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Superspace description of low-temperature phases in the system Bi_2O_3-MoO_3

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The superspace formalism is a well-established method for the structural analysis of aperiodic crystals [1]. Moreover, this approach has also been applied to systems with flexible composition. Although, in some cases these systems can be described as conventional periodic crystals, the superspace formalism allows a unitary description in which the structure and the composition are related through modulation vectors and crenel functions of the atomic domains. Such approach has been successfully applied to different families [2],[3].

In this context, some low-temperature phases in the binary system Bi_2O_3-MoO_3 have been studied recently [4]. The generic formula for the system is $Bi_{2n+4}Mo_nO_{6(n+1)}$ (with n=3, 4, 5, 6) and they are reasonable candidates for this description. On one hand, the unit cells of these compounds are related with a fluorite-like structure. On the other, electron diffraction pattern consists of Bragg peaks which can be classified into main and satellite reflections, as in the case of a modulated structure.

Starting from the model proposed for the member with n=3 [5], the embedding of the three-dimensional structure has been carried out. Two possible descriptions have been considered. The first one is based on the fluorite-like structure of the compound δ-Bi_2O_3. The second description is developed from the Aurivillius structure of the compound Bi_2MoO_6. Since the coordination environments of Bi and Mo atoms are very different, the second model has been considered more convenient because oxygen atoms are represented by several atomic domains associated either with Bi or Mo atoms. This model has also been applied to compounds n=4, 5 and 6.

The actual atomic structures have been determined through the application of the Rietveld method using a combination of synchrotron X-ray and neutron powder data for each compound. Two superspace models are proposed. On one hand, a model for odd members (n=3, 5) with superspace group F2(α0γ) and modulation vector $\mathbf{q} = \frac{1}{3n+4}(-1,0,n+1)$. On the other, another model for even members (n=4, 6) with superspace group F2/m(α0γ)0s and modulation vector $\mathbf{q} = \frac{2}{3n+4}(1,0,2n+3)$. On both models, Bi and Mo cations share the average position with occupancies $\frac{2n+4}{3n+4}$ and $\frac{n}{3n+4}$ respectively. The occupational modulation for cations is represented by complementary crenel functions, giving rise to the cationic distribution proposed for these compounds [5]. Positional modulations obtained in the superspace models are very large, especially for the oxygen atomic domains close to Mo atoms.

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Long range ordering in the spin crossover compound [Fe(5-NO_2-sal-N(1,4,7,10))]

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The studies of Fe(II) complexes with multi-step spin transition are particularly important in understanding the mechanism of a cooperative interaction responsible for the spin transitions in solid state. Based on theoretical considerations and Monte Carlo simulation, it has been shown that a two-step or incomplete spin transition must be accompanied by a structural phase transition (change of the space group) or additional short or long range ordering of molecules in high spin and low spin state [1]. In the former case diffuse scattering or creation of satellite reflections should be observed. The complex under study fully conforms to the above theoretical predictions.

The compound crystallizes in two forms: monoclinic [2] and orthorhombic [3]. In the first form, a two-step spin transition is accompanied by two structural phase transitions at 140 and at 180 K [2]. In the orthorhombic form at 200 K, we have observed an incomplete spin transition ($\gamma_{HS} = 2/3$) and in addition, very weak satellite reflections [3].

The orthorhombic form of the complex crystallizes in the space group Pccn ($Z = 4$). Below the spin transition temperature, the same splitting of the Bragg peaks is observed, which indicates that the structure transforms to monoclinic and week satellite reflections appear. They create superstructure where *a* and *b* lattice parameters are three times larger while *c* remains the same [3]. The rules for systematic absence allowed to perform an initial refinement in $P2_1/c$ space group using three-dimensional space groups (SG) and SHELX program [4]. Analysis of the obtained result showed that molecules in high and low spin state during spin transition are ordered. The bond lengths Fe-N and Fe-O are the criteria for distinguishing which molecules occur in the high spin or in the low spin state. Because the unit cell of superstructure is nine times larger than the unit cell of the high temperature phase and satellite reflections are very weak, the final accurate analysis of the superstructure was performed in JANA2006 [5] using (3+1)-dimensional P2/n(αβ0)00 super space group (SSG).

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Keywords: Fe(II), spin transition, phase transition

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Commensurate 3D Ln–pmdc–ox open frameworks

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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, $\{[Ln(\mu_3\text{-pmdc})(\mu\text{-ox})_{0.5}(H_2O)_2]\cdot 2.25H_2O\}_n$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er; pmdc = pyrimidine-4,6-dicarboxylato, ox = oxalato). 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 x 7 Å 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.

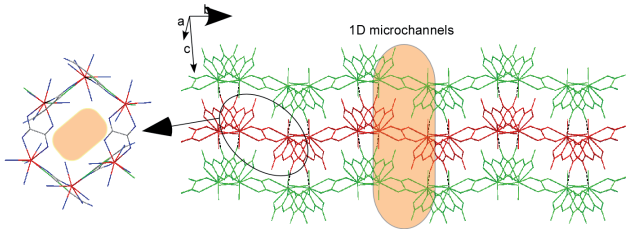

Figure 1. View of the overall 3D open framework showing the microchannels.

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Keywords: commensurate, lanthanide, luminescence

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Thermally Induced Structural Changes in Modulated $Ca_{0.28}Ba_{0.72}Nb_2O_6$ (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 $Ca_{0.28}Ba_{0.72}Nb_2O_6$ 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 (Ca^{2+} and Ba^{2+}). The X-ray single crystal diffraction patterns of $Ca_{0.28}Ba_{0.72}Nb_2O_6$ exhibit weak first order satellite reflections in addition to the main reflections indicating the existence of a two dimensional structural modulation like in isotypic $Sr_{1-x}Ba_xNb_2O_6$ 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 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 ½ 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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Anion deficient perovskites $(Pb,Bi)_{1-x}Fe_{1+x}O_{3-y}$ modulated by crystallographic shear planes

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$BiFeO_3$ is one of the rare perovskites combining ferroelectric and magnetic ordering in a single phase material. Being a room-temperature multiferroic, $BiFeO_3$ is a playground for the investigation of the physical phenomena behind multiferroicity [1]. The main instability