

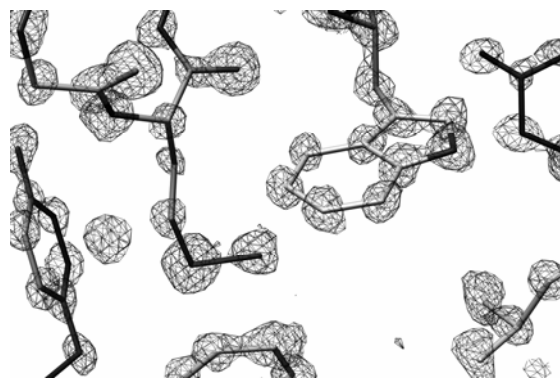
The M1 site is an antiprism sharing faces with two AO₆ octahedra. The M2 site is a large cage bounded by 8 oxygens.

MS33 P01

Atomic resolution structure of HEWL in complex with tris-dipicolinate lanthanide Guillaume Pompidor^a, Olivier Maury^b, Jean Vicat^a, Richard Kahn^a, ^a*Institut de Biologie Structurale, CEA-CNRS-UJF, UMR 5075, Grenoble, France.* ^b*Laboratoire de Chimie, UMR 5182, ENS-Lyon, France.*
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Keywords: macromolecular phase determination, atomic resolution crystallography, lanthanide

Tris-dipicolinate lanthanide complex, Na₃[Ln(DPA)₃], where DPA stands for pyridine-2,6 dicarboxylate, was used to obtain derivative crystals of hen egg-white lysozyme (HEWL). Derivative crystals were prepared by co-crystallization using conditions close to those leading to the native tetragonal HEWL crystals by adding in the crystallization drops solutions of Ce or Lu complexes to a final concentration of 50-100 mM. The crystals, belonging to a new monoclinic form of lysozyme, space group C2, were diffracting to a resolution never achieved with lysozyme crystals. Diffraction data for the Ce and Lu derivative crystals were recorded to resolutions of 0.80 and 0.85 Å, respectively. Taking advantage of the anomalous signal of Lu ($f'' = 7.8 e^-$ at $\lambda = 0.85 \text{ \AA}$), experimental phases were determined by the SAD method using the program *SHARP* [1]. Most of the atoms in the structure could be individually observed in the experimental electron-density map, similar in quality to the final 2Fo-Fc map.



Experimental electron-density map of lysozyme at 0.85 Å resolution (contours at 2.0 σ)

The structures were refined against anomalous diffraction data using the program *SHELX* [2]. Among 5 sites found for the lanthanide complexes, 2 sites turned out to be almost fully occupied. The tris-dipicolinate lanthanide complexes, located at the interface between protein molecules are involved in the crystal packing. Strong interactions between each lanthanide complex and different lysozyme molecules strengthen the packing thus enhancing the diffracting power of the crystals.

[1] La Fortelle, E. de, Bricogne, G., *Methods Enzymol.*, 1997, 276, 472. [2] Sheldrick, G., Schneider, T. *Methods Enzymol.*, 1997, 277, 319.

MS35 P06

A comparative study of natural and synthetic calcium sulphates F. Karim^a, M. Waqif^a and L. Saadi^a, ^a*Laboratory of Condensed Matter and Nanostructures, Team of Study and Valorization of Mineral Resources and Synthetic Materials Evar-mimas, Department of Chemistry, Faculty of Science and Technology Guéliz, Marrakech, Morocco.*
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Keywords : Gypsum, calcium sulphate, medical plasters, mineralogy , chemistry.

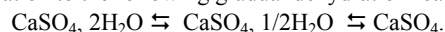
In the past, plaster obtained by calcination of gypsum, has been used as biomaterial. However, there has been limited research on the Moroccan gypsum, although the Moroccan gypsum reserves are very significant.

Our study respectively refers to a physicochemical characterization of gypsum samples from three different areas of Morocco: Midelte (GMB), Immentanoute (GIB) and Safi (GRST). These samples were compared with medical plaster (PMC).

The mineralogy and chemistry of all samples were studied by X-ray Diffraction (XRD), IR X-ray fluorescence, DTA and TGA. The morphology of gypsum was studied by Scanning Electron Microscopy (SEM).

The chemical analyses revealed that the three natural gypsum samples GMB, GIB, GRST and PMC, are made up mainly by calcium sulphate and calcium oxide. These natural samples are characterized by a high purity comparable to sample PMC. SiO₂, Al₂O₃ and MgO, are present in very small abundances, in mineral impurities such as traces of clays and carbonates as was confirmed by XRD on bulk samples.

From thermal behavior point of view, samples GMB, GIB, GRST and PMC show almost the same thermal phenomena with increasing temperature. Using XRD it was possible to assign modifications in gypsum during calcination to the following gradual dehydration reactions:



In conclusion the Moroccan natural samples studied consist mainly of gypsum associated with traces of clay and carbonates. Their raw materials are characterized by high purity and their mineralogy and chemistry are comparable to those of the medical plaster.

MS41 P28

Crystal structures of the K_{1,125}Rb_{1,875}La(VO₄)₂ and Rb_{1,435}Cs_{1,565}La(VO₄)₂ vanadates . L. Rghioui^{a,b}, L. Benarafa^a, S. Zaydoun^a and L. El Ammari^c. ^aLaboratoire de Spectroscopie infrarouge, Département de Chimie, Faculté des Sciences, B.P. 1014, Rabat, Maroc. ^bEquipe Physico-chimie de la matière condensée, Département de Chimie, Faculté des Sciences, B.P. 4010 Beni M'hamed, Meknès, Maroc. ^cLaboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, B.P. 1014, Rabat, Maroc
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Keywords : analysis of disordered structures, infrared spectroscopy, single-crystal structure

The new vanadates K_{1,125}Rb_{1,875}La(VO₄)₂ and Rb_{1,435}Cs_{1,565}La(VO₄)₂ have been synthesized by the reactive flux method. Their crystal structures were determined by single crystal X-ray diffraction. Both

compounds and $K_3Nd(PO_4)_2$ are isostructural and crystallize in the monoclinic system with space group $P2_1/m$ and Pearson symbol $mP28$.

Least square refinements gave rise to the above indicated formulas which are consistent with the chemical analysis results. The structure of those vanadates is built up of two independent VO_4 tetrahedra sharing edge or corner with LaO_7 polyhedron. However, a small difference between the two structures has been observed. Indeed, the $Rb_{1,435}Cs_{1,565}La(VO_4)_2$ structure includes three larger sites in nine- and ten-coordinate environments, two disordered nine-coordinate Cs/Rb positions with occupancies 0.33/0.17 and 0.45/0.05, respectively, and one ten-coordinate Rb position, whereas, in that of $K_{1,125}Rb_{1,875}La(VO_4)_2$ the potassium and rubidium ions are disordered over two large cation positions with nine and ten-neighbouring oxygen (occupancies rates Rb/K are 0.33/0.17 and 0.11/0.39, respectively) and one rubidium with eleven-coordinate environments. The V-O and La-O bond lengths vary from 1.674 to 1.733 Å and from 2.397 to 2.616 Å, respectively, in both structures. These values are compatible with those published in the literature for similar vanadates without disorder like $K_2CsLa(VO_4)_2$.

The infrared and Raman spectra of these two compounds have been established and interpreted. The attribution of vibrational spectra was proposed by a study of Raman and infrared spectra. This attribution was confirmed by an analysis in normal coordinates. The simulation of the vibration spectra can be regarded as satisfying since the average deviation between the calculated frequencies and the observed ones is approximately 1,5%.

MS41 P29

Mechanism of cation migration at high temperature in chabazite Michele Zema, Serena C. Tarantino, Gabriele Montagna *Dipartimento di Scienze della Terra, University of Pavia, Italy*
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Keywords: zeolite structures; HT XRD; cation distribution

Chabazite is one of the most widespread natural zeolites, reported from a variety of occurrences (in vugs of plutonic rocks, volcanic rocks and metamorphic rocks). It shows a framework structure consisting of parallel stacks of six-membered double rings in the sequence ABC. Chabazite is rhombohedral $R\bar{3}m$, but due to some (Si,Al) ordering there is a deviation from the trigonal towards the triclinic symmetry [1]. However, this ordering appears to be rather random as due to randomly arranged domains with perfect (Si,Al) ordering. The high temperature structural behaviour of a natural chabazite from Talisker Bay, Skye Island (Scotland), having composition $(Ca_{1,1}Na_{0,4}K_{0,7})[Si_{8,6}Al_{3,4}O_{24}]\cdot 14.4H_2O$, as determined by EMPA and thermogravimetric analyses, has been characterized by means of in situ high temperature single-crystal X-ray diffraction. Lattice constants have been measured in the 25-700°C temperature range at regular intervals and complete XRD data collections have been performed at $T = 25, 100, 125, 175, 250, 300, 425, 600^\circ C$. Chabazite is characterized by negative thermal expansion, with a volume reduction of 2.8% in the T range investigated; cell volume contraction as a function of temperature is not continuous: (1) from RT up to 100°C

cell volume decreases linearly as a consequence of linear decreases of both a_H and c_H (hexagonal setting) lattice constants; (2) between 100 and 200°C the c_H parameter increases and causes a slightly positive thermal expansion; (3) in the range 200-250°C a steep contraction of cell volume is associated to a significant broadening of diffraction profiles; (4) at $T > 250^\circ C$ diffraction profiles are again sharp and narrow, and thermal expansion up to 700°C is nil. Structure refinements revealed that at room temperature cations occupy the C2 and C4 sites, in which they are partly coordinated by oxygen atoms of the framework and partly by extraframework water molecules, and the C3 site which can be considered as an aquoion. All these positions are located within the largest cage of the chabazite framework. As long as the dehydration process of chabazite proceeds with increasing temperature, cationic sites become unstable. Cations migrate from C3 and C4 towards the C2 sites as temperature increases from RT to 200°C. At $T > 250^\circ C$ also the C2 site is unstable due to the loss of the water molecules participating to its coordination sphere. Therefore cations migrate towards smaller cavities where coordination is assured by oxygen atoms of the framework only. Such mobility is then responsible for the broadening of diffraction profiles observed at this temperature. In particular, cations now occupy the 6-membered double ring (C1 site) and a peripheral position within the 8-membered ring (C5 site). To our knowledge, this latter position had never been reported as a cationic site in earlier works. Reversal experiments demonstrated that the whole process is reversible under the conditions of this study; by decreasing temperature water enters the structure again and cations migrate back to their original positions. The hydration/dehydration process represents then the driving force for the cation migration at high temperature in chabazite.

[1] Mazzi and Galli *Jb. Miner. Mh.* 1983, H10, 461.

MS41 P30

Thermoelastic behaviour of Li_2VOSiO_4 Serena C. Tarantino^a, Michele Zema^a, Tiziana Boffa Ballaran^b, Paolo Ghigna^c, ^a*Dipartimento di Scienze della Terra, University of Pavia, Italy*, ^b*Dipartimento di Chimica Fisica, University of Pavia, Italy*, ^c*Bayerisches Geoinstitut, Universität Bayreuth, Germany*
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Keywords: high-pressure diffraction; high-temperature diffraction; silicate structures

Li_2VOSiO_4 is a synthetic analogue of the mineral natisite, a Na-Ti orthosilicate. The general network of Li_2VOSiO_4 , with two formulae per unit, is formed by piling up parallel $[VOSiO_4]_n^{2-}$ layers of VO_5 square pyramids and SiO_4 tetrahedra held together by intercalated Li cations located in distorted octahedral sites. The layer is a 4-connected net with alternating corner-sharing V and Si polyhedra. Each V^{4+} square pyramid (hemioctahedron) shares its four equivalent equatorial O atoms with four different SiO_4 groups and the remaining axial O atom belongs to a vanadyl group. The vanadyl O atoms alternately point up and down relative to a layer. Structural analogies can be found in several minerals such as sulfohalite, metaautunite and phosphates such as α -VOPO₄. All of them have the same topology in the *ab* projection: corner linked