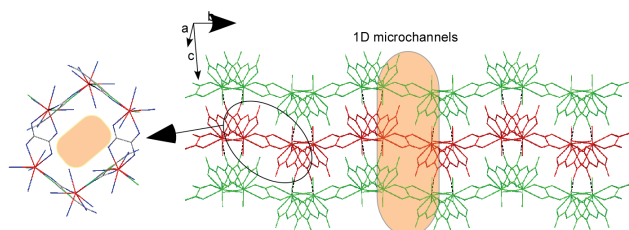


One of the goals of crystal engineering is to make it possible to design and synthesize MOFs with predetermined topology and properties, usually through judicious selection of multitopic organic ligands as the spacers and metal ions or clusters as the junctures [1]. As functional metal centers, rare earth metals are attracting more and more attention due to their fantastic coordination properties and special chemical characteristics arising from 4f electrons [2], [3]. Many coordination polymers based on rare earths have been synthesized, and most of them exhibit amazing optical and magnetic properties, enabling them as fluorescent probes and electroluminescence devices [4], [5].

We report herein a family of 11 isostructural 3D metal-organic compounds,  $\{[\text{Ln}(\mu_3\text{-pmdc})(\mu\text{-ox})_{0.5}(\text{H}_2\text{O})_2] \cdot 2.25\text{H}_2\text{O}\}_n$  (Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er; pmdc = pyrimidine-4,6-dicarboxylate, ox = oxalate). The most striking feature of these structures is that they undergo a phase transition from the monoclinic  $P2_1/n$  space group at room temperature towards a modulated commensurate structure upon cooling up to 100 K with the superspace group  $P2_1/n(\alpha 0 \gamma)0s$  and  $t = (0 \ 0 \ 1/3)$ , in such a way that the modulated commensurate unit cell is related to the room temperature one as being three unit cells piled up along the  $c$  axis. The dimension of the channel and the occupancy of the water molecule placed in these channels are modulated. The metal centers are joined by means of bis-bidentate pmdc and ox ligands to lead to neutral Shubnikov hexagonal plane nets, which are joined together through the coordination of the non-chelating carboxylate oxygen atom belonging to the adjacent layers. The overall three-dimensional open framework possesses channels along the crystallographic  $a$  axis that are filled by solvent water molecules. The available space within these channels of approximate dimensions of  $5 \times 7 \text{ \AA}$  represents a 20.1% of the unit cell volume. The topological analysis of the crystal structure carried out by means of the TOPOS program package indicates a *ins* like 3D network (3,4-c net), the Schläfli symbol being  $\{6^3\} \{6^5.8\}$ .

Europium and terbium compounds exhibit bright red and green luminescence under excitation at 488 nm, respectively.



**Figure 1.** View of the overall 3D open framework showing the microchannels.

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**Acknowledgements.** This work has been supported by the Ministerio de Ciencia e Innovación (MAT2008-05690/MAT), the Gobierno Vasco (IT477-10) and UPV/EHU (predoctoral fellowships). We also thank technical and human support provided by SGIKER (UPV/EHU, MICINN, GV/EJ, ESF).

**Keywords:** commensurate, lanthanide, luminescence

## MS88.P11

*Acta Cryst.* (2011) **A67**, C759

### Thermally Induced Structural Changes in Modulated $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$ (CBN28)

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The incommensurately modulated crystal structure of relaxor ferroelectric CBN28 was refined at elevated temperatures up to 330°C in the 3+2 dimensional superspace group  $P4bm(pp1/2, -pp1/2)$ . Single crystals grown by the Czochralski method were used.

The crystal structure of  $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$  is isotypic with the tetragonal tungsten bronzes. Corner-sharing octahedra form a framework, which leaves space for three types of cavities. The Me1 site is coordinated by 12 oxygen atoms, the Me2 site by 15 O atoms and the Me3 position by nine oxygen atoms. The latter is not occupied in the tetragonal bronze type and the Me1 and Me2 sites are incompletely filled with the larger cations ( $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ ). The X-ray single crystal diffraction patterns of  $\text{Ca}_{0.28}\text{Ba}_{0.72}\text{Nb}_2\text{O}_6$  exhibit weak first order satellite reflections in addition to the main reflections indicating the existence of a two dimensional structural modulation like in isotypic  $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$  with  $x$  ranging from about 0.25 to 0.75. The wave vectors are  $q_1 = \alpha a^* + \alpha b^* + \frac{1}{2} c^*$  and  $q_2 = -\alpha a^* + \alpha b^* + \frac{1}{2} c^*$  with  $\alpha \sim 0.3$  [1], [2].

The modulation consists of a wavy distribution of barium and calcium atoms as well as vacancies on the incompletely occupied Me2 site with 15-fold oxygen coordination. The occupational modulation is coupled with a modulation of the atomic displacement parameters and a very weak modulation of the positional parameters of Me2. The surrounding oxygen atoms show strong positional modulations with an amplitude up to ca. 0.4 Å resulting in a cooperative tilting of the  $\text{NbO}_6$  octahedra. The Me1 site and the octahedrally coordinated niobium atoms are hardly affected by the modulations.

With increasing temperatures, the electric polarization is reduced by way of approaching 0 or  $\frac{1}{2}$  of the  $z$  parameters of all atoms, which are special positions in the centrosymmetric space group  $P4/mbm$  (no. 127). However, not all atoms arrive exactly at these equipoints at the Curie temperature near 270°C. Above  $T_C$ , the average structure can better be described in  $P4bm$  (no. 100) or in the non-polar space group  $P-4b2$  (no. 117) [3] than in  $P4/mbm$ . The modulations persist above  $T_C$ . The intensities of the satellite reflections, however, can only be refined in the superspace group  $P4bm(pp1/2, -pp1/2)$  indicating that no true change of symmetry takes place at 270°C. The amplitudes of the positional modulations decrease at temperatures above  $T_C$  while the atomic displacement parameters increase indicating enhanced vibrational motions at the expense of the static displacements. Lattice parameters and the wavelength of the modulation change only slightly upon heating.

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**Keywords:** incommensurate, modulation, ferroelectricity

## MS88.P12

*Acta Cryst.* (2011) **A67**, C759-C760

### Anion deficient perovskites $(\text{Pb,Bi})_{1-x}\text{Fe}_{1+x}\text{O}_{3-y}$ modulated by crystallographic shear planes

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$\text{BiFeO}_3$  is one of the rare perovskites combining ferroelectric and magnetic ordering in a single phase material. Being a room-temperature multiferroic,  $\text{BiFeO}_3$  is a playground for the investigation of the physical phenomena behind multiferroicity [1]. The main instability

resulting in ferroelectricity in BiFeO<sub>3</sub> is driven by a lone pair of the Bi<sup>3+</sup> cation [2,3]. Due to similarity between the electronic structures of Bi<sup>3+</sup> and Pb<sup>2+</sup>, the substitution of Pb for Bi provides a potential way to modify the electric and magnetic properties of the mixed lead-bismuth ferrites.

Anion-deficient perovskites (Pb,Bi)<sub>1-x</sub>Fe<sub>1+x</sub>O<sub>3-y</sub> were prepared as single phases in the compositional range from Pb<sub>0.857</sub>Bi<sub>0.094</sub>Fe<sub>1.049</sub>O<sub>2.572</sub> to Pb<sub>0.409</sub>Bi<sub>0.567</sub>Fe<sub>1.025</sub>O<sub>2.796</sub>. Variation of the anion content in the compounds is carried out through a long-range-ordered arrangement of crystallographic shear (CS) planes, which incommensurately modulate the basic perovskite structure. Using a combination of electron diffraction and high-resolution scanning transmission electron microscopy, a superspace model was constructed describing a periodic arrangement of the CS planes of any possible orientations. The model was verified by refinement of the Pb<sub>0.650</sub>Bi<sub>0.308</sub>Fe<sub>1.042</sub>O<sub>2.675</sub> crystal structure from neutron powder diffraction data ((3+1)D S.G. X2/m( $\alpha 0\gamma$ ), X = [1/2, 1/2, 1/2, 1/2], a = 3.8999(2)Å, b = 3.8924(2)Å, c = 4.0897(2)Å,  $\beta$  = 91.947(3)°, q = 0.05011(7)a\* + 0.09188(6)c\* at T = 550K, R<sub>p</sub> = 0.043, R<sub>wp</sub> = 0.056). The (Pb,Bi)<sub>1-x</sub>Fe<sub>1+x</sub>O<sub>3-y</sub> structures consist of perovskite blocks separated by CS planes confined to nearly the (50)<sub>p</sub> perovskite plane. Along the CS planes, the perovskite blocks are shifted with respect to each other over the 1/2[110]<sub>p</sub> vector that transforms the corner-sharing connectivity of the FeO<sub>6</sub> octahedra in the perovskite framework to an edge-sharing connectivity of the FeO<sub>5</sub> pyramids at the CS plane, thus reducing the oxygen content. Variation of the chemical composition in the (Pb,Bi)<sub>1-x</sub>Fe<sub>1+x</sub>O<sub>3-y</sub> series occurs mainly due to a changing thickness of the perovskite block between the interfaces. The Pb, Bi, and Fe atoms are subjected to strong displacements occurring in antiparallel directions on both sides of the perovskite blocks, resulting in an antiferroelectric-type structure. This is corroborated by the temperature-, frequency-, and field-dependent complex permittivity measurements. Pb<sub>0.650</sub>Bi<sub>0.308</sub>Fe<sub>1.042</sub>O<sub>2.675</sub> demonstrates a remarkably high resistivity > 0.1 TΩcm at room temperature and orders antiferromagnetically below T<sub>N</sub> = 608(10)K.

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**Keywords:** perovskite, incommensurate, ferrite

## MS89.P01

*Acta Cryst.* (2011) **A67**, C760

### Protein Data Bank on the Semantic Web

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The Protein Data Bank (PDB) provides a wealth of structural information on biological macromolecules. However, modern biomedical research demands integrative approaches to elucidate the complexity of living systems, which in turn requires gathering various kinds of information from a wide range of sources. In such a context, no single database, such as the PDB, is useful by itself. Given the ever increasing number of databases, and the ever increasing amount of data made available in each of these databases, compiling all the databases into a single archive is not feasible, if not impossible. Therefore, an approach that allows distributed data resources to be integrated on demand seems more appropriate. The Semantic Web is one such framework.

In the Semantic Web, data are provided in the RDF (Resource Description Framework) format, possibly accompanied by an ontology specified in RDFS (RDF Schema) or OWL (Web Ontology Language). Ontologies allow Semantic Web agents to infer new information that is

not explicitly stated in a database. In RDF, each datum is expressed as a triple of subject (URI for data resource), predicate (describing relations between two data), and object (URI or literal data).

In this poster, we present our attempt to convert PDB data into RDF with an OWL ontology converted from the PDB exchange dictionary. RDF files for all PDB entries were automatically generated from the corresponding PDBML files by using an XML style sheet, which was also automatically generated from the PDBML XML Schema by using another XML style sheet. An OWL ontology was generated from the PDBML XML Schema in a semi-automatic manner. Extensive cross-references are provided in RDF-formatted PDB entries, including those within each PDB entry, and between related PDB entries, and pointers to the PDB Chemical Component Dictionary, as well as pointers to external resources such as UniProt, PubMed, NCBI Taxonomy, and Bio2RDF. Each mmCIF category element in each PDB entry is given a dereferenceable URL so that agent programs can actually obtain the data on the Web by following the links. We discuss some technical issues concerning how to manage several billion triples in a daily basis in addition to some potential problems in the current PDB data encountered during the conversion from PDBML to RDF. The Web interface to PDB/RDF will be available at <http://pdj.org/rdf/>

**Keywords:** database, web, computation

## MS90.P01

*Acta Cryst.* (2011) **A67**, C760

### Freezing of disordered hydrogen-bonding networks observed in nucleotide hydrates

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Nucleotides, basic components of nucleic acid, crystallize frequently in highly hydrated states. Layered structure is usually formed where an organic layer of nucleotides and an inorganic layer of water molecules and counter ions align alternately. Hydrogen bonds play a key role to construct layered structures in both organic and inorganic layers.

Disodium inosine 5'-monophosphate (Na<sub>2</sub>IMP) and disodium uridine 5'-monophosphate (Na<sub>2</sub>UMP) crystallize as octahydrate and heptahydrate, respectively. We have been examining humidity- and temperature-dependence of crystal structures by X-ray and neutron diffraction, gravimetric and thermal analyses. At room temperature, a considerable part of water molecules and counter ions disorder dynamically. The disordered sites are classified into several networks, and it indicates that disordered water molecules and sodium ions displace collectively switching their networks. With lowering temperature, the unit cell of each hydrate doubles and the disordered sites disappear at -150 °C. Freezing mechanism of hydration water will be discussed based on temperature dependence of interaction schemes.

**Keywords:** hydrogen bond, dynamic disorder, nucleotide

## MS90.P02

*Acta Cryst.* (2011) **A67**, C760-C761

### Experimental Charge Density of Selected Amino Acids.

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According to reports [1], [2], a phase transitions in crystals of d-