Poster Presentation

MS047.P14

Ammonium Sulphate phase transition studied by ab initio calculations

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New ferroelectric materials are mostly desired because of their application in ferroelectric random access memories (FeRAM), ferroelectric field-effect transistors (FeFET) and other new advanced electromechanical and optical devices. [1] Recently the domination of perovskite type materials as the only useful ferroelectrics was broken by the discovery of novel hybrid inorganic-organic, organic and supramolecular ones, with high values of spontaneous polarization. [2] The current course in the strategy of ferroelectric crystal engineering is to mimic the known mechanisms of phase transition (eg. KDP's one), reproducing it with tectons providing greater physical response. Recent studies shown that hydrogen-bonded ferroelectrics are one of the most prospective materials. [2] The main goal of our work is to clarify the Ammonium Sulphate's (AS) mechanism of ferroelectric phase transition with modern quantum chemical calculation methods. Despite many surveys AS ferroelectricity is still not well understood. Simultaneously AS can be the precursor of new MOF ferroelectric materials.

The phase transition of AS occurs at Tc = 223 K. [3] Above critical temperature, in paraelectric (PE) phase, it belongs to Pnam centrosymmetric space group. Below Tc in ferroelectric (FE) phase it belongs to the polar Pna2(1) space group. All currently performed ab initio calculations are based on the series of single-crystal X-ray diffraction measurements, which were completed during cooling from 298 K to 148 K.

Born-Oppenheimer molecular dynamics simulations were aimed to give an accurate description of the thermal evolution of AS structure. The analysis of dynamic changes occurring in AS structure was performed by simulations in different point groups and several conditions in NVT ensemble. Moreover, the molecular dynamic ramping temperature calculations were done and gave us a possibility to explain the structural changes along AS phase transition. The use of symmetry 1 allows to keep the orientation of ions and their arrangement, according to the experimental structure for both phases. Application of point group symmetry 1 in the calculations led to the reconstruction of all H-bond interactions in both phases.

Quantitative methods for classifying chemical bonding were used to get a profound information about the structure and bonding. This was done in the framework of QTAIM method. Wave-function were calculated for geometries taken from two experimental data sets representing crystal structures in PE and FE phases.

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Keywords: H-bonded ferroelectrics, phase transition, ab initio calculations