

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}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 ± 0.05 K. The accuracy of setting the angular positions of the goniometer is 0.001° . 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

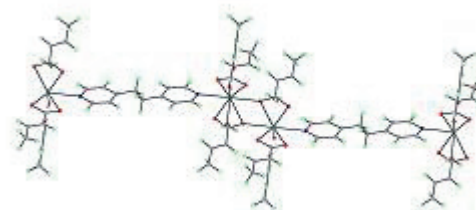
Structural properties of Gd(III) and Y(III) complexes with diimines and crotonate as bridging ligands.

M.T.Garland,^a A.M.Atria,^b R.Baggio,^c ^aFacultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago. (Chile). ^bFacultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago. (Chile). ^c Comisión Nacional de Energía Atómica Argentina. CNEA, (Argentina). E-mail: mtgarlan@dfi.uchile.cl

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.

Tatyana I. Mel'nikova,^a Galina M. Kuz'micheva,^a Victor B. Rybakov,^b Nadezhda B. Bolotina,^c A. Cousson,^d ^aLomonosov State Academy of Fine Chemical Technology, Moscow, (Russia). ^bLomonosov State University, Moscow, (Russia). ^cShubnikov Institute of Crystallography RAS, Moscow, (Russia). ^dLaboratoire Leon Brillouin, Cea/Saclay, (France). E-mail: melti@list.ru

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 (γ - Bi_2O_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,

Bruker, $\nu=400-1000\text{ cm}^{-1}$;

Electron microscopy (JEM-2100; INCA Penta FETx 3 OXFORD INSTRUMENTS).

Both defective and defect-free sillenite phases $\text{Bi}_{24}\text{M}_2\text{O}_{40}$ have been obtained. Vacancies in the *M* site for $M = \text{Fe}^{3+}$, Si^{4+} , Mn^{4+} compensate by the vacancies in the O(3) site. The formation of vacancies in the Bi site has been found for the sillenite with $M = \text{V}^{5+} - (\text{Bi}_{23.4(1)}\square_{0.6})[\text{Bi}_{0.02(1)}\text{V}_{0.98}^{5+}]_2\text{O}_{40}$.

The difference between the crystallochemical properties of the atoms *M* and *M'* leads to the two types of phenomena:

1. *Dissymmetrization* of the sillenite phases – the transition from sp.gr. I23 to sp.gr. P23 (phase with sp.gr. P23 are formed in the region of stability of phase with sp.gr. I23): $\text{Bi}_{24}(\text{Si}^{4+}_{0.9(1)}\text{Mn}^{4+}_{1.1})\text{O}_{40} - \Delta r = r(\text{Mn}^{4+}_{\text{IV}}) - r(\text{Si}^{4+}_{\text{IV}}) = 0.13\text{ \AA}$; $\Delta \text{FC} = \text{FCSi}^{4+} - \text{FCMn}^{4+} = 0$.

2. *Dissociation* on the two isostructural solid solutions with different composition:

– for sillenite with nominal composition $\text{Bi}_{24}\text{Mn}_2\text{O}_{40} \rightarrow \text{Bi}_{24}(\text{Mn}^{4+}_{-0.8}\text{Bi}^{3+}_{-0.2})_{40-8} + \text{Bi}_{24}(\text{Bi}^{3+}_{-0.8}\text{Mn}^{4+}_{-0.2})_{40-8}$ ($\Delta r = 0.47\text{ \AA}$, $\Delta \text{FC} = 1$) (this effect was observed by using synchrotron radiation and electron microscopy).

– for sillenite with nominal composition $\text{Bi}_{24}\text{P}_2\text{O}_{40} \rightarrow \text{Bi}_{24}(\text{P}^{5+}_{-0.8}\text{Bi}^{3+}_{-0.2})_{40-8} + \text{Bi}_{24}(\text{Bi}^{3+}_{-0.8}\text{P}^{5+}_{-0.2})_{40-8}$ ($\Delta r = 0.69\text{ \AA}$, $\Delta \text{FC} = 2$) (this effect was observed by X-ray diffraction study).

It was found that some ions of transition elements in the sillenites can have different FC: $M = \text{Fe}^{3+}$, Ti^{4+} , Mn^{4+} , Mn^{5+} , Cr^{4+} , V^{4+} , V^{5+} .

The transition sp gr. I23→sp.gr. P23 is due to both structure peculiarities (a presence of several atoms in *M* position of sillenite structure) and preparation conditions simultaneously ($T=400^\circ\text{C}$): sp. gr. I23 for cube+tetrahedron morphology ($\text{Na}_2\text{SiO}_3 = \text{Mn}(\text{NO}_3)_2$ in the initial charge) and sp.gr. P23 for tetrahedron morphology ($\text{Na}_2\text{SiO}_3 \ll \text{Mn}(\text{NO}_3)_2$) and cube ($\text{Na}_2\text{SiO}_3 \gg \text{Mn}(\text{NO}_3)_2$) one.

Keywords: sillenites, composition, structure

MS81.P52

Acta Cryst. (2011) A67, C722

Diffraction methods for investigation of the real structure of langasite family

Elena Domoroshchina,^a Irina Kaurova,^a Galina Kuz'micheva,^a Viktor Rybakov,^b Alain Cousson,^c Oksana Zaharko,^d ^a*Lomonosov State Academy of Fine Chemical Technology, Moscow, (Russia)*. ^b*Moscow State University, Moscow, (Russia)*. ^c*Laboratoire Leon Brillouin, Cea/Saclay, Gif-sur-Yvette, (France)*. ^d*Laboratory for Neutron Scattering, Paul Scherrer Institut, Zurich, (Switzerland)*. E-mail: elena7820@gmail.com

Langasite family crystals, represented by general chemical formula $\text{A}_3\text{BC}_3\text{D}_2\text{O}_{14}$, are a class of excellent candidates for piezoelectric and high temperature applications. However, the application of these compounds depends on the type and concentration of point defects, which does not coincide with the composition of the initial charge.

Crystals of $\text{La}_3\text{Ga}_5\text{SiO}_{14} = \text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$ -LGS, $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14} = \text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$ (LGT), $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14} = \text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ (LGN) and $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ (CNGS) initial compositions with diameter up to 3" were grown by the Czochralski technique (Crystal-3M growth system) in <0001> and <01-11> directions (Ir-crucibles) in Ar+1-2%O₂ (LGS, LGT, LGN) or pure Ar (CNGS, LGS) growth atmosphere both without subsequent annealing and with vacuum and air annealing. A complex investigation by different diffraction methods (X-ray and neutron diffraction studies of single crystals; X-ray study of ground into powder samples), IR-spectroscopy and X-ray microanalysis allow to determine for the first time:

- vacancies in dodecahedral positions – $\text{V}_{\text{La}}^{\text{IV}}$ ($\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$) and $\text{V}_{\text{Ca}}^{\text{IV}}$ ($\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$);
- vacancies in trigonal-pyramidal positions – $\text{V}_{\text{Ga}}^{\text{IV}}$

($\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$) and $\text{V}_{\text{Si}}^{\text{IV}}$ ($\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$);

- vacancies in oxygen positions – $\text{V}_{\text{O}}^{\text{IV}}$ – O(1) ($\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$), O(3) ($\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$) and O(2) ($\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$, $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$, $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$);

- different ratio of $\text{Ga}^{3+} : \text{M}^{5+}$ in octahedral position ($\text{La}_3(\text{Ga}_{0.5}\text{M}_{0.5})\text{Ga}_5\text{O}_{14}$, $M = \text{Ta}, \text{Nb}$) and different ratio of Ga : Si in trigonal-pyramidal position ($\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$);

- antistructural defects in octahedral ($\text{Ga}_{\text{Nb}}^{\text{IV}}$), tetragonal ($\text{Si}_{\text{Ga}}^{\text{IV}}$) and trigonal-pyramidal ($\text{Ga}_{\text{Si}}^{\text{IV}}$) positions of ($\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$) crystal structure;

- interstitial atoms Ca_i ($\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$);

- the possibility of microtwins formation (two unit cells connected by the translation – $\frac{1}{2}z$) was revealed for $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ and $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ crystals;

- the possibility of the $\text{La}(\text{Ta},\text{Ga})\text{O}_3$ phase allocation on the outer and inner surfaces of the $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$ crystal annealed in vacuum at 1200 °C which leads to green color of crystals due to the Ta^{3+} ions presented in the phase composition;

- the color of $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$, $\text{La}_3(\text{Ga}_{0.5}\text{Nb}_{0.5})\text{Ga}_5\text{O}_{14}$ and $\text{Ca}_3\text{NbGa}_3\text{Si}_2\text{O}_{14}$ crystals depends on the post-growth treatment conditions (vacuum annealing- colorless crystal, air annealing- orange crystal). The increase of oxygen vacancies content changes the crystal color from light-yellow to orange, the further increasing one leads to the color changes from orange to colorless. The crystals with large content of oxygen vacancies are colorless. The coloration was tentatively attributed to an *F*-center consisting of an oxygen vacancy and an electron: $(\text{V}_{\text{O}}^{\text{IV}}, \text{ne}^{\cdot})^{\times}$. The crystals are colorless for $\text{V}_{\text{O}}^{\text{IV}} > (\text{V}_{\text{O}}^{\text{IV}}, \text{ne}^{\cdot})^{\times}$ and exhibit a color for $\text{V}_{\text{O}}^{\text{IV}} < (\text{V}_{\text{O}}^{\text{IV}}, \text{ne}^{\cdot})^{\times}$.

Keywords: piezoelectrics, composition, structure

MS81.P53

Acta Cryst. (2011) A67, C722-C723

Structure elucidation and aqueous speciation of water-soluble $\text{M}_3\text{S}_4\text{M}$ (Mo,W) clusters bearing hydroxypropyl diphosphine ligands

Tomás F. Beltrán,^a Manuel G. Basallote,^b M. Jesús Fernández-Trujillo,^b Jose Angel Pino,^b Carolina Corao,^a Rosa Llusar,^a Maxim Sokolov,^a Cristian Vicent,^a ^a*Departament de Química Física i Analítica, Universitat Jaume I, Campus de Riu Sec, 12071 Castelló, (Spain)*. ^b*Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real, 11510 Cádiz, (Spain)*. E-mail: tbeltran@qfa.uji.es

The chemistry of water-soluble transition-metal complexes containing phosphine ligands is of interest because of the potential usefulness of these complexes in biphasic (aqueous-organic) catalysis and biomedicine.[1] Two-phase catalysis can solve basic problems in homogeneous catalysis such as the separation and further recycling of the catalyst, making these processes environmentally friendly.

In particular, phosphines with hydroxyalkyl groups such as 1,2-bis(bis(hydroxypropyl)-phosphino)ethane (dhprpe) have enabled the development of a wide spectrum of water-soluble transition/organometallic complexes.[2]

Here we present the structural characterization of new group six trinuclear $[\text{M}_3\text{S}_4\text{X}_3(\text{dhprpe})_3]^+$ ($M = \text{Mo}, \text{W}$; $X = \text{Cl}, \text{Br}$) clusters combining x-ray diffraction and spectroscopic techniques. A water speciation study is also shown. Depending on pH, new cluster structures are obtained as a result of dhprpe ligand deprotonation.