12-Amorphous, Imperfectly Ordered and Quasi-periodic Materials

PS-12.02.10 MOLECULAR ORIENTATION IN PLASTIC CRYSTAL OF 1-BROMOADAMANTANE. By H. Takakura*, M. Shiomo and N. Akiwa, Department of Physics, Kyushu University, Higashi-ku, Fukuoka, Japan.

Some of adamantane 1-monosubstituted derivatives have plastic phase just below melting point. 1-bromoadamantane (C11H15Br, Br-ADM) is one of the suitable compounds for studying molecular orientation and phase transition property because bromine atom has relatively large X-ray scattering amplitude. Br-ADM has semi-ordered and ordered phases below plastic phase [Clar, T., et al., J. Chem. Soc. Faraday Trans., 1977, 73, 1224-1231]. X-ray single crystal Bragg data in three phases were measured at 244K, 298K and 340K. Temperature dependence of lattice parameters were also determined from 244K to 346K. The plastic phase crystallizes in the cubic space group (Pm3m, a = 10.079(1)Å). The Crystal structure was analyzed by using rigid-model and then we proceed to maximum entropy (ME) analysis. The most plausible ME-map is shown in Fig. 1. It can be deduced that the molecule orients its molecular principal Br-C axis along a six equivalent < 100 > direction rotating around the molecular principal Br-C axis. Moreover, it seems that the center of mass of each split molecule slightly deviates along the four-fold axis. The semi-ordered phase crystallizes in the orthorhombic space group (Pmcn, a = 12.102(2)Å, b = 6.902(1)Å, c = 13.624(2)Å) where tumbling motion of molecules around the Br-C axis occur. The ordered phase crystallizes in the monoclinic space group (Pbcn, a = 10.134(1)Å, b = 6.685(1)Å, c = 12.315(2)Å, β = 90.05(1)°) and the Br-C axis orient alternatively in (011) and (011) directions parallel along the c-axis. This structure is quite similar to that of Cl-ADM (Poulin, M. et al., Acta Cryst., 1989, B45, 404-411) which shows only ordered phase below the plastic phase.

Fig. 1 The most plausible ME-map in (001) plane.

PS-12.02.11 INVESTIGATION OF THE REAL STRUCTURE OF NON-STOCHIOMETRIC SPINELS WITH DIFFERENT COMPOSITIONS. By S. V. Tsybul'ko, L. P. Solov'yeva and G. N. Kryukova, Institute of Catalysis of the Russia Academy of Sciences, Novosibirsk, Russia

The structure of several nanometersized non-stoichiometric spinels has been investigated by X-ray powder profile analysis (Rietveld and Warren-Averbach methods) and HREM. The Mg-Al spinel was derived from the aluminum hydroxide which has been modified by magnesium (9.45%MgO·90.65%Al₂O₃) at 1273 K. Vacancies in the 8a tetrahedral and 16d octahedral positions and atoms in the 8b (tetrahedral A') and 16e (octahedral B') positions have been found. The structure formula is (Mg₈₋ₓAlₓ)₄⁺Al₃⁺[Al₉₋₅yAl₃₋₅]₆⁻[P₉₋₇yP₅₋₇]₀⁻. It was found that the cations occupy A' and B' positions due to the formation of stacking faults. The model of stacking faults has been proposed. The Zn-Al spinel was derived at 1023 K from α-Al₂O₃ and β-Zn(OH)₂. The particles of this spinel consist of incoherent microblocks with sizes of 50 Å. The structure formula has been determined as (Zn₉₋₅yAlₓ)₄⁺[Al₃₋₅yAl₉⁻₅]₆⁻[P₉₋₇yP₅₋₇]₀⁻, where the vacancies are at the octahedral sites. Two anions (ca. from 0.2 up to 4) seem to be OH- groups. The Co₃O₄ spinel was prepared from cobalt nitrate. The structure formula of this sample is Co₂⁺[Co₃O₄₋₁]⁻[Co₃O₄₋₂], where x is assigned to the 16e octahedral position. Due to the presence of cations at the 16e position there are clusters or stacking faults with the structure of CoO in this sample.

PS-12.02.12 CONNECTION BETWEEN THE AVERAGE HEXAGONALITY AND ANOMALOUS PHOTORESPONSE OF FAULTED SBS 2101 POLYTYPE.

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According to recent investigations [M. Farkas-Jahnke, Z. Márkus, 1993, to be published] the lattice parameters of ZnS polype crystals can be related to the hexagonality of their stacking. As the hexagonality means the proportions of the hexagonal stackings to the whole number of stackings, this concept can be used also for polype with stacking faults, and the average value of lattice parameter parallel to the hexagonal c-axis of the crystal can be correlated to the average hexagonality of a randomly faulted lattice region. The average hexagonality of the investigated region, and also the relative rate of occurrences of four and five layer structure elements can be obtained by using a direct method based on the diffracted intensity distribution measured along low lines with Miller indices h-k-3n on oscillating X-ray patterns of the crystals. In such faulted regions of the lattice, where a random distribution of hexagonal and cubic stackings are present, the lattice will have an average hexagonality, and corresponding a common average lattice parameter value. This corresponds to an energy gap between the hexagonal and the cubic energy gap value.

Photoreactivity measurements were taken from crystal parts connecting pure 2H, 4H, 6C other periodic polype type to such randomly faulted regions. Appearance of photactivity could be correlated to these adjoining pure and faulted regions and also to the presence of asymmetrical structure elements /bdc or hlc stackings/ among the layer structure elements of the faulted lattice.