Topological analogues of nyerereite.

We use the topological representation of the initial crystal structure as a three-periodic net, where the connectivity between atoms is automatically determined according to the domain algorithm (Blatov, 2016). The topology of a complex carbonate is determined for a net of metal atoms and ligand centers of mass, which is constructed on the basis of metal-ligand coordination bonds. To do this, CO3 groups were transformed into [C] pseudoparticles by tightening the O atoms, with all bonds involving these atoms, to the central atoms C. Such a representation is described by an underlying net, (Alexandrov et al., 2011) which is the net of the barycenters of the structural groups. The topology of an underlying net is determined in an automated mode by comparison of a set of topological indices of the net with those for the reference nets from the ToposPro TTD collection (Alexandrov et al., 2019).

The topological analysis, devoted to the study of possibile analogues for carbonate structures, has been performed for the simple carbonates (e.g. Blatov, 2011). In our earlier works we have shown similarity of the crystal structure of nyerereite with the crystal structure of fairchildite [$K_2Ca(CO_3)_2$] and have noted that the similar structures were not found among orthoborates (Gavryushkin et al., 2016); whereas, the iso-structural analogues among orthoborates were found for $Na_2Ca_3(CO_3)_4$ (Gavryushkin et al., 2014) and $Na_4Ca(CO_3)_5$ (Rashchenko et al., 2018).

The net of nyerereite is characterized by the unique topological index 5, 6, 8, 9T2. Only two instances with this index have been found in ICSD, namely the α-$Na_2Ca(CO_3)_2$ and β-$Na_2Ca(CO_3)_2$ (Gavryushkin et al., 2016). The analysis of the subnet formed by the metal atoms showed that Na in the crystal structure of nyerereite forms 10-coordinated net **tca,** whereas Ca forms 8-coordinated net **hex**. Carbon atoms are arranged in the dense 12-coordinated net with **tcj** topology.

As it was earlier shown by Bolotina et al. (2017), the crystal structure of nyerereite can be presented as the stacking of layers of $CaCO_3$ and Na_2CO_3 in composition. Our investigation has shown that $CaCO_3$ layers are characterized by 2D 3-coordinated topology of the honeycomb – **hcb** (Figure 5). This topological motive is typical for inorganic compounds, in particular for graphite

nitrated where C is referred to the R-$3m$ symmetry (Nixon et al., 1966) and In_2Se_3 for which $R3m$ and R-$3m$ space groups have been proposed (Vilaplana et al., 2018). In 2D layers of Na_2CO_3, each atom of Na coordinates three CO_3 groups, and each CO_3 group is connected to six Na atoms with the resulting 3,6-coordinated **kgd** underlying net. The layers of **kgd** topology are characteristic for the well-known crystal structure of mineral portlandite $Ca(OH)_2$ – P-$3m1$ space group (Nagai et al., 2000). Moreover, the crystal structures of **kgd** topology were found among carbonates such as Tl_2CO_3 – $C2/m$ symmetry (Marchand et al., 1975) and $BaCa(CO_3)_2$ (ewaldite) – $P6_3mc$ space group (Donnay et al., 1971).

Topological analysis has also revealed several groups of ternary carbides, containing layers of **kgd** or **hcb** topology interchanging with the layers of the other topologies. Below we consider the most representative groups of such compounds. The first one is $Me(1)Me(2)C_2$ – $Amm2$ (Me(1) = Fe, Co, Ni et al, Me(2) = REE, An) for which 36 structures were found. Atoms Me(1) and C are arranged in layers of **hcb** topology and the net of atoms Me(1) and Ca is characterized by the **hex** topology. On the other hand, there is the class of compounds $Me(1)_2Me(2)C$ – $P6_3/mmc$ [Me(1) = Ti, Cr, V, Nb et al., Me(2) = Al, Ga, Cd, Ge et al.] with 29 structures where the net of Me(1) and C has the **kgd** topology, while Me(1) and Na has the **tca** topology.

The topological type **tca**, found for the Na atoms in the nyerereite crystal structure, is not popular among carbonates or carbides. It was found among oxy-carbonates with large cations La, Dy, Gd: $Dy_2O_2(CO_3)$ – $P6_3/mmc$ (Kutlu and Meyer, 1999), $La_2O_2(CO_3)$ – $P6_3/mmc$ (Attfield and Férey, 1989). Also the **tca** topology was found for the earlier mentioned carbides $Me(1)_2Me(2)C$ – $P6_3/mmc$ for the subnet of Me(1) atoms. In contrast, the topology of the subnet of C atoms in the crystal structure of nyerereite (**hex**) is typical for many carbides, as the topology of the net formed by the atoms of metal and carbon (we have found more than 100 structures of binary and ternary carbides). In carbonates, this topology has been found for the net of Ca atoms in the vaterite structures of $CaCO_3$ – $P6_522$ (Wang and Becker, 2009), as well as for atoms of Ca and Ba in $BaCa(CO_3)_2$ – $P3_21$ (mineral

paralstonite). This topology is more popular among the nets formed by carbon atoms. More than 20 double carbonates and oxy-carbonates with this topology were found.

The topology **tcj**, found for the net of carbon atoms in nyerereite structure, is observed only for the nets of carbon atoms for two double carbonates: $Na_5Y(CO_3)_4 - P2_1/c$ and $Na_2Cd(CO_3)_2 - Cmcm$. Carbon atoms in crystal structures of carbides are characterized by 12-coordinated close-packed **fcu** topology (*fcc* in crystal chemical notation).