MS27 Minerals and Materials Under Extreme Conditions

MS27-03

Polymerization of CO_4 groups in carbonates

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Abstract

The building blocks of 'conventional' carbonates such as calcite or magnesite are trigonal planar $[CO_3]^{2-}$-groups [1,2]. These CO_3-groups remain stable as isolated groups up to pressures of ~70 GPa. At higher pressures and high temperatures above ~2000 K the formation of $[CO_4]^{4-}$-groups was observed and explained by the formation of carbon with *sp*^{3}-hybridized orbitals [2]. In contrast to *sp*^{2}-hybridized CO_3-groups, CO_4-groups may polymerize based on half-occupied orbitals that allow for additional bonding. However, extensive investigation of the polymerization of CO_4-groups was hindered by experimental difficulties to achieve such extreme conditions. In contrast to CO_4-groups, polymerizations of other orthoanions $[MO_4]$ have been extensively investigated in the past. $[SiO_4]^{4-}$-tetrahedra are the main building blocks in silicates and play a major role in crystallography and mineralogy [3,4]. Tetrahedral SiO_4-groups can polymerize and build pairs, chains, rings, sheets or networks [3,4]. In addition to the SiO_4-tetrahedra in silicates, further anions such as $[BO_4]^{5-}$ -groups of borates are key-components in basic chemistry and polymerize with BO_4-groups and even with other BO_3 building blocks [5].

Recently, we demonstrated the synthesis of carbonates containing CO_4-groups at moderately high pressures (20-30 GPa) by reacting carbonates with either oxides or CO_2 [6-8]. These carbonates have chemical compositions other than the well-known 'conventional' carbonates ($MeCO_3$) and are either enriched in a metal oxide or CO_2 [6-8]. Some of them can even be recovered at ambient conditions [6,7]. The favorable synthesis pressure conditions allowed us to investigate different structural aspects and the polymerization of CO_3-groups in large detail. As a result of the polymerization, carbonates with isolated CO_4-tetrahedra or carbonates with groups, rings, chains or pyramids can be formed (see the figure). The structural variety of those carbonates resembles that of silicates and some borates. In the present study, we will give an overview of carbonates containing CO_4-groups and present crystal-chemical aspects of CO_4-groups in comparison to SiO_4 and other MO_4 complex anions.

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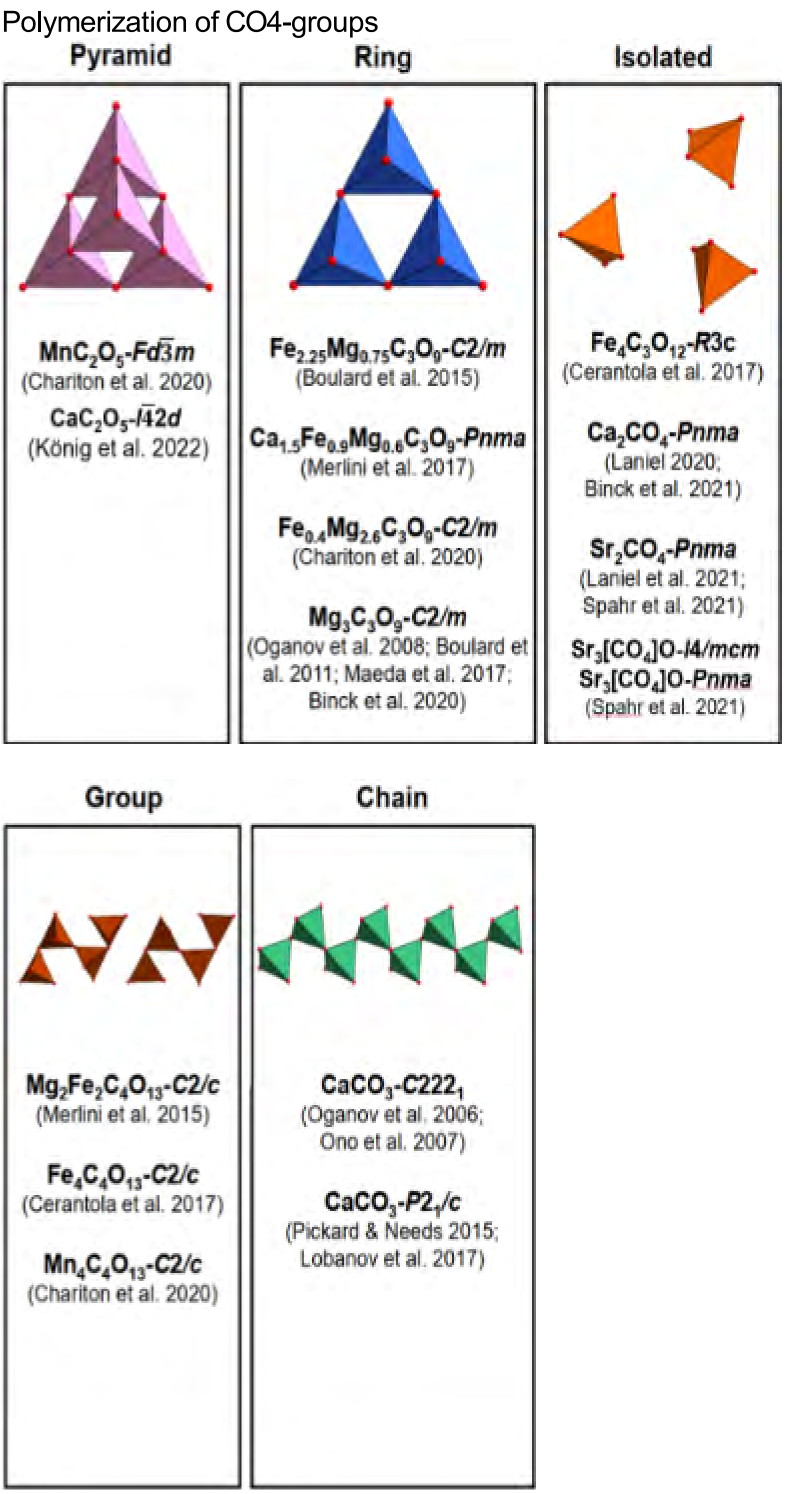
Polymerization of CO4-groups
Pyramid
Ring
Isolated
MnC_2O_5-$Fd\bar{3}m$
(Chariton et al. 2020)
CaC_2O_5-$I\bar{4}2d$
(König et al. 2022)
$Fe_{2.25}Mg_{0.75}C_3O_9$-$C2/m$
(Boulard et al. 2015)
$Ca_{1.5}Fe_{0.9}Mg_{0.6}C_3O_9$-$Pnma$
(Merlini et al. 2017)
$Fe_{0.4}Mg_{2.6}C_3O_9$-$C2/m$
(Chariton et al. 2020)
$Mg_3C_3O_9$-$C2/m$
(Oganov et al. 2008; Boulard et al. 2011; Maeda et al. 2017; Binck et al. 2020)
$Fe_4C_3O_{12}$-$R3c$
(Cerantola et al. 2017)
Ca_2CO_4-$Pnma$
(Laniel 2020; Binck et al. 2021)
Sr_2CO_4-$Pnma$
(Laniel et al. 2021; Spahr et al. 2021)
$Sr_3[CO_4]O$-$I4/mcm$
$Sr_3[CO_4]O$-$Pnma$
(Spahr et al. 2021)
Group
Chain
$Mg_2Fe_2C_4O_{13}$-$C2/c$
(Merlini et al. 2015)
$Fe_4C_4O_{13}$-$C2/c$
(Cerantola et al. 2017)
$Mn_4C_4O_{13}$-$C2/c$
(Chariton et al. 2020)
$CaCO_3$-$C222_1$
(Oganov et al. 2006; Ono et al. 2007)
$CaCO_3$-$P2_1/c$
(Pickard & Needs 2015; Lobanov et al. 2017)