transitions were detected at high temperature, with removal of superlattice peaks and symmetry increase. An *ab initio* periodic quantum-mechanical simulation of possible locally ordered structures was then performed, by use of the B3LYP hybrid functional and of an all-electron basis set of atomic orbitals [4]. The two compositions $Li_{0.5}La_{0.5}TiO_3$ and $Li_{0.3125}La_{0.5625}\square_{0.125}TiO_3$ were considered, with 4 to 16 formula-units of LLTO per primitive unit-cell, and with symmetry lowered to monoclinic *Pm*. Several different La-Li-$\square$ ordering patterns within the (001) layers of A-cages were devised. The structures were fully optimized by energy minimization, so as to localize the preferred lithium sites for each ordering scheme. Maps of the electrostatic potential were also computed in ionized Li-free model structures, in order to study the electric field acting on Li^+ ions. It was found that the anti-phase octahedral tilt is reproduced only for layers with mixed La-Li composition, and not for full La-Li ordering in different layers. Further, the positions adopted by lithium depend significantly on the locally ordered environment, so that the two sites appearing in the experimental average structure can be assigned to specific ordered configurations on the basis of the theoretical results obtained. The most populated Li site, close to the O_4 windows separating adjacent A cavities in the layer, corresponds to La-poor local configurations, and is actively involved in the ion migration process. The other one, closer to the cage centre, is related to La-rich local environments, and is a trapping location less favourable to the transport mechanism.

[1] Inaguma Y., Chen L., Itoh M., Nakamura T., Uchida T., Ikuta H., Wakihara M. *Solid State Commun.* 1993, 86, 689.
[2] Catti M., Sommariva M., Ibberson R.M. *J. Mater. Chem.* 2007, 17, 1300.
[3] Sommariva M., Catti M. *Chem. Mater.* 2006, 18, 2411.
[4] Dovesi R., Saunders V.R., Roetti C., Orlando R., Zicovich-Wilson C., Pascale F., Civalleri B., Doll K., Harrison N.M., Bush I.J., D'Arco Ph., Llunell M. CRYSTAL06: *User's Manual*; http://www.crystal.unito.it

MS17 P04

Structural and crystallographic characterization of compacted and induction melted Cu-Al alloys *Yacine Debili, Kebbache Ismahane University Annaba, BP 12 eL-HADJAR, 23000, Annaba, Algeria*
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Keyword : Cu-Al alloys ,Cu9Al4, Hume-Rothery phase

We have elaborated several copper based (Cu-Al) alloys with various aluminum compositions (25.2, 25.85, 26.02, 26.50, and 26.86 % at. Al) by fusion melting after cold compaction of Al and Cu powder, and we have been interested by structural and crystallographic characterization which permits us to identify the intermetallic compounds appearing during solidification as AlCu phase (monoclinic), Cu_9Al_4 phase (Sc) and Cu_3Al phase (Orthorhombic).
Cu_9Al_4 is an electronic compound belonging to Hume-Rothery phase.The α(Cu) lattice parameter decrease in an anomalous way as deviation from vegard's low with Al content between (25.20%at. Al and 26.86%at. Al)

MS17 P05

The microstructure of low-aqueous liquid detergents by X-ray diffraction Ruud den Adel[a], Eli Roijers[a], John

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Keywords: low-aqueous liquid detergents, microstructure, X-ray diffraction

To build up knowledge about the phase behaviour and microstructure of liquid detergents, different compositions are measured using the ternary phase diagram with axes water, solvent and surfactants percentages. In this ternary phase diagram the liquid crystalline (LC) and an isotropic area can be distinguished. The phase diagram is determined by classical light microscopy, using polarised light. The liquid crystalline phase scatters light and has an appearance in the range of milky to translucent. The isotropic phase is transparant. Of interest is the region up to 5% water.
The X-ray powder diffraction measurements are performed on the Bruker D8-Discover in a theta/theta configuration. A copper anode is used, and the K- alpha radiation with wavelength 0.15418 nm is selected. Long spacings are measured by performing X-ray diffraction in the transmission mode. The X-ray source and the detector are positioned in front of each other (Theta1 and Theta2 = 0 degrees). To prevent the detector being hit by the primary beam a leaden beam stopper is precisely positioned in the middle and just in front of the detector. The sample is placed in a sample holder between Mylar film.
In this ternary phase diagram the following sets of samples are described:
a.) Along the water axis
b.) Along the organic solvent axis
c.) 80% surfactants along the water-solvent axis
d.) 60% surfactants along the water-solvent axis
e.) 40% surfactants along the water-solvent axis
f.) Along the line from 100% surfactants to 50%water/ 50%solvent
It is found that the concentrated surfactants system shows an order of surfactant molecules in the reversed micellar L2-phase and the swelling of the surfactant mixtures is dominated by water. On increasing the water level the layer thickness increases and the disorder of the surfactant molecules decreases.
On increasing the organic solvent level the layer thickness remains constant, the disorder of the surfactant molecules increases and/or the domain sizes decreases.
The transition from the lamellar liquid crystalline into the isotropic phase is a gradual change in microstructure.

MS17 P06

Structure Prediction-versus-Determenation of B-site Doped La-Sr-Mn Perovskite A. A. Ramadan[(a)], M. El-Hagry[(a)], A. M. Moustafa[(b)], Y. A. Shoker[(a)] and A. M. El-Shabiny[(b)] [(a)] *Phys. Dept., Helwan Univ., Helwan, Cairo, Egypt.* [(b)] *Phys. Dept., National Research Center, Dokki, Cairo, Egypt*
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Keywords: *Ab-initio* powder structure determination, Prediction, Perovskite structures.

Ab-initio crystal structure determination from X-ray powder diffraction data suffers from limitations and is associated with interinsic challenges. However, in recent years there has been substantial progress in this approach. The crystal structure of Cu-doped $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_3$ (x = 0.0, 0.1 and 0.2) peroveskite was predicted starting only

from the stoichiometry and determined using powder data. The optimal structure model was predicted by minimization of the global instability index of the difference between the calculated bond valency sum and the formal valency (oxidation state) of each ion (optimize the bonding in the structure) using SPuDS program [1]. Three expected space groups (R-3c, I4/mcm and Pnma) and the corresponding lattice parameters and fractional atomic coordinations were given. On the other hand, the experimental diffraction pattern was indexed by CRYSFIRE and the possible best space groups (R-3c, P2/c and C2/m) and the corresponding lattice parameters were specified by CHEKCELL program. These three space groups were used one-by-one in turn to determine the aproximate structure solution by "direct-space" approach using Monte Carlo method [2, 3] and a combined cost function of global optimization of the difference between the calculated and the measured diffraction pattern and of the potential energy of the system, which is implemented in ENDEAVOUR program [4]. The predicted structures as well as the aproximate ones were refined by Rietveld method using FULLPROF program. Almost, acceptable fitting with good reliability factors (R_{wp} and χ^2) was reached in all cases. However, in order to pick out the most reliable space group, careful inspection of the tick marks that represent the positions of the possible Bragg reflections in Reitveld plot was considered; their presence where no peaks or their absence where weak peaks are observed. The rhombohedral (R-3c) space group was found to be the reasonable accepted choice for $La_{0.77}Sr_{0.23}MnO_3$, which is the common space group between the two approaches. Considering the number of diffraction peaks as well as their positions and relative intesities, the three samples showed almost the same XRD patterns. So, the accepted model was applied successfully for the two Cu-doped samples. The light Cu B-site doping does not change the crystal structure; only a small increase in lattice volume occures due to the larger average ionic size of Cu (Cu^{2+} and Cu^{3+}) relative to Mn (Mn^{3+} and Mn^{4+}). In conclusion, the prediction methods, as a useful guide, coupled with direct-space methods and proper cost function is an approach of great help in *ab- initio* structure determination from powder data.

[1] M. W. Lufaso and P. M. Woodward, *Acta Cryst.*, B57, 725-738 (2001)
[2] Yu. G. Andreev, P. Lightfoot and P. G. Bruce, *J. Appl. Cryst.* 30, 294-305 (1997).
[3] K. D. M. Harris, *J. Chin. Chem. Soc.* 46, 23-34 (1999).
[4] V. Brodski, R. Peschar and H. Schenk, *J. Appl. Cryst.* 36, 239-243 (2003).

MS17 P07

A_2FeSbO_6 (A=Sr,Ca) double perovskites oxides: Crystal structures, phase's transitions and ^{57}Fe Mössbauer spectroscopy study. A. Faik[a], J. M. Igartua[a], J. Pizarro[b] and J. J. S. Garitaonandia[a]. [a]*Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, Apdo. 644, Bilbao 48080, Spain.* [b]*Dpto. de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Apdo. 644, E-48080 Bilbao, Spain.*
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Keywords: transition-metal perovskites; Mössbauer spectroscopy; perovskite structures.

A_2FeSbO_6 (A=Sr,Ca) double perovskite have been elaborated by the standard solid state reaction method.

Rietveld analysis of X-ray powder data at room temperature, shows that Sr_2FeSbO_6 crystallize in the monoclinic system (space group $P2_1/n$) with unit cell parameters a = 5.6148(1) Å; b = 5.5954(4) Å; c = 7.9002(1) Å; β = 90.02(4)° the ordering scheeme is 92%, in good agreement with the crystal structural data from the first synthesis of this compound[1]. The Ca_2FeSbO_6 phase has been synthesized for the first time, and from conventional x-ray powder diffraction data, it has been found that it crystallizes in the $P2_1/n$ monoclinic space group; the Rietveld analysis results show the following cell parameters: a =5.4425(1)Å; b = 5.5413(6) Å; c = 7.7451(8) Å; β = 90.06(3)°. The Fe and Sb cations are almost completely ordered in the B sites (95%). ^{57}Fe Mössbauer spectroscopy measurements, at room temperature, showed a single Fe^{3+} cation in two six-coordinated sites, with the same ordering degree deduced from the powder diffraction data: 92% for Sr_2FeSbO_6, and 95% for Ca_2FeSbO_6.

The temperature evolution of the crystal structure of A_2FeSbO_6 (A=Sr,Ca) has been studied using both x-ray powder diffraction and ^{57}Fe Mössbauer spectroscopy. A_2FeSbO_6 (A=Sr,Ca) were found to present the $P2_1/n$ (monoclinic) – I4/m (tetragonal) – Fm-3m (cubic) phase transitions sequence observed for similar materials Sr_2MWO_6 (M=Ca,Zn,Co) [2, 3]. The first phase transition, from the monoclinic structure with the $P2_1/n$ space group to tetragonal structure with I4/m space group, is starts to take place at ≈400 K, for Sr_2FeSbO_6, with a temperature interval, 400 to 420 K, in which both phases, monoclinic and tetragonal, co-exist; for Ca_2FeSbO_6, the phase transition takes place at 920 K, with no co-existence interval. The mechanism of these phase transition is related to the mismatch between the size of the A cation and the cuboctahedral space between the FeO_6 and SbO_6 octahedra: the smaller size of the Ca^{2+} cation, with respect to that of Sr^{2+} cation, leads to a structure with a higher monoclinic distortion, at room temperature for the calcium containing compounds. This fact can explain the higher phase-transition temperature, 920 K for Ca_2FeSbO_6, compared to that 420 K for Ca_2FeSbO_6. The second phase transition, from the tetragonal structure with I4/m space group to the cubic structure with the Fm-3m space group, observed above 500 K for the strontium compound and above 1150 K for the calcium compound.

[1] Edmund J. Gussen, Jaap F. Vente, Peter D. Battle and Torence C. Gibb. J. Mater. Chem., 1997, 7(3),459-463.
[2] M. Gateshki, J. M. Igartua and E. Hernández-Bocanegra. J.phys.: Condens. Matter 2003, 15, 6199-6217.
[3] M. Gateshki and J. M. Igartua, J.phys.: Condens. Matter 2004, 16, 6639-6649.