of x=0.7, 0.8 and 0.9 was almost same one of NH_4IO_3. Meanwhile, the crystal structure of the middle compositions (x=0.4, 0.5 and 0.6) was different from both of $RbIO_3$ and NH_4IO_3.

The measurement of DSC in temperature range from room temperature to 135°C, $Rb_{1-x}(NH_4)_xIO_3$ with x=0.0 to 0.6 indicate no anomaly. However, single anomaly in DSC measurement was observed in the each sample of x=0.7 to 1.0. From a reported temperature of ferroelectric phase transition in NH_4IO_3 [3], it was considered that these DSC anomalous temperatures were equivalent to temperature of the ferroelectric phase transition. These temperatures of ferroelectric phase transition were decreased with decreasing the value of composition x from x=1.0 to x=0.7. The values of the entropy change at the ferroelectric phase transition of x=0.8, 0.9 and 1.0 were obtained from the value of these heat anomaly in DSC measurement of each samples. As a result, it was considered these ferroelectric phase transition was an order-disorder type.

Now, we are carrying out the low temperature DCS measurement and the identification of the crystal structure of middle composition region (x=0.4, 0.5 and 0.6). In congress, we will show the crystal structures and DSC measurements, and will discuss the phase diagram and the mechanism of phase transition in $Rb_{1-x}(NH_4)_xIO_3$ mixed crystals.

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Keywords: rubidium_ammonium_iodate_mixed_crystal, X-ray_ diffraction, differential_scanning_measurement

MS81.P66

New molybdenum peroxocomlexes as a promising catalysts

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Molybdenum organometallic complexes and oxides catalyze epoxidation reactions in homogenous and heterogenous catalysis. In addition, molybdenum complexes, in particular peroxomolybdates show structural and functional analogy to enzymes containing Mo atom, therefore are active in various reactions [1]. Most of the molybdenum catalysts play an important role in environment protection. They are used in desulphurization of petroleum and coal derived products, as sulphur dioxide causes a serious deterioration of air quality [2].

In our laboratory almost a dozen of a new peroxomolybdates have been obtained, they have been thoroughly investigated by X-ray and spectroscopic methods [3]. Recently, three new peroxocomplexes were synthesized from ammonium molybdate solution with addition of nicotinic acid and hydrogen peroxide (compounds **I-III**, see Table 1). In Figure 1a) anion coordination polyhedron and in 1b) asymmetric unit of peroxocomplex **I** are presented. The molybdenum atom is coordinated by seven oxygen atoms, among them there are two peroxo-groups lying in the same plane, one terminal O atom and two bridging oxygen atoms. Compound **I** is an ammonium salt, compound **II** is a salt of the same acid with protonated nicotinic acid. In Table 1 summary of crystal data of new peroxo-molybdenum complexes are presented.
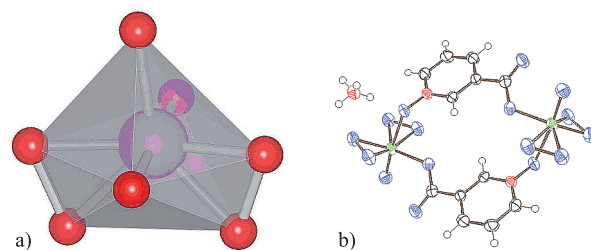

Figure 1, a) Anion coordination polyhedron and b) asymmetric unit of compound **I** (Mo-green, O-blue, N-red, C-grey).

Table 1. Crystal data of new peroxo-molybdates with nicotinic acid.

C h e m i c a l formula	$C_{12}H_{18}Mo_2N_4O_{16}$ **I**	$C_{24}H_{22}Mo_2N_4O_{22}$ **II**	$C_{12}H_{12}Mo_2N_2O_{16}$ **III**
SG	P-1 (2)	P2$_1$/c (14)	Pc (7)
C e l l parameters [Å, °]	a=6.687(4) b=6.965(4) c=12.012(7) α=76.421(4) β=77.434(4) γ=69.478(4)	a=7.504(2) b=28.473(7) c=7.777(2) β=111.425(1)	a = 5.416(3) b = 5.350(2) c =16.976(7) β = 106.230(3)
V [Å³], Z	503.66(2), 1	1546.82(3), 2	472.29(4), 2
R1; wR2	0.0422; 0.0902	0.0282; 0.0622	0.0508; 0.1342

Some peroxo-nicotinic acid complexes of Mo, have been investigated by Djordjevic et al., [4], their samples were not investigated by X-ray methods, but with the use of chem. analysis, spectroscopic, ^{1}H and ^{13}C NMR studies they proposed structures which differ from ours.

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MS81.P67

Indialite and cordierite in glass ceramics for millimeterwave dielectrics

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Dielectrics for millimeterwave communications are expected to have low dielectric constant and high quality factor (high *Q*). Cordierite ceramics is a candidate for millimeterwave dielectrics, because of low dielectric constant 4.7, and high *Qf* more than 200,000 GHz. Cordierite has two polymorphs: disordered phase indialite (hexagonal, *P6/mcc* (No. 192)) and ordered phase cordierite (orthorhombic, *Cccm* (No.66)). As Ni-doped cordierite ceramics with good dielectric properties tend to disordered, indialite was expected to have high *Qf*. As indialite

is known to be precipitated from glass phase, we got glass ceramics with high *Qf*. In this paper, phase relations in the glass ceramics are examined by powder X-ray diffraction patterns.

Powders obtained from glass melted at 1550 °C are crystallized for 10 h at 1200, 1300 and 1400 °C, and for 50 h at 1200 °C. The powder diffraction data are collected with the multiple detector system on beam line BL4B2 at the Photon Factory in Tsukuba (Toraya *et al.*, 1996). As corundum phase are precipitated in all samples, it was used for internal standard. These samples are analyzed by Rietveld method using RIETAN-FP by Fujio Izumi. Initial atomic parameters for indialite, cordierite and corundum are sited from ICDD-PDF4+ cards.

Sample #1: 1200 °C, for 10 h was analyzed by two models: (1) Indialite + Corundum, and (2) Cordierite + Corundum. As 100 - diffraction peak profile of indialite shows slight asymmetric, it was considered that the symmetry of indialite becomes lower. But model (2) has a 311-diffraction peak which was not observed in the diffraction pattern. So, this crystal structure is similar to indialite, and cordierite percentage ρ is 3.5 %. Sample #2: 1300 °C for 10 h was analyzed by four models: (1) Indialite + Corundum, (2) Cordierite + Corundum, (3) Indialite + Cordierite + Corundum, and (4) Cordierite I + Cordierite II + Corundum. In the case of model (3), the fittings of some refrections were not sufficient. So, two cordierite I and II with different lattice parameters are applied. The cordierite percentage ρ is 32.5 %. Sample #3: 1400 °C for 10 h was analyzed by three models: (1) Cordierite + Corundum, (2) Indialite + Cordierite + Corundum, and (3) Cordierite I + Cordierite II + Corundum. In the case of model (3), the cordierite percentage ρ is 83.3 %. Sample #4: 1200°C for 50 h was analyzed by three models: (1) Indialite + Corundum, (2) Cordierite + Corundum, (3) Indialite + Cordierite + Corundum. In the case of model (3), the cordierite percentage is 21.2 %.

Here, cordierite percentage $\rho = (a/\sqrt{3}b-1)/(17.0448/9.7127\sqrt{3}-1)$, *a* and *b*: lattice parameter of cordierite obtained, *a*=17.0448 A, *b* = 9.77605 A, and *c* = 9.34498 A are lattice parameters of pure cordierite [ICDD-PDF#01-089-1487].

The cordierite percentage increases according to temperature and crystallizing time. And the quality factor *Qf* is depending on the indialite (with high symmetry) percentage 1- ρ. High symmetry affects to *Q* factor more than ordering.

Keywords: millimeterwave microwave dielectrics, indialite and cordierite, rietveld refinement

MS81.P68

Phase formation in deformed iron-based alloys under saturation by N and C

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The diffusion saturation of iron-based alloys by nitrogen and carbon is widely used in industry for increase of strength, hardness, wear and corrosion resistance of metal products. Inexhaustible and unrealized potentialities of such treatment are opened when applying it under strain and stress condition [1]. The topical question in this direction is clarification of mechanisms of N and C diffusion and phase formation in strained iron and iron-based alloys.

The structure, phase composition and properties of surface diffusion layers formed in the preliminary deformed α-Fe and Fe-Cr, Fe-Ti, Fe-Cr-Ti, Fe-Ni alloys after diffusion saturation by N and C were studied. Preliminary plastic deformation (PPD) was realized by rolling with deformation degrees: ε = 3, 5, 8, 10, 15, 20, 25, 30, 35, 40, 50, 60,

70 %. The following gaseous saturation with nitrogen and carbon was performed from ammonia and propane-butane at T = 623÷853 K.

According to the SEM, TEM, XRPD investigations the diffusion layer is a combination of surface layers of different nitride (ξ-, ε-, γ′-) phases, nanostructured (γ′ + ε) – eutectoid layer and a zone of internal saturation (α_{N-C} – *phase* with *bcc* structure). According TEM the eutectoid consists of γ′-phase (*fcc* structure with lattice parameter a=0.378±0.004 nm) and ε-phase (*hcp* structure). The lattice constant of the α-solid solution of N in Fe is a=0.286 ±0.004 nm.

PPD considerably effects on the phase formation, structure, microhardness and thickness of nitrided layers. The thickness of ε-phase layer depends on deformation degree and changes in the range of 25-43 μm. The nitrided layers formed in Fe-Ni alloys some differ from those in α-Fe. These differences consist in the presence of additional layer of ξ-phase on the surface. The diffusion layers in Fe-Cr-Ti alloys consist of a surface layer of ε-phase ($Fe_{2-3}N$ type) with hexagonal lattice or θ-phase with orthorhombic lattice isostructural to cementite (Fe_3C type) crystal lattice and a zone of solid solution of nitrogen and carbon in α-phase.

The distribution of carbon and nitrogen atoms in Fe after deformation and nitriding were studied using Mössbauer spectroscopy An analysis of the hyperfine parameters has shown that the NGR spectra consist of several components relating to iron atoms in α-Fe and iron nitrides (ε-, γ′-phases).

The microhardness test of nitrided layers has discovered the narrow intervals of deformations of 3-8 % and 20-30 % in which the considerable rise (in about 2 times) of microhardness of the surface diffusion layer after nitriding of α–Fe exist. The high microhardness of the diffusion layers results from the formation of the ε- and γ′-nitrides. Iron doping with Ni leads to changing of the ε-, γ′-phases composition.

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Keywords: deformation, diffusion, nitride

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Structure types of intermolecular tin halide interactions in diorgaotin dihalides

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