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Bilbao Crystallographic Server - new databases and computer tools

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The Bilbao Crystallographic Server [1] is a free web site with crystallographic databases and programs available at *http://www.cryst.ehu.es*. The server is built on a core of databases that contains data of the *International Tables for Crystallography*, Vol. A (*Space-group Symmetry*), Vol. A1 (*Symmetry Relations between Space Groups*) and Vol. E (*Subperiodic Groups*). More specialized crystallographic software is also available and distributed in shells according to different topics: group-sub-group relations (subgroups and supergroups of space groups, splitting of Wyckoff positions), solid-state applications (pseudo-symmetry search and selection rules) or representation theory. There are symmetry tools for the construction of irreducible representations of space groups and point groups, for the analysis of their correlations for a group-subgroup pair, and for the reduction into irreducible constituents of Kronecker products of representations [2].

The aim of the contribution is to report on new databases and tools available on the server. The space-group database has been extended to include the data on the non-conventional settings of the monoclinic and orthorhombic space groups. In addition, the series of maximal isomorphic subgroups of the space groups (indices up to 27) are made online accessible. Recently, the computer program SITESYM has been implemented on the server. It is based on the so-called site-symmetry approach that establishes symmetry relations between the localized states (local atomic displacements) and crystal extended states (phonons, electrons, *etc*.) over the entire Brillouin zone [3]. The method applies the procedure of induction of representations of the space group of the crystal from the representations of the site-symmetry groups of constituent units (atoms, clusters and layers) according to which the local excitations are transformed. The site-symmetry approach has proved to be efficient in the analysis of phonon and electron spectra in crystals with large number of atoms in the unit cell where the traditional symmetry methods turn to be complicated.

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New topologies of metal based croconates:Syntheses, crystal structures and thermal behaviours

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Most of the microporous materials are built from phosphates or carboxylates, and the use of oxocarbons, such as croconates, has been much less investigated. New families of open-framework materials have been recently obtained from the assembly of building blocks MO_7, MO_8 or MO_9 polyhedra and croconate $C_5O_5^{2-}$ anions. The crystal structures, determined from single-crystal possess various dimensionalities and topologies. The present study describes the crystal structures of five families:

- Yttrium croconate hydrate, $[Y(H_2O)_6]_2(C_5O_5)_3.3H_2O$, Z = 1, $P1$. The structure, isotypical to lanthanide related croconates [1], contains isolated $[Y(H_2O)_6]_2(C_5O_5)_3$ entities in which YO_8 square-based antiprisms are connected via monodentate croconates.

- Piperazinediium cerium(III) croconate hydrate, $(C_4H_{12}N_2)_2[Ce(H_2O)_3]_2(C_5O_5)_5.2.5H_2O$, Z = 8, $C2/c$; piperazinediium lanthanum croconate hydrate, $(C_4H_{12}N_2)_2[La(H_2O)_3]_2(C_5O_5)_5.3H_2O$, Z = 2, $P2/c$; dabcodiium cerium(III) croconate hydrate, $(C_6H_{14}N_2)_2[Ce(H_2O)_3]_2(C_5O_5)_5.6H_2O$, Z = 2, $P2/c$. The structures are built from anions $Ce_2(C_5O_5)_5^{4-}$ made of MO_9 polyhedra sharing one vertex and also connected to each other by three bis-chelating croconates. Anions are stacked up to form corrugated chains in between which amines and water molecules are located.

- Calcium croconate trihydrate, $Ca(C_5O_5).3H_2O$, Z = 8, $Pbca$; The compound is a polymorph of an already reported croconate [2]. $[CaO_8]_2$ dimers are connected by bis-chelating croconates to form highly corrugated layers which interpenetrate.

- Calcium croconato oxalate hydrate, $Ca_2(C_5O_5)(C_2O_4).H_2O$, Z = 4, $Pnma$. The structure is built from CaO_7 and CaO_8 polyhedra sharing edges in the form of zigzag chains. Adjacent chains are connected both by polyhedra vertices and oxalate groups. The resulting layers are bridged by croconates leading to a 3D open-framework.

-Lanthanide(III) croconato oxalate hydrate, $Ln_2(C_5O_5)_2(C_2O_4)(H_2O)_8.2H_2O$ (Ln = Ce, La), Z = 2, $P2_1/n$. MO_9 polyhedra are connected by croconates and oxalate groups to form a 3D neutral framework. Free water molecules are located inside the tunnels of the structure.

The different topologies as well as the role of amines, oxalates and van der Waals interactions between stacked croconates will be discussed. The thermal behaviours studied by thermogravimetry and thermodiffractometry will allow to evidence possible zeolite-like properties.

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