

FA5-MS01-P23

Structure Refinement of Kochsándorite, A Basic Double-Carbonate Mineral. István E. Sajó. *Chemical Research Centre of the Hungarian Academy of Sciences, Budapest, Hungary.*
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Kochsándorite, $\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$, a recently discovered mineral species [1] of the dundasite group crystallizes in *Pnma* space group. Of this mineral group dundasite is the only member for which the structure is known [2]. In the lack of proper sized crystals the structure of the other members of the group (dresserite, strontiodresserite, kochsándorite) was not determined, however they are supposed to be isostructural with dundasite [1]. High quality powder diffraction data of kochsándorite were collected in a focusing mirror – capillary geometry instrumental setup using Cu $K\alpha$ radiation. Initial atomic coordinates were taken from the dundasite structure and geometrical constraints were used for bond lengths during refinement. The resulting structure exhibits partial similarity with the members of dawsonite group. The nature and origin of this similarity is discussed.

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Keywords: rietveld refinement; powder diffraction; mineral structure

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New High Temperature Phases of the Type $\text{M}(\text{Py})_n\text{Cl}_2$ Edith Alig^a, Lothar Fink^a, Tuncay Yeşilkaynak^b, Nevzat Külcü^b. ^a*Institute Inorganic and Analytical Chemistry, Goethe-University Frankfurt, Germany.* ^b*Mersin University, Faculty of Arts and Sciences, Department of Chemistry, Mersin-Turkey.*
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Several compounds of the type $[\text{M}(\text{II})(\text{Py})_n]\text{Cl}_2$ with (M= Ni, Cu; $2 < n < 4$) were synthesized. Thermal decomposition led to various high temperature phases with different pyridine contents. For the copper compound $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2$ [1] a new phase, $[\text{Cu}(\text{C}_5\text{H}_5\text{N})]\text{Cl}_2$, was observed at temperatures above 170°C. At 230°C, ongoing decomposition resulted in another phase with less amount of pyridine. Above 270°C a mixture of different copper phases occurred, after that at 330°C Cu_2OCl_2 and, finally, CuO was observed ($T > 430^\circ\text{C}$). For the nickel compound, $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}_2$, [2] the thermal treatment resulted in the pyridine complex $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2$ at 130°C and another phase, $[\text{Ni}(\text{C}_5\text{H}_5\text{N})]\text{Cl}_2$, at temperatures above 190°C. At 310°C NiCl_2 was present while NiO was the stable phase above 490°C. Structural characterisation of the nickel and copper phases will be reported.

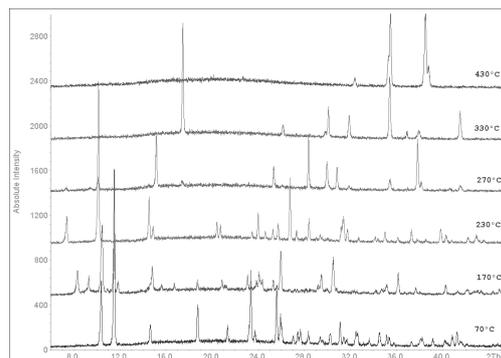


Fig.1: Thermal decomposition of $[\text{Cu}(\text{Py})_2]\text{Cl}_2$

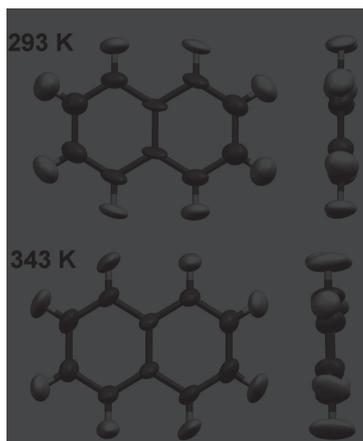
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Refinement of TLS Matrices from Powder Diffraction Data: Application to Naphthalene. Ivan Halasz^a, Robert E. Dinnebier^a. ^a*Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany.*
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Analysis of thermal motion of molecules in crystals with the assumption of a rigid body can be approached in two ways: (1) TLS matrices can be refined from the independently refined ADPs of each atom and (2) ADP parameters can be *a priori* constrained to conform to the rigid body assumption. In the latter case the translational (T), librational (L) and the correlation (S) matrices contain the refineable parameters and the ADPs are then calculated from them [1,2]. The approach (2) is, regarding the number of required parameters, a compromise between the usual practice with powder diffraction data which is to describe the thermal motion of all atoms by a common isotropic Debye-Waller factor and an independent anisotropic refinement of each atom customary with single crystal data sets. The flexible macro scripting language of TOPAS [3] has been used to implement the refinement of TLS matrices from the approach (2) for powder diffraction data and has been applied to crystalline naphthalene for data collected between 293 K and 343 K. The refinement of elements of TLS matrices is performed in the Cartesian coordinate system followed by calculation of each atom's ADPs in the crystal coordinate system. Results are compared to previous studies [4,5] on thermal motion in crystalline naphthalene and the feasibility of this approach for routinely collected laboratory powder diffraction data is estimated. The macro scripts are readily applied to other molecular compounds for which the results of refinement of TLS matrices are also presented.



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Keywords: powder diffractometry; thermal motion in crystal; TLS matrices

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Substitution Effects in Some Bismuth Based Rare Earth Manganites. Kiril Krezhov^a, Stefan Kovachev^a, Daniela Kovacheva^b, Erzhebet Svab^c, Françoise Bourée^d, Gilles André^d. ^a*Institute for Nuclear Research and Nuclear Energy*. ^b*Institute of General and Inorganic Chemistry, Sofia, Bulgaria*. ^c*Research Institute for Solid State Physics and Optics, Budapest, Hungary*. ^d*Laboratoire Leon Brillouin, CEA/Saclay, Gif-sur-Yvette, France*.

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In consistence with other authors we established that the characteristic signs attributed to the charge ordering (CO) and orbital ordering (OO) in the parent manganites $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ appear at $T_{\text{CO}} \approx 320$ K and $T_{\text{CO}} \approx 525$ K, respectively [1]. We investigated the magnetic ordering and CO/OO phenomena with respect to temperature and chemical doping in $\text{Bi}_{0.25}\text{R}_{0.25}\text{AA}_{0.5}\text{MnO}_3$ (R = La, Nd, Ho, Er, Tm) (A-site doping [1-3]) and $\text{Bi}_{0.5}\text{AA}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ (B-site doping [4-6]), where AA stands for Ca or Sr. For both sets of Bi-based manganites prepared as polycrystalline powders by controlled solid-state reaction we correlated the structural findings from high-resolution X-ray and neutron powder diffraction with results for transport and magnetic properties. At 295 K $\text{Bi}_{0.25}\text{R}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ are in paramagnetic phase of small monoclinic distortion allowing for structural description in orthorhombic Pnma symmetry. A significant anisotropic distortion of the MnO_6 octahedra occurs in the characteristic manner associated with the particular orbital order of manganese ions at half doping level. The findings corroborate the conclusion that the effective Bi^{3+} ionic radius in Bi-Ca manganites is close in value to that of Nd^{3+} indicating that the lone pair character of $6s^2$ Bi^{3+} orbitals is rather constrained than dominant. Except for

$\text{Bi}_{0.25}\text{La}_{0.25}\text{Ca}_{0.5}\text{MnO}_3$ which undergoes a ferromagnetic transition at $T_{\text{C}} = 281$ K followed by a transition to an antiferromagnetic state at lower temperatures, the rest compounds become antiferromagnetic. At 10 K the ground magnetic state of most Ca-Bi compounds could be acceptably described by the insulating antiferromagnetic CE ordering. The RT cell parameters of $\text{Bi}_{0.5}\text{Ca}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0 \leq x \leq 0.6$) change monotonously with increasing x . The compounds are antiferromagnetic with T_{N} which decreases with increasing Fe-substitution. For $x \geq 0.1$ the antiferromagnetism is accompanied by a weak ferromagnetism. The CO-OO order in the neat form is suppressed at very low Fe-substitution ($x \leq 0.05$). Room temperature diffraction data of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{Fe}_x\text{Mn}_{1-x}\text{O}_3$ ($0 \leq x < 1.0$) show that the crystal structure is orthorhombic for $x \leq 0.3$ and cubic for $x > 0.4$. Unit cell volume increases with x . The charge/orbital order was observed for the compound without Fe. The magnetic state of the compounds with different Fe-content changes from paramagnetic to weak antiferromagnetic below T_{N} , in the range 116 K - 155 K. All Ca-Fe and Sr-Fe compounds are semiconductors between 100 K and 600 K and there was no magnetoresistivity effect in fields up to 7 kOe.

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Molecular and Crystalline Structures of Three (S)-4-alkoxycarbonyl-2-azetidiones Containing Long Alkyl Side Chains From Synchrotron X-ray Powder Diffraction Data. Luis E. Seijas^a, Asiloé J. Mora^a, Gerzon E. Delgado^a, Francisco Lopéz-Carrasquero^b, Michela Brunelli^c, Andrew N. Fitch^d. ^a*Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101, Venezuela*. ^b*Laboratorio de Polímeros, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101, Venezuela*. ^c*ILL Institut Laue-Langevin, BP 156, 38042 Grenoble cedex 9, France*. ^d*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble cedex, France*.

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The (S)-4-alkoxycarbonyl-2-azetidiones are optically active β -lactam derivatives of aspartic acid, which are used as precursors of carbapenems-type antibiotics and poly- β -aspartates. The crystal structures of three (S)-4-alkoxycarbonyl-2-azetidione with alkyl chains with