Diorganotin dihalides, R_2SnHal_2 with Hal = Cl, Br, I, belong to the basic chemicals in organotin(IV) chemistry because they are versatile precursors for the preparation of other diorganotin compounds like complexes, hydrolysis products, hydrides and so on. Since the first structural characterization of Me_2SnCl_2 in 1970 by Davies et al. [1] some dozens structures of dihalides were determined but no general classification scheme was evolved. In solid state, many of these dihalides exits as monomers without any intermolecular tin-halide interactions because of intramolecular Lewis-base Lewis-acid adduct formation or because of steric hindrance but especially the common ones with hydrocarbon rests are dominated by intermolecular tin halide interaction with strong effects on intramolecular bond angles and lengths. For this kind of interaction which is often termed *secondary bonding* [2] or *supramolecular architecture* [3] two main types of arrangements were found: 1) side by side with the dipole moments more or less antiparallel (*a*) to each other or 2) one after another with two equal or different tin halide interactions and a more or less parallel (*p*) ordering of the dipole moments.

In the course of a systematical study on the crystal structures of diorganotin dihalides we obtained – in addition to the already known structure types - a lot of new ones which gave us the possibility to develop a general classification scheme for the intermolecular tin-halide interaction. To discriminate the different structure types, our scheme takes into account the dipole-dipole interaction represented by the angle bisector between the halide atoms, the crystallographic symmetry elements between the interacting molecules and a tin-halide respectively tin-tin aggregation plane. The poster will show the limitations and options of our scheme covering oligomeric ($2a$, $4a$) arrangements, the different chainlike ones built up by monomers with parallel ($P_0 - P_2$) or antiparallel ($A_0 - A_3$) orientations of the dipole moments, the chainlike ones built up by dimers [C2($2a_1$)] as well as the band [B(pp)] and sheet [S($2a_1$)] like structure types.

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Keywords: organotin, halides, classification

MS81.P70

Crystal structures of few new β-octamolybdates

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Octamolybdates are important and interesting group of compounds. Among the molybdates, they are the most numerous group of compounds. In addition, there are several types of octamolybdates. Why are they important to study, when their applications are not especially numerous yet?. The reason is a desire to understand the rules governing the formation of certain polymetallate anions. These rules are quite complex, the type of anion depends on the reaction time, concentration and type of reactants. An additional element is the richness of anionic forms and their potential applications in crystal engineering. For a deeper understanding of principia of polymetallate construction, structural studies of a group of newly obtained compounds, have been undertaken. We investigated octamolybdates of aniline derivatives with the general formula NH_2-Ph-$R_{(1\ or\ 2)}$ and mm2 symmetry.

Synthesis: aqueous solution of molybdic acid and amine, acidified with HCl or CH_3COOH was boiled under reflux for 1-24hrs.

Among the most surprising findings is the fact that; short-term synthesis using 4-methylaniline results in octamolybdate, while the result of a long (24hr) synthesis is pentamolybdate. Similar results were observed in the case of 4-iodoaniline. Interestingly, using 3,5-dimethylaniline exclusively trimolybdate is produced, regardless of the reaction time. In the case of 4-fluoroaniline and 4-chloroaniline, 24-hour reactions conducted under the same conditions, have resulted in a complex polycrystalline material, which has not been fully explored yet.

Among anilinium octamolybdates only β-isomers were obtained.

The results indicate that, the creation of a specific polymolybdate type depends on many factors, and structural 'synthons' present in the 'reacting system', may help to describe the resulting structure. However, on their basis, it is much harder to predict resulting anionic species.

All compounds were synthesised for the first time in our laboratory. Structural studies were performed mainly by single crystal methods (Bruker-Nonius), phase composition and structural studies for compound **5** by powder diffraction methods. All compounds were also characterised by IR spectroscopy, SEM, XRD vs. temp and DSC investigations. Some crystallographic data are listed below:

1. $Mo_8O_{26}.4\{NH_2$-C_6H4-$CH_3\}$ – tetrakis(p-toluidynium) β–octamolybdate, Sg. P 2_1/c (14), 8.388(2), 26.669(4), 9.346(3) Å, 103.65(3)º, V=2031.8 Å, Z=2

2. $Mo_8O_{26}.4\{NH_2$-C_6H_4-$F\}$ – tetrakis(p-fluoroanilinium) β–octamolybdate, Sg. P-1(2) 10.567(4), 14.605(3), 15.724(5)Å, 117.16(2), 96.67(4), 97.80(4)º, V=2095.8(8) Å^3, Z=2

3. $Mo_8O_{26}.4\{NH_2$-C_6H_4-$Cl\}$ – tetrakis(p-chloroanilinium) β–octamolybdate, Sg. P-1(2) 10.586(3), 14.705(5), 16.407(4) Å, 116.26(2), 93.43(2), 98.38(3)º, V=2243 Å^3, Z=2

4. $Mo_8O_{26}.4\{NH_2$-C_6H_4-$(CH_3)_2\}$ – tetrakis(2,6-dimethylanilinium) β–octamolybdate, Sg P-1(2), 10.508(5), 11.578(5), 11.686(5)Å, 118.59(5), 93.74(5), 101.146º,V=1204Å, Z=1

5. $Mo_3O_{10}.2\{NH_2$-C_6H_4-$(CH_3)_2\}$ – bis(3,5-dimethylanilinium) trimolybdate, Sg. P-1(2) 8.936(3), 16.729(4), 7.580(2) Å, 92.20(2), 93.138(3), 98.18(3)º, V=1118.4(4)Å, Z=2

Keywords: molybdate, isopolymetallate, catalysis

MS81.P71

Crystal structure of $C_4H_8ONH_2$-$PbBr_3$ by neutron and X-ray diffraction experiments

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$C_4H_8ONH_2$-$PbBr_3$ has a lead-based inorganic-organic perovskites structure. One-dimensional chains of face shearing $PbBr_6$ octahedra are isolated by $C_4H_8ONH_2^+$ cations to be quantum wire, so this material can be regarded as a naturally self-organized one-dimensional system. The crystal structure of the material is orthorhombic with space group of $P2_12_12_1$. $PbBr_6$ octahedra are strongly distorted because of the existence

of oxygen atom of the cations. It is interesting that the structure of inorganic part is highly influenced by the existence of organic molecules in this type of inorganic-organic hybrid materials.

We have been studying the crystal structure and chemical bonding in the material by combining the data obtained by single crystal neutron and X-ray diffraction experiments. It is difficult to decide the atomic positions of organic part in the material from only X-ray diffraction data because heavy lead atom is coexisting in the structure. Neutron diffraction is suitable way to analyze the crystal structure of this type of materials. Neutron diffraction data was collected at 120K using time-of-flight single crystal neutron diffractometer "iBIX" constructed at J-PARC. X-ray diffraction data was also collected using imaging-plate single crystal X-ray diffractometer at 120K. From the obtained crystal structure, orientation of the cations and distortion tendency of $PbBr_6$ octahedra suggests the existence of chemical bonding between lead and oxygen atoms. In addition, the existence of hydrogen bonding between the nitrogen atoms of the cation and bromide atoms of inorganic chain is also suggested. Electron density distribution analysis by maximum entropy method was performed to investigate the nature of chemical bondings in the material. Overlapping of electron density is seen between lead and bromide atoms because of covalent characteristic of the bonding. On the other hand, because no overlapping of electron density is seen between lead and oxygen atoms, it is expected that the bonding has ionic characteristic. Each of inorganic chains is connected by electrostatic interaction through the cations.

Keywords: inorganic-organic, single crystal, bonding

MS81.P72

Synthesis, structural reinvestigation and physical properties of alkali hexatitanate

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The alkali hexatitanate having the tunnel structure form a class of compounds that can exhibit interesting physical properties such as bronze-type TiO_2, [1], [2] and Li ion conductor in ramsdellite-type $Li_2Ti_3O_7$, [3], [4] as well as their intriguing structural features. In the tunnel-type alkali and alkaline earth hexatitanate $A_2Ti_6O_{13}$ (A = H, Li, Na, K, Sr and Ba) systems, several compounds are reported until now. $H_2Ti_6O_{13}$ and $Li_2Ti_6O_{13}$ is known as metastable form by ion-exchange method. However, crystal structure and physical properties of $H_2Ti_6O_{13}$ and $Li_2Ti_6O_{13}$ has not been reported. In the present study, we successfully synthesized polycrystalline sample of $H_2Ti_6O_{13}$ and $Li_2Ti_6O_{13}$ by ion-exchange method from $Na_2Ti_6O_{13}$ [5]. The crystal structure was determined ab-initio structure determination by powder X-ray and neutron diffraction data. In addition, the structural validity was confirmed by bond valence sums calculation, and the data of MAS-NMR, and the results of the present first-principles calculation by the FLAPW method. The result of crystal structure on $Li_2Ti_6O_{13}$ showed LiO_4 plain tetra coordinates. This Li-O coordination is not normal, and different from that in other $A_2Ti_6O_{13}$ compounds. On the other hand, the crystal structure of $H_2Ti_6O_{13}$ showed OH-O hydrogen bonding, and ordered arrangement of proton is seen in the crystal structure.

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Keywords: oxide, structure solution, powder diffraction

MS81.P73

Critical behaviour of Ti doped manganite $La_{0.67}Ba_{0.33}MnO_3$

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The critical properties of Ti doped $La_{0.67}Ba_{0.33}MnO_3$ around the paramagnetic ferromagnetic phase transition were investigated based on the data of static magnetic measurement around Curie temperature T_c. It is found that the mean-field model is the best one to describe the critical phenomena around the critical point. The magnetic data analyzed in the critical region using the Kouvel-Fisher method yield the critical exponents in $La_{0.67}Ba_{0.33}Mn_{0.98}Ti_{0.02}O_3$ of $\beta=0,589\pm0,015$ with $T_c=310,852\pm0.190$ (from the temperature dependence of spontaneous magnetization below T_c) and $\gamma=1,020\pm0,024$ with $T_c=310,111\pm0.143$ (from the temperature dependence of inverse initial susceptibility above T_c) and $\delta=2.741$ is determined separately from the isothermal magnetization at T_c. These critical exponent obtained by this method obey the Widom scaling relation $\delta=1+\gamma/\beta$, implying that the obtained values of β and γ are reliable.

Keywords: critical, perovskite, modelling

MS81.P74

The structure and magnetic properties of the solid-solution: $Na_2(Zn,Co)SiO_4$

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Na2ZnSiO4, a homeotype of wurtzite, is of interest as a host structure for the creation of potentially interesting magnetic materials. The solid-solution series Na2(Zn(1-x) ,Cox)SiO4 was synthesized by high temperature ceramic methods. The resulting blue compounds possessed band gaps of ~1.7 eV, independent of Co2+ doping percentage. Initial powder X-ray data were collected on a Rigaku Miniflex II diffractometer with copper Kα radiation and later high resolution data were collected on the 11-BM diffractometer at the Advanced Photon Source, Argonne National Laboratory with a wavelength of 0.413606 Å. The resultant data verified that the Co2+ and Zn2+ ions were randomly distributed forming a single Zn-Co phase from 0 < x < 0.50. Rietveld analysis converged to X2 of 1.89 and R = 2.49 %. All atoms possessed tetrahedral environments, but those associated with the sodium ions were highly distorted. The high resolution data revealed a more complicated structure than predicted with evidence for aperiodicity in the crystal structure. Magnetic moment versus temperature data were collected from 2 K to 350 K under 1000 G field. The data conformed to a Curie-Weiss plot (1/χ vs. T), which represents primarily paramagnetic behavior although the positive Y intercept indicates the presence of short-range antiferromagnetic interactions at high temperature. At low temperatures, a paramagnetic-antiferromagnetic interchange occured with a Néel temperature at 5 K. Keywords: solid-solution, rietveld, anitiferromagnetism