PS11.05.14 PEROVSKITE-TYPE (Nd_x , Sm_{1-x})AlO_3: EFFECTS OF INIOC RADII AND TEMPERATURES ON THE STRUCTURE CHANGE. Hiroyuki Horiuchi[1], AkiraYoshikawa[1], Akihiro Saito[1], Toetsu Shishido[2], Masahiko Tanaka[3] and Tsuguo Fukuda[2]. 1) Mineralogical Inst., Faculty of Science, University of Tokyo, Hongo, Bunkyo, Tokyo 113, Japan, 2) Institute for Materials Res., Tohoku University, Katahira, Aoba, Sendai 980, Japan, 3) Photon Factory, National Lab. for High Energy Physics, Oho, Tsukuba, Ibaragi 305, Japan

Effects of the ionic substitution of Nd for Sm on the structure change of perovskite-type (Nd_x, Sm_{1-x})AlO_3 was investigated by means of a high resolution powder X-ray diffraction technique developed by Sasaki et al.[1], and the similar structure change which was caused by changing temperatures was also discussed based on the results of high-temperature powder X-ray diffraction experiments. The substitution of Nd for Sm changes the average size of rare earth ions in the structure, as a result, this was effective to the cause for an apparent phase transition from orthorhombic to trigonal structure at around $x = 0.7$. On the other hand, (Nd_x, Sm_{1-x})AlO_3 showed an actual phase transition from orthorhombic to trigonal structure at the temperature which was intimately related to the amount of ionic substitution. The relationship between phase transition temperature and chemical composition was decided as $T(°C) = -1075_x+795$ from the phase transition temperatures of (Nd_x, Sm_{1-x})AlO_3 for x=0.0, 0.4 and 0.7. This structure change is a kind of a first-order phase transition as suggested by O'Bryan *et al.*[2] for $SmAlO_3$. As a result, the phases of $RAlO_3$ with larger rare-earth ions (R) will be assumed to be higher temperature and/or lower pressure structures compared with those with smaller R ions from structural point of view.

1) S.Sasaki et al.(1992) Rev. Sci. Instrum. **63**, 1047-1050.
2) O'Bryan et al. (1990) Jour. Mater. Res., **5**, 183-189.

PS11.05.15 OPTICAL INSTABILITY IN INCOMMENSURATE BARIUM SODIUM NIOBATE CRYSTAL. S. V. Ivanova, Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, Moscow 117924, Russia

The distribution of the intensity of the radiation which had passed through the crystal $Ba_2NaNb_5O_{15}$ (BSN) was investigated in a range of 20-500°C. The oscillations of the light scattering intensity near the temperatures of 200°C and 500°C was discovered if the laser beam was propagated in the crystal perpendicular to the ferroelectric c axis and had polarisation direction parallel to this one. Period of oscillations depends on the rate of the temperature change. The second order phase transitions were discovered at 200°C and 500°C using elastic light scattering method /1/.

The experiment consist in direction of the light beam of Ar ion laser (λ =514.5nm , P=30-300mW) on the crystal and registration the scattering intensity passed through its on a screen behind the crystal. Single crystals were grown in Moscow University by the Czochralski method. The samples 2 x 3 x 5 mm were oriented in the [001], [100] and [010] directions.

Ferroelectric crystal BSN with tetragonal tungsten bronze type of structure has been noted for its excellent non-linear optical and electrooptical properties and interesting sequence of the phase transition on cooling, 4/mmm-4mm-mm2. The highest one, at 585°C, is a ferroelectric transition, the other, at about 300°C, is a ferroelastic one. The existence of incommensurate phase in BSN has been postulated and confirmed of different methods /2/.

The dynamics of beam formation and changes in the dielectric material on the microscopic level near the phase transition temperatures of about 200°C and 500°C are not well understood.

1. J.Schneck, J. C. Toledano, C. Joffrin, A. Aubree, B. Joukoff and A. Gabelotaud. Phys. Rev. B, 25, 1766 (1982)
2. S. V. Ivanova. Ferroelectrics, 170, 203 (1995)

PS11.05.16 DIFFRACTION AND PHENOMENOLOGICAL STUDIES OF THE PHASE TRANSITION IN THE MOLECULAR CRYSTAL $[P(CH_3)_4]_2ZnBr_4$. S. Jerebets, R. D. Willett, Chemistry Department, Washington State University, Pullman, WA 99164, USA

$[P(CH_3)_4]_2ZnBr_4$ is a member of the β-K_2SO_4 family. It undergoes a second order phase transition (T=368.7(8)K) from orthorhombic Pmcn phase with cell parameters a=9.505(1)Å, b=16.476(1)Å, c=13.401(2)Å, V=2098.82(34)Å^3 to monoclinic $P12_1/c1$, a=9.502(3)Å, b=16.013(2)Å, c=13.114(3)Å, β=90.47(2)°, Z=4 (at room temperature). This corresponds to a phase transition with a distortion at k = 0. The compound has been investigated by single crystal x-ray diffraction in the temperature interval from 293K to 411K. The behavior of the lattice parameters as a function of temperature was obtained. A Landau free energy function proposed for the phase transitions in A_2BX_4-family compounds has been reexamined and applied to describe the observed sequences of phases driven by $B_{1g}(0)$-representation. The phase diagram in the adopted parameter space is presented and analyzed. The temperature dependence of specific heat and the elastic stiffness constants associated with the order parameter derived from the given free energy function are shown. Intensity data will be collected to determine the structural temperature dependence, which will facilitate better understanding of the changes in the structure through the phase transition.

PS11.05.17 THE THERMAL MACROSTRUCTURE CHANGES IN THE NATURAL PHLOGOPITE CRYSTALS. V.M.Kalikhman, G.A.Kuznetsova, M.S.Metsik. Irkutsk State University, Irkutsk, Russia.

The thermal changes in real macrostructure of phlogopite in the temperature range from 300 to 1300 K have been investigated by the high-temperature X-ray diffractometry method. The monocrystals content the microadmixture of vermiculite and chlorite phase.

The microstructural changes have been determined as the half-width of basal difractional reflections B_{0012}. B_{0012} of only few natural and synthetic fluorphlogopite crystals have been determined to be the same in the thermal range before the formation of high-temperature phase. Another group of specimens was characterized by increase B_{0012} in the temperature range 350-470 K. Lastly B_{0012} was changes for big group of the investigated crystals at the temperature over 600 K. The half-width of difractional reflections B_{0012} has been determined to be constant for the nonadmixtural phlogopite crystals .The low-temperature increase B_{0012} has been observed for the phlogopite crystals with vermiculite admixture. It corresponded to the decrease of phlogopite layer thickness because of vermiculite phase dehydrotation and followinges water migration out of the crystal .The chang of B_{0012} were observed in phlogopite monocrystals contenting the chlorite microadmixture at the temperature over 600 K. Thus individual thermal characterictics of monocrystal phlogopite macrostructure have been determined to be depend strongly on admixtural crystal phase.

PS11.05.18 ISOMORPHIC PHASE TRANSITIONS IN $Li_xV_2O_5$ INTERCALATION COMPOUNDS. H. Katzke, W. Depmeier, Mineralogical Institute, University of Kiel, Olshausenstr. 40, D-24098 Kiel, Germany

The intercalation of lithium ions into the layered structure of V_2O_5 is within certain stoichiometry ranges the result of a topotactic electron/cation-transfer reaction which is used in high density/high capacity solid state batteries operating at ambient temperature.

The intercalation leads in dependence of the external conditions to a series of composition and temperature induced structural phase transitions. These structural phase transitions can be understood by consideration of the symmetry relations between the various phases. They can be described in terms of group-subgroup relationships, despite the fact that most of the phase transitions are first order and several transitions are even isomorphous.