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

#### FA5-MS01-P26

**Substitution Effects in Some Bismuth Based Rare Earth Manganites.** Kiril Krezhov<sup>a</sup>, Stefan Kovachev<sup>a</sup>, Daniela Kovacheva<sup>b</sup>, Erzhebet Svab<sup>c</sup>, Françoise Bourée<sup>d</sup>, Gilles André<sup>d</sup>. <sup>a</sup>*Institute for Nuclear Research and Nuclear Energy*. <sup>b</sup>*Institute of General and Inorganic Chemistry, Sofia, Bulgaria*. <sup>c</sup>*Research Institute for Solid State Physics and Optics, Budapest, Hungary*. <sup>d</sup>*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  $\text{MnO}_6$  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  $\text{Bi}^{3+}$  ionic radius in Bi-Ca manganites is close in value to that of  $\text{Nd}^{3+}$  indicating that the lone pair character of  $6s^2$   $\text{Bi}^{3+}$  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  $T_{\text{N}}$  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  $T_{\text{N}}$ , 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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**Keywords:** charge order; magnetic structure; manganites

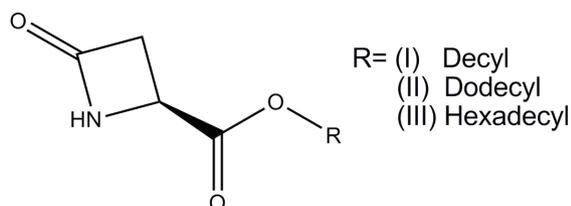
#### FA5-MS01-P27

**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<sup>a</sup>, Asiloé J. Mora<sup>a</sup>, Gerzon E. Delgado<sup>a</sup>, Francisco Lopéz-Carrasquero<sup>b</sup>, Michela Brunelli<sup>c</sup>, Andrew N. Fitch<sup>d</sup>. <sup>a</sup>*Laboratorio de Cristalografía, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101, Venezuela*. <sup>b</sup>*Laboratorio de Polímeros, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101, Venezuela*. <sup>c</sup>*ILL Institut Laue-Langevin, BP 156, 38042 Grenoble cedex 9, France*. <sup>d</sup>*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble cedex, France*.

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

10, 12 and 16 carbon atoms were solved using parallel tempering and refined against X-ray powder diffraction data using the Rietveld method. The azetidinone ring in the three compounds display a pattern of asymmetrical bond distances and an almost planar conformation, these characteristics are compare with periodic solid-state and gas phase DFT calculations. The compounds form 1-D, 2-D and 3-D networks of H-bonds of the type N—H•••O (and C—H•••O) as their side-chain augment. The compounds pack as corrugated sheets, separated by approximately 4.40 Å, which piled up along the [0 0 1] direction



**Keywords:** powder diffraction; structure solution;  $\beta$ -lactams

#### FA5-MS01-P28

**Solving Crystal Structures Using Symmetry-Mode Collective Coordinates.** Danel Orobengoa<sup>a</sup>, Juan Rodriguez-Carvajal<sup>b</sup>, Juan Manuel Perez-Mato<sup>a</sup>, Mois I. Aroyo<sup>a</sup>, Abdessamad Faik<sup>c</sup>, Josu Mirena Igartua<sup>c</sup>. <sup>a</sup>Dpto. Física de la Materia Condensada, UPV, Bilbao, Spain. <sup>b</sup>Diffraction Group, Institut Laue-Langevin, Grenoble Cedex 9, France, <sup>c</sup>Fisika Aplikatua II Saila, Zientzia Fakultatea, Euskal Herriko Unibertsitatea, Bilbao, Spain.

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The computer program Amplimodes performs symmetry-mode analysis of any pseudosymmetric structure and it is freely accessible on the Bilbao Crystallographic Server ([www.cryst.ehu.es](http://www.cryst.ehu.es)) [1]. A new option, recently added to Amplimodes, allows automatic generation of input files for FullProf[2]. The refining program has also been adapted to work with the basis of symmetry modes constructed and used by AMPLIMODES. This allows performing crystal structure refinements using symmetry-adapted collective coordinates as refinable parameters. This represents a new way of treating the experimental diffraction data that captures the physics of these structures, which in many cases are the result of real or virtual phase transitions.

If the studied structure is pseudosymmetric, it can be seen as the result of a distortion with respect to a higher symmetry configuration. The space groups of the reference G and the distorted H structures are group-subgroup related (G>H). AMPLIMODES lists all the possible symmetry modes participating in the distortion. Their components are referred to the unitary basis of the H phase. Thus, the coordinates of the atoms on the H phase can be written as:  $r_i(H) = r_i(G) + \sum_m (A_m \varepsilon(m,i))$ , where  $r_i(G)$  are the ideal atomic coordinates of the G phase referred to the H basis and  $A_m$  and  $\varepsilon(m,i)$  are the amplitudes and the polarization vectors

of the symmetry modes. The set of polarization vectors  $\varepsilon(m,i)$  is provided by the file produced by AMPLIMODES, and  $A_m$  are the collective coordinates refined by FullProf, substituting the individual atomic coordinates.

This approach can be very useful for determining low symmetry structures with strong pseudosymmetry [3]. A hierarchy is expected among distortions of different symmetry as well as an essential invariance of their polarization vectors with the variation of external conditions (temperature, pressure, etc.), making the refinement more robust and stable when the data are insufficient or of low quality (e.g. powders or twinned crystals).

In this communication the method will be presented in more detail and illustrated with a few examples.

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**Keywords:** refinement; symmetry-modes; bilbao crystallographic server

#### FA5-MS01-P29

**Crystal Structure and Superconducting Properties in  $YNi_{1-x}M_xB_2C$  (M = Al, Cr, Co).** Antoni Winiarski<sup>a</sup>, Anna Winiarska<sup>a</sup>, Andrzej Ślebarski<sup>a</sup>, Zofia Drzazga<sup>a</sup>, August Chełkowski<sup>a</sup>. <sup>a</sup>Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland.

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Superconductivity, magnetism and structural properties of  $RE(Ni_{1-x}Me_x)_2B_2C$  (RE – rare earth metal, Me – metal) have been studied by several authors, e.g. [1], [2], [3]. Polycrystalline  $YNi_{1-x}M_xB_2C$  (M = Al, Cr, Co) samples were prepared by arc melting under Ar atmosphere and annealed at 1323 K for 100 hours. The stoichiometry and homogeneity of the samples were checked by XPS method. The samples with small values of x are superconductors. They crystallize in the tetragonal space group I4/mmm. Temperature dependence of the lattice parameters was measured in the temperature range from 12 K to 297 K using a Siemens D5000 X-ray Diffractometer with  $Cu_{K\alpha}$  radiation. The Rietveld method was applied to calculate the crystal lattice parameters. Electrical resistance and transition temperature to superconductivity  $T_c$  were measured using four-probe method in the temperature range of 4.2 K – 297 K. We found anomalies in change of the lattice parameters in  $YNi_{1-x}Co_xB_2C$  for the x parameter less than 0.03. The change in the lattice parameters is hardly visible in the x range 0 – 0.03. We suggest explaining observed effect in the term of crystal lattice defects. The lattice parameters for  $YNi_{1-x}Co_xB_2C$  samples with x > 0.3 decrease linearly in the superconducting region.

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