

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 $M = \text{V}^{5+} - (\text{Bi}_{23.4(1)}\square_{0.6})[\text{Bi}^{3+}_{0.02(1)}\text{V}^{5+}_{0.98}]_2\text{O}_{40}$.

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

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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 $\text{V}_{\text{O}}^{\text{IV}} < (\text{V}_{\text{O}}^{\text{IV}}, \text{ne}^{\cdot})^{\times}$.

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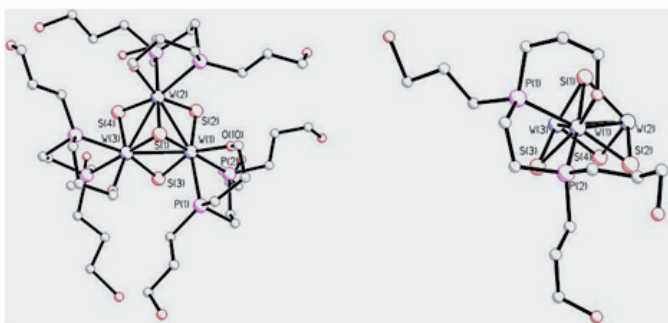
Structure elucidation and aqueous speciation of water-soluble $\text{M}_3\text{S}_4\text{M}$ (Mo, W) clusters bearing hydroxypropyl diphosphine ligands

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.



[1] N. Pinault, D.W. Bruce, *Coord. Chem. Rev.* **2003**, *241*, 1-25. [2] J. Chatt, J.G. Leigh, R.M. Slade, *J. Chem. Soc. Dalton Trans.* A. G. Algarra, M.G. Basallote, M. J. Fernandez-Trujillo, E. Guillamon, R. Llusar, M.D. Segarra, C. Vicent, *Inorg. Chem.* **2007**, *46*, 7668-767.

Keywords: water soluble clusters, hydroxyalkyl phosphines, crystal structure

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Incommensurate structure analyses of Bi-Te and Sb-Te binary system

Kazuyuki Shakudo,^a Kouichi Kifune,^a Yoshiki Kubota,^a Toshiyuki Matsunaga,^b Noboru Yamada,^b Masaki Takata,^c ^a*Department of Physical Science, Osaka Prefecture University, Gakuen-cho, Sakai, Osaka.* ^b*Panasonic Corporation, Moriguchi, Osaka.* ^c*RIKEN/SPring-8 Center, Sayou-cho, Hyogo (Japan).* E-mail: s_k.shakudo@p.s.osakafu-u.ac.jp

Sb-Te binary compounds are well known as base materials for optical data storage media. They have long-period cubic close-packed ABC stacking structures [1]. Two kinds of fundamental structural units form an intergroth along the stacking direction at the atomic level. Chemical formulae of Sb-Te binary compounds are expressed as $(Sb_2)_n(Sb_2Te_3)_m$, where n and m are integers. The period of stacking structure is considered to be determined by the ratio of the two atomic species. However, our recent study revealed that stacking period of this system changes with temperature [2]. Bi-Te binary compounds which have similar crystal structures also show this tendency. We then performed synchrotron powder diffraction experiments and crystal structure analyses in order to clarify the temperature dependence of these stacking period in Sb-Te and Bi-Te binary systems.

$Bi_{14}Te_{15}$, $Bi_{10}Te_{11}$, Bi_8Te_9 and Bi_3Te_4 compounds were synthesized by melting method and $Sb_{67}Te_{33}$ and $Sb_{60}Te_{40}$ compounds were synthesized by sputtering method, as specimens. Powder X-ray diffraction experiments were carried out using a large diameter Debye-Scherrer camera with an imaging plate at the SPring-8 BL02B2 beamline. Temperature of powdered specimens were controlled by blowing high-temperature N_2 gas. Measurements were carried out every 50 K from room temperature to 773 K.

The specimens synthesized by sputtering method were amorphous and they crystallized with increasing temperature. It was found from the peak positions of diffraction pattern that the specimens have incommensurate structure at early stage of crystallization. Crystal structure analyses were performed under the superspace group approach, using JANA2006[3]. The basic unit cell consists of cubic close-packed three layers, and modulation of the atomic displacement is characterized by a single modulation vector $q = \gamma c^*$, where γ is a modulation period.

In the case of $Sb_{67}Te_{33}$ compound, as-deposited specimen was amorphous up to 388 K. It crystallized into an incommensurate

structure with $\gamma = 1.633$ at 423 K. The γ value then continuously changed with increasing temperature and drastically rised from 1.633 to 1.656 at around 700 K. However, it did not change in the following cooling down measurement. Final γ value 1.656 showed very good accordance with that expected from its composition. Similarly, as for all other specimens, changes of γ values and stacking structures were demonstrated.

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Structural conditionality of proton conductivity in $M_mH_n(XO_4)_{(m+n)/2}$ crystals

Irina Makarova, Tatiyna Chernaya, Igor Verin, Vadim Grebenev, Valentina Dolbinina, *Shubnikov Institute of Crystallography of Russian Academy of Sciences, Moscow (Russia).* E-mail: secr@ns.crys.ras.ru.

Compounds $M_mH_n(XO_4)_{(m+n)/2}$ ($M = K, Rb, Cs, NH_4; X = S, Se, P, As$) are of considerable interest for extending current knowledge about the nature of hydrogen bonds and their influence on the properties of crystalline compounds. At the same time, these compounds are of importance for applied research due to the formation of phases with conductivity of the 10–2 Ω/cm order of magnitude at relatively low temperatures. The characteristic features of this crystal family are low-temperature ferroelectric or antiferroelectric phase transitions, which result in the ordering of protons in the two-minimum hydrogen-bond potential, and high-temperature superionic phase transitions associated with the disordering of the positions of hydrogen atoms. “Superprotonic” crystals form a specific class of compounds, in which changes in hydrogen bonds in the course of phase transitions result in radical changes in the physical and physico-chemical properties. This crystal family is unique in a class of proton conductors since proton conductivity is property of their structure, instead of consequence of impurity doping process.

X-ray structural data allow to draw a conclusion on the distinction of structural mechanisms of conductivity in $M_mH_n(XO_4)_{(m+n)/2} \cdot H_2O$ compounds. In $K_3H(SO_4)_2$ crystals high proton conductivity is caused by the formation of dynamically disordered hydrogen-bond network similarly to $Rb_3H(SeO_4)_2$ [1], [2], which enables protons to move over vacant crystallographically equivalent positions, and also by the formation of a multiphase state at further heating (with the retention of the crystal state). In $K_9H_7(SO_4)_8 \cdot H_2O$ crystals an essential contribution to conductivity is brought also by crystalline water and K atoms.

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