

There is a great interest in the multiferroic compounds and in mechanisms of the magnetic-ferroelectric coupling in view of promising wide technological applications of such materials. Recently, a cascade of the magnetic and structural phase transitions were discovered in the new multiferroic  $\text{GdFe}_3(\text{BO}_3)_4$  [1], [2], [3]. A single-crystal X-ray structural study [2] showed the presence of two different iron helicoidal chains at 90 K, which becomes identical at room temperature. However, the relationship between magnetism and structure of  $\text{GdFe}_3(\text{BO}_3)_4$  is still unclear.

In this work, the single-crystal of gadolinium iron borate  $\text{GdFe}_3(\text{BO}_3)_4$  was investigated by the  $^{57}\text{Fe}$  Mössbauer spectroscopy and X-ray diffraction in the temperature range between 5 and 295 K. Computer analysis of the Mössbauer data shows the presence of two close but nonequivalent sites for the Fe ions in the whole temperature range 5 - 295 K. Temperature dependences of the hyperfine parameters of the Mössbauer spectra indicate some structural and magnetic anomalies at  $T < T_N$  and near the structural phase transition points, that are well correlated with our single-crystal X-Ray data.

The unit cell parameters of  $\text{GdFe}_3(\text{BO}_3)_4$  single crystal were determined in a temperature range from room temperature to 30 K on a HUBER-5042 four-circle X-ray diffractometer equipped with a DISPLEX DE-202 two-stage closed-cycle cryostat (ADP Cryogenics Inc.), which affords the temperature stabilization within  $\pm 0.05$  K. The accuracy of setting the angular positions of the goniometer is  $0.001^\circ$ . The unit cell parameters were measured at  $T = 295$  K and in the 220 - 30 K range with the 5 - 10 K intervals. The measurements were based on 32 diffraction reflections at  $19^\circ < \theta < 22^\circ$ . It was found that the  $a$  and  $b$  unit cell parameters do not change until the phase transition at 155 K, and then they decrease dramatically with lowering temperature. After that they reduce as  $a \sim T^2$ -law. Yet, the  $c$  parameter decreases uniformly from the room temperature down to 155 K, and then some anomalies appear near 80 K when it starts to increase. The unit cell volume shows properly the phase transition at 155 K and has some anomalies in the 80 - 60 K interval.

**Acknowledgments:** This work is supported by the Russian Foundation for Basic Research grant and 11-02-00636-a and by the Program of Russian Academy of Sciences under the Project "Strongly correlated electronic systems".

[1] R.Z. Levitin, E.A. Popova, R.M. Chtsherbov, A.N. Vasiliev, M.N. Popova, E.P. Chukalina, S.A. Klimin, P.H.M. van Loosdrecht, D. Fausti, L.N. Bezmaternykh, *JETP Lett* **2004**, *79*, 9, 423. [2] S.A. Klimin, D. Fausti, A. Meetsma, L.N. Bezmaternykh, P.H.M. van Loosdrecht, T.T.M. Palstra, *Acta Cryst. B* **2005**, *61*, 481. [3] D. Fausti, A.A. Nugroho, P.H.M. van Loosdrecht, S.A. Klimin, M.N. Popova, *Phys. Rev. B*, **2006**, *74*, 024403.

**Keywords:** multiferroics, phase transitions, low temperature

## MS81.P50

*Acta Cryst.* (2011) **A67**, C721

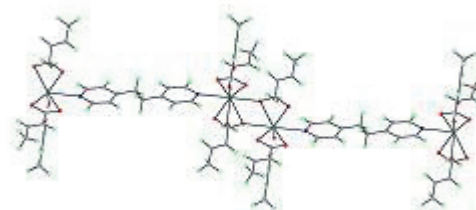
### Structural properties of Gd(III) and Y(III) complexes with diimines and crotonate as bridging ligands.

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As a part of our research of lanthanide complexes we have prepared and determined the crystal and molecular structure of five crotonate Gadolinium and Yttrium complexes displaying crotonates bridges. The diimines are 2,2-bipyridine (bpy), 1,2-bis(4-pyridyl)ethane (bpy-etha), and 1,2-bis(4-pyridyl)ethene (bpy-ethy)

The first one  $\{\{\text{Gd}(\text{crotonate})_3(\text{H}_2\text{O})(\text{bpy})_{1/2}\}_2\}$  (**1**) is a dimer, built up around a symmetry center, and each cation is coordinated to three crotonate groups binding in dissimilar coordination modes (purely chelating, tridentate, and purely bridging). There is in addition a bpy unit, also chelating the cation through both nitrogens and protruding outwards at both sides of the dimer [1].

The complexes  $\{\{\text{Gd}(\text{crotonate})_3(\text{H}_2\text{O})(\text{bpy-etha})_{1/2}\}_n\}$  (**2**),  $\{\{\text{Gd}(\text{crotonate})_3(\text{H}_2\text{O})(\text{bpy-ethy})_{1/2}\}_n\}$  (**3**),  $\{\{\text{Y}(\text{crotonate})_3(\text{H}_2\text{O})(\text{bpy-etha})_{1/2}\}_n\}$  (**4**), and  $\{\{\text{Y}(\text{crotonate})_3(\text{H}_2\text{O})(\text{bpy-ethy})_{1/2}\}_n\}$  (**5**) are polymers. They crystallize in the triclinic space group P-1, and the asymmetric units are composed of a nine coordinated Ln cation, three crotonate ligands, one aqua and half of a whole diimine unit bisected by a symmetry centre.  $[\text{Ln}(\text{crotonate})_3(\text{H}_2\text{O})]$  groups are linked by a double  $\text{O}_{\text{crotonate}}$  bridge into centrosymmetric dimeric units, in turn connected by the corresponding pyridine groups into chains running along  $[-201]$  (Figure)



[1] A.M. Atria, R. Baggio, M.T. Garland, J.C. Muñoz, O. Peña, *Inorganica Chimica Acta* **2004**, *357*, 1997-2006.

**Keywords :** complexes, lanthanides, structures .

## MS81.P51

*Acta Cryst.* (2011) **A67**, C721-C722

### Sillenites: composition, structure, morphology, crystal growth.

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The phases  $\text{Bi}(1)_{24}\text{M}_2\text{O}_{40}$  or  $\text{Bi}(1)_{24}(\text{M},\text{M}')_2\text{O}_{40}$  with sillenite structure ( $\gamma$ - $\text{Bi}_2\text{O}_3$ , sp.gr. *I23*,  $z=13$  or  $\text{Bi}(1)_{24}\text{Bi}(2)_2\text{O}_{40}$ ,  $z=1$ ; coordination polyhedron of Bi(1) is distorted semi-octahedron  $\text{Bi}(1)\text{O}_5$  -  $\text{Bi}(1)\text{O}(1)_3\text{O}(2)\text{O}(3)$ ) and of Bi(2) or M - tetrahedron  $\text{Bi}(2)\text{O}(3)_4$  or  $\text{MO}(3)_4$ ) have physical properties (photoconductivity, piezo- and electrooptical effects and so on) depending on the crystallochemical properties (ionic radius -  $r(\text{M}_{\text{IV}})$ , and formal charge - FC) of M and M' atoms. The aim of this paper is structural characterization of the compounds in the sillenite family.

Basic methods for structural characterization of sillenites with nominal composition  $\text{Bi}_{24}\text{M}_2\text{O}_{40}$  ( $\text{M}=\text{Al}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+}, \text{Si}^{4+}, \text{Ge}^{4+}, \text{Ti}^{4+}, \text{Mn}^{4+}, \text{Cr}^{4+}, \text{V}^{5+}$ ) and  $\text{Bi}_{24}(\text{M},\text{M}')_2\text{O}_{40}$  ( $\text{M}=\text{Al}^{3+}, \text{Fe}^{3+}, \text{Si}^{4+}, \text{Ge}^{4+}, \text{Ti}^{4+}, \text{Cr}^{4+}, \text{V}^{5+}$ ,  $\text{M}'=\text{Mn}^{4+}, \text{V}^{5+}$ ) were:

*Diffraction study.*

- X-ray structure analysis - single crystals: CAD-4 and Xcalibur; ground into fine powder samples: HZG-4A;
- neutron study - single crystal: 5C2, Orphee reactor;
- synchrotron radiation - the 'Belok' station on the synchrotron radiation source from the bending magnet in the Sibir-2 storage ring;

*Spectroscopy study.*

- Raman-spectroscopy - single crystals: Horiba Jobin Yvon LABRAM HR800,  $\nu=100$ - $1000 \text{ cm}^{-1}$ ;
- IR-spectroscopy - ground into fine powder samples: Equinox 55,