Bruker, ν=400-1000 см$^{-1}$;

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

Both defective and defect-free sillenite phases $Bi_{24}M_2O_{40}$ have been obtained. Vacancies in the *M* site for $M = Fe^{3+}$, 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=V^{5+} – $(Bi_{23.4(1)}\square_{0.6})[Bi^{3+}{}_{0.02(1)}V^{5+}{}_{0.98}]_2O_{40}$.

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. I*23* to sp.gr. P*23* (phase with sp.gr. P*23* are formed in the region of stability of phase with sp.gr. *I*23): $Bi_{24}(Si^{4+}{}_{0.9(1)}Mn^{4+}{}_{1.1})O_{40}$ –$\Delta r = r(Mn^{4+}{}_{IV}) - r(Si^{4+}{}_{IV}) = 0.13$Å; ΔFC = FCSi^{4+} - FCMn^{4+}= 0.

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

– for sillenite with nominal composition $Bi_{24}Mn_2O_{40} \rightarrow Bi_{24}(Mn^{4+}{}_{\sim0.8}Bi^{3+}{}_{\sim0.2})_{40-\delta} + Bi_{24}(Bi^{3+}{}_{\sim0.8}Mn^{4+}{}_{\sim0.2})_{40-\delta}$ (Δr = 0.47Å, ΔFC = 1) (this effect was observed by using synchrotron radiation and electron microscopy).

– for sillenite with nominal composition $Bi_{24}P_2O_{40} \rightarrow Bi_{24}(P^{5+}{}_{\sim0.8}Bi^{3+}{}_{\sim0.2})_{40-\delta} + Bi_{24}(Bi^{3+}{}_{\sim0.8}P^{5+}{}_{\sim0.2})_{40-\delta}$ (Δr = 0.69Å, ΔFC = 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: $M = Fe^{3+}$, Ti^{4+}, Mn^{4+}, Mn^{5+}, Cr^{4+}, V^{4+}, V^{5+}.

The transition sp gr. *I*23→sp.gr. *P*23 is due to both structure peculiarities (a presence of several atoms in *M* position of sillenite structure) and preparation conditions simultaneously (*T*=400°C): sp. gr. *I*23 for cube+tetrahedron, morphology (Na_2SiO_3=$Mn(NO_3)_2$ in the initial charge) and sp.gr. *P*23 for tetrahedron morphology (Na_2SiO_3<<$Mn(NO_3)_2$) and cube (Na_2SiO_3>>$Mn(NO_3)_2$) one.

Keywords: sillenites, composition, structure

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Diffraction methods for investigation of the real structure of langasite family

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Langasite family crystals, represented by general chemical formula $A_3BC_3D_2O_{14}$, 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 $La_3Ga_5SiO_{14} = La_3Ga_4(GaSi)O_{14}$-LGS, $La_3Ga_{5.5}Ta_{0.5}O_{14} = La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$(LGT), $La_3Ga_{5.5}Nb_{0.5}O_{14} = La_3(Ga_{0.5}Nb_{0.5})Ga_5O_{14}$ (LGN) and $Ca_3NbGa_3Si_2O_{14}$ (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%O_2 (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 – V_{La}''' ($La_3Ga_4(GaSi)O_{14}$, $La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$, $La_3Ga_{5.5}Nb_{0.5}O_{14}$) and V_{Ca}'' ($Ca_3NbGa_3Si_2O_{14}$);
- vacancies in trigonal-pyramidal positions –V_{Ga}''' ($La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$, $La_3(Ga_{0.5}Nb_{0.5})Ga_5O_{14}$) and V_{Si}'''' ($Ca_3NbGa_3Si_2O_{14}$);
- vacancies in oxygen positions - $V_O^{\bullet\bullet}$- O (1) ($La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$), O(3) ($La_3Ga_4(GaSi)O_{14}$, $La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$, $La_3Ga_{5.5}Nb_{0.5}O_{14}$) and O(2) ($La_3Ga_4(GaSi)O_{14}$, $La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$, $La_3Ga_{5.5}Nb_{0.5}O_{14}$, $Ca_3NbGa_3Si_2O_{14}$);
- different ratio of Ga^{3+} : M^{5+} in octahedral position ($La_3(Ga_{0.5}M_{0.5})Ga_5O_{14}$, M=Ta, Nb) and different ratio of Ga : Si in trigonal-piramidal position ($La_3Ga_4(GaSi)O_{14}$);
- antistructural defects in octahedral (Ga_{Nb}''), tetragonal ($Si_{Ga}^{\bullet}$) and trigonal-piyramidal (Ga_{Si}') positions of ($Ca_3NbGa_3Si_2O_{14}$) crystal structure;
- interstitial atoms Ca_i ($Ca_3NbGa_3Si_2O_{14}$);
- the possibility of microtwins formation (two unit cells connected by the translation - ½ z) was revealed for $Ca_3NbGa_3Si_2O_{14}$ and $La_3(Ga_{0.5}Nb_{0.5})Ga_5O_{14}$ crystals;
- the possibility of the $La(Ta,Ga)O_3$ phase allocation on the outer and inner surfaces of the $La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$ 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 $La_3Ga_4(GaSi)O_{14}$, $La_3(Ga_{0.5}Ta_{0.5})Ga_5O_{14}$, $La_3(Ga_{0.5}Nb_{0.5})Ga_5O_{14}$ and $Ca_3NbGa_3Si_2O_{14}$ 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: $(V_O^{n\bullet}, ne')^x$. The crystals are colorless for $V_O^{n\bullet} > (V_O^{n\bullet}, ne')^{\times}$ and exhibit a color for $V_O^{n\bullet} < (V_O^{n\bullet}, ne')^{\times}$.

Keywords: piezoelectrics, composition, structure

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Structure elucidation and aqueous speciation of water-soluble M_3S_4 M= (Mo,W) clusters bearing hydroxypropyl diphosphine ligands

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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 $[M_3S_4X_3(dhprpe)_3]^+$ (M= Mo, W ; X=Cl, 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.