MS88.P08

Acta Cryst. (2011) A**67,** C758

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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Keywords: superspace formalism, modulated structures, homologous series

MS88.P09

Acta Cryst. (2011) A**67,** C758

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

MS88.P10

Acta Cryst. (2011) A**67,** C758-C759

Commensurate 3D Ln–pmdc–ox open frameworks

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