

intercalated $\text{Na}_{1-x}\text{CoO}_{2-x}$, spin-state transitions of the Co^{3+} ion in LaCoO_3 , a metal-insulator (MI) accompanied by structural transition in $\text{LnBaCo}_2\text{O}_{5.5}$ (where Ln is a rare earth). We present our recent results on crystal growth of cobaltites: $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{LnBaCo}_2\text{O}_{5+x}$ using Optical Travelling Solvent Floating Zone method. The crystals were studied by different techniques and some of results will be discussed. A very small Sr doping level (0.2%) drastically changes magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ as found using inelastic neutron scattering and magnetisation measurements. This can be explained assuming that the slight hole doping in LaCoO_3 matrix creates magnetic polarons, which leads to a spin-state transition of Co^{3+} . On the background of the spin-state and orbital-ordering transitions of the Co^{3+} ion in $\text{LnBaCo}_2\text{O}_{5+x}$, the system shows a metal-insulator transition accompanied by structural one at temperatures above room temperature, three different magnetic phases below room temperature and a structural transition at temperature above MI transition. All these properties can be tuned by a kind of the rare earth ion and oxygen stoichiometry. Structural, magnetic and transport studies of layered cobaltites $\text{LnBaCo}_2\text{O}_{5.5}$ (Ln=Tb, Nd) especially near metal-insulator transition will be presented.

Keywords: crystal growth, crystal structure and properties, transition metal-rare earth oxides

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Micro-crystallographic structure of $\text{Sr}_2\text{RuO}_4/\text{Sr}_3\text{Ru}_2\text{O}_7$ eutectic crystals grown by floating zone method

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Directional solidification at high temperature gradients by Infrared Image Furnace of $\text{Sr}_2\text{RuO}_4/\text{Sr}_3\text{Ru}_2\text{O}_7$ eutectic crystals has shown that mainly two distinct eutectic morphologies occur, a regular lamellar structure and a wavy lamellar structure. High resolution X-ray analysis has shown that the two phases are stacked in a multilayer structure along their c-axis. The analysis of X-ray diffraction patterns by the Rietveld method has been used to determine the percentage of each phase in crystals grown starting from a different composition of the polycrystalline rod. The morphology of crystals with different fraction of Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$ phase has been investigated by optical and electron microscopy. Electron back scatter diffraction (EBSD) technique was used to characterize the crystallographic match at the interface between Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$ phases. In particular the crystallographic match has been investigated for interfaces along plane parallel and perpendicular to the growth direction. Moreover, the misorientations for sharp and wavy lamellar structure have been thoroughly investigated with EBSD technique.

Keywords: eutectic crystallization, float zone growth, back-reflection electron Kikuchi pattern

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Chirality realized only in the crystalline state: Inorganic and organic compounds

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Some compounds exhibit chirality only in the solid state through chiral supramolecular arrangement of achiral compounds or through trapping a chiral conformation of a flexible achiral compound. The chirality must be measured in the solid state, however, the macroscopic anisotropies of crystals, Linear Birefringence (LB) and Linear Dichroism (LD) cause parasitic artifact signals in CD (Circular Dichroism). Thus, we have designed and built a Universal Chiroptical Spectrophotometer (UCS-1¹, UCS-2²) and devised a set of procedures for obtaining artifact-free CD and CB (circular birefringence) based on the Mueller matrix method. We have studied inorganic crystals, $\alpha\text{-Ni}(\text{H}_2\text{O})_6 \cdot \text{SO}_4$ and $\text{Ni}(\text{H}_2\text{O})_6 \cdot \text{SeO}_4$, which exhibit natural optical rotatory power only in the crystalline state. Using UCS-1, we could show that true CD and CB signals satisfy the Kramers-Kronig relationship.³ Further we have discovered a remarkable sign inversion of single crystal CD in one of the Ni *d-d* transitions at near liquid nitrogen temperatures, although the crystal structure hardly changes.⁴ With UCS, we have also observed birefringence of a chiral cubic crystal of class T, NaClO_3 and NaBrO_3 , along the [100] directions for the first time and proved that the anisotropy is of an intrinsic nature. Only the non-birefringent axis is along the [111] directions.⁵ Photocyclization of dynamically achiral organic compounds also produces enantioselective reaction products if carried out in chiral crystal environment.⁶

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Structure-property relationship in the crystals of chiral amino acids and their racemic counterparts

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Understanding structure-property relations in crystalline amino

acids is an important challenge. The structure-forming units in the crystals of amino acids are similar to those in the biopolymers: robust head-to-tail chains of molecules linked by hydrogen bonds are preserved even on polymorphic transformations. Packing of the head-to-tail chains can mimic polypeptide structures: helical structures, β -sheets, amyloids. Knowledge about the temperature and pressure-induced changes in these crystals can help to understand better the contributions to the dynamic properties of proteins related to the intrinsic motions of structural fragments. Besides, crystalline amino acids are important materials with non-linear optical and piezoelectric properties. The structures and properties of the chiral and racemic crystals of amino acids are remarkably different. In the present contribution we illustrate this using several selected examples (L- and DL-serine, L- and DL-cysteine, L- and DL-alanine, L- and DL-phenylalanine, L- and DL-phenylglycine) studied at variable temperatures (the range 3-450 K) and variable pressures (up to 1-10 GPa, depending on the compound and the technique) by single-crystal and powder X-ray diffraction, IR-, Raman, inelastic neutron scattering spectroscopy, and calorimetry. The differences in the structural response to variations in temperature and pressure (different values of compressibility and thermal expansion, different strain anisotropy, different stability with respect to phase transitions induced by cooling, heating or increasing pressure). The study was supported by Integration projects #49 and #110 of SB RAS, a grant from RFBR (05-03-32468) and grants from BRHE (NO-008-XI and RUX0-008-NO-06).

Keywords: crystalline amino acids, structure-properties relations, head-to-tail chains

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Chiroptical properties of *N*-benzoylglycine crystals

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Despite the fact that *N*-benzoylglycine is an achiral molecule, chiral crystal is spontaneously formed. The molecules are helically arranged through the hydrogen bond chains in the crystal. We measured the optical rotatory dispersion by High Accuracy Universal Polarimeter (HAUP). The magnitudes of optical rotation along the helical axes were larger than those perpendicular to the helical axes.

Keywords: chiroptical properties, *N*-benzoylglycine crystals, chiral crystal

MS.14.4

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A solution to the problem why chiral hydrophobic amino acids form crystals with $Z' = 2$

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Chiral amino acids that do not have functional groups in their side chains (hydrophobic amino acids) regularly form crystals with two molecules in the asymmetric unit (with different side-chain conformations as shown for L-valine). In contrast, racemates of

the same compounds always form crystals with $Z' = 1$. What is the origin of the difference between enantiomeric and racemic crystals? No attempts have apparently been made to answer this fundamental question concerning the essential building blocks of life. The present investigation shows that by using a combination of crystallographic, statistical and theoretical methods it is indeed possible to explain the observed behaviour, and furthermore tell why these amino acids do not undergo racemic separation upon crystallization, but rather choose to form racemates in the solid phase.



Keywords: *ab-initio* calculations, amino acids, crystal packing

MS.14.5

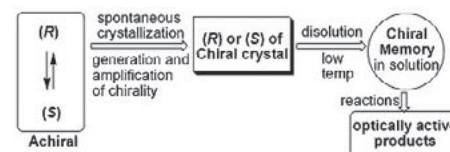
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Control of chirality by spontaneous crystallization and absolute asymmetric synthesis in fluid media

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Asymmetric generation influenced by a chiral crystalline environment is considered an attractive methodology for obtaining optically active compounds from achiral compounds. In recent years, the solid-state photochemical reaction using chiral crystals in a variety of new systems has progressed to such an extent that it can now be regarded as an important branch of organic chemistry. Furthermore, a new methodology using molecular chirality in crystal as a source of chiral memory in solution was explored. The chirality can be effectively transferred to optically active products by asymmetric reactions involving a nucleophilic carbonyl addition and intermolecular photochemical reaction. Now we have found that achiral coumarin-3-carboxamide crystallized in a chiral fashion, and the molecular chirality could be transferred to products by intermolecular 2+2 photocycloaddition reactions, cyclopropanation, and the reaction with carbenes in fluid media with high enantiomeric excesses.



Keywords: chiral space groups, asymmetric synthesis, organic synthesis

MS.15.1

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Small beams can play big roles in macromolecular crystallography

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