen, R. J. Ward, M. R. Hampson, R. K. B. Gover, J S. O. Evans, *Acta Cryst. B*, **60**, 32 (2004).
49. R. F. Klevtsova, P. V. Klevtsov, *Kristallografiya*, **15**, 953 (1970).
50. R. Vidya, P. Ravindran, P. Vajeeston, H. Fjellvag, A. Kjekshus, *Physical Review, Serie 3. B – Condensed Matter*, **72***,* 014411 (2005).
51. A. W. Kolsi, M. Quarton, W. Freundlich, *Journal of Solid State Chemistry*, **36**, 107 (1981).
52. G. Giester, *Mineralogy and Petrology*, **53**, 165 (1995).
53. Y. Piffard, S. Oyetola, S. Courant, A. Lachgar, *Journal of Solid State Chemistry*, **60**, 209 (1985).
54. D. R. Nandini, K. Vidyasagar, *J. Chem. Soc., Dalton Trans*, **18,** 3013 (1998).
55. E. J. Graeber, A. Rosenzweig, *Am. Mineral.*, **56**, 1917 (1971).
56. T. Balić-Žunić A. Garavelli, P. Acquafredda, E. Leonardsen, S. P. Jakobsson, *Mineralogical Magazine*, **73(1)**, 51 (2009).
57. P. B. Moore, T. Araki, *Am. Mineral.*, **57**, 1355 (1972).
58. J. Alkemper, H. Fuess, *Zeitschrift fuer Kristallographie*, **213**, 282 (1998).

КРИСТАЛОХИМИЯ НА СЪЕДИНЕНИЯ С “GLASERITE” ТИП СТРУКТУРА

Р. Николова*, В. Костов-Китин

Институт по минералогия и кристалография, Българската академия на науките,
ул. „Г. Бончев“, бл. 107, 1113, София, България

Постъпила февруари, 2013 г.; приета май, 2013 г.

(Резюме)

Обобщени и са кристалохимични данни за повече от 100 съединения с “glaserite” тип структура. Предложена е ревизирана кристалохимичната обща формула на “glaserite” тип съединения (GTC) – $X_{(\square;1)}Y_{(\square;2)}[M(TO_4)_2]$, която дава информация за две важни структурни характеристики на GTC. Първата е, че основната структурна единица в този тип съединения е слой – ${}^{2}_{\infty}[M(TO_4)_2]$, в който всички атомни позиции са напълно заети. Втората е, че заетостта на X и Y позиции зависи от заряда на слоя и тези позиции могат или да бъдат изцяло заети и двете заедно или по отделно, като и да бъдат незаети, ако заряда на слоя е нулев. Предложени са точни критерии за “glaserite” тип топология (GTT), които позволяват разграничаване на GTT от други такива, изградени от сходни или еднакви слоеве. Границите на структурна стабилност на “glaserite” тип съединения е описан от гледна точка на установените до сега катионен състав и заетост на междуслойните катионни позиции. Възможностите за деформация на GTT при запазване на основните и характеристики е оценена чрез геометрични критерии, основани на решетъчни параметри и определени разстояния и ъглови. Установеното голямо разнообразие в структурните параметри, химичния състав и условията на образуване на “glaserite” тип съединения са добра предпоставка за получаване на нови материали с подобна топология, предлагаща възможности за нереконструктивни фазови преходи. Ключови думи: глазерит, “glaserite” тип топология, “glaserite” тип съединения.