

MS26 Aperiodic and modulated structures

Chairs: Prof. Sven Lidin, Prof. Alla Arakcheeva

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Phase transitions in organic-inorganic hybrids

Anna Gagor¹

1. Institute of Low Temperatures and Structure Research PAS,
Wrocław, Poland

email: a.gagor@int.pan.wroc.pl

The organic-inorganic hybrids from the halometallate family are explored as functional materials. Many of them crystallize in polar space groups exhibiting non-linear optical, piezoelectric and ferroelectric properties. The iodometallates stand out from other halide connections having useful optical properties like thermochromism and photochromism. The revival of the interest in these materials has vitality been boosted by the application of $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ in III generation 'perovskite' solar cells [1].

Hybrids that bear Pb^{2+} , Sn^{2+} , Sn^{3+} , Bi^{3+} , Sb^{3+} halide units in combination with organic counter-ions exhibit tremendous structural diversity due to the variety of the anionic substructures that may be adopted. The basic units: MX_6 octahedrons or MX_5 square pyramids may form numerous discrete or polymeric connections including edge-sharing, vertex sharing, and face-sharing motifs. The poly-anionic structures depend on the size and symmetry of organic cations, quantity, and distribution of proton and donor centers, and the size of the halogen atoms. Depending on the cation symmetry, size and amount of the dipole moment and donor potential the cations are dynamically disordered. The change in the dynamic states of the cations entails changes in the symmetry generating phase transitions. The interplay between the short-range intermolecular forces, the flexibility of the anionic units and associated with them steric effects, as well as the thermally activated dynamic of cations may stand at the origin of the formation of complex structures, including modulated phases, and complex phase sequences.

In this contribution phase transitions in the ferroelectric $(4\text{-NH}_2\text{C}_5\text{H}_4\text{NH})\text{SbCl}_4$ (4-APCA) and thermochromic $(\text{CH}_3\text{C}_3\text{N}_2\text{H}_4)\text{SbI}_4$ hybrids are presented. 4-APCA is modulated within three structural phases [2]. The incommensurately modulated phase is stable between 270 and 304 K. At 270 K, a *lock-in* phase transition is observed for the commensurate ferroelectric phase. Further cooling leads to commensurate–incommensurate transformation which is accompanied by the formation of a dense domain structure which disappears after the conversion to the low-temperature phase. The differences between the structures of the subsequent phases should be perceived as the mutual displacements of the anionic groups and rearrangements of 4-AP mediated by the hydrogen bonds. The crystals of $(\text{CH}_3\text{C}_3\text{N}_2\text{H}_4)\text{SbI}_4$ undergo a phase transition to incommensurately modulated phase around 295 K which is associated with a subtle distortion of $[\text{SbI}_4]_n^-$ chains of edge-shared

octahedrons [3]. The driving force is the change in stereochemical activity of the Sb^{3+} lone-pair. The ordering of 2-MIm^+ counter-cations takes place at lower temperatures and affects the lattice with a step-like contraction in all directions.

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