

**HYDROTHERMAL GROWTH OF PIEZOELECTRIC CRYSTALS
HOMEOTYPES OF α -QUARTZ**

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Growth and study of α -SiO₂, AlPO₄, GaPO₄ and α -GeO₂ single crystals with quartz structure are realized. Comparison of the crystal growth conditions (influence of solvents, T-P parameters, seed sizes and orientations, etc.), crystal quality (controlled by Polarized microscopy, IR-spectroscopy, X-ray topography, etc.), and piezoelectric properties in this material family have allowed to allocate and explain the main features on chemical side of hydrothermal crystal growth and physical properties of grown crystals. By this way during last years growth conditions were optimized and new growing solutions for α -quartz homeotype crystals were found. More interesting results, as some piezoelectric properties of GaPO₄ and α -GeO₂, such are coupling coefficient and piezoelectric constants, were observed to be higher than the α -quartz one. The study and development of new techniques of hydrothermal crystal growth for GaPO₄ and α -GeO₂ single crystals open opportunities for the synthesis of new α -quartz homeotype crystals with optimum properties for application in piezo-engineering.

**Keywords: HYDROTHERMAL CRYSTAL GROWTH,
PIEZOELECTRIC MATERIALS, PIEZOELECTRIC PROPERTIES**

**USING SAXS AND WAXD FOR *IN SITU* OBSERVATION OF
CRYSTALLISATION FROM LIQUID PHASES**

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Our understanding of the process of phase transformation and creation of crystalline materials from liquid phase precursors has been continually limited and updated by the size and timescales at which available experimental techniques can probe a transforming system. This contribution describes in situ studies of the process of crystallization following the time development of both size and structure in nucleating systems using synchrotron small and wide-angle x-ray scattering. The design and choice of operating equipment and nucleating systems was governed by the need to maximize the diffraction and scattering signals from experiments in which the mass fraction of solid phase was expected, at least initially, to be low. Accordingly experiments were performed at the highest possible supersaturation where the nucleation rates and hence mass of crystalline phase is maximized and with crystallizing components which are inherently good x-ray scatterers. The contribution will describe the use of stopped flow and continuous steady state plug-flow reactors to perform crystallizations which result from rapid reaction or 'drown outs'; a specially constructed batch classifying crystallizer with stirrer and classifying zone for slow cooling crystallizations; lindemann tubes to allow controlled cooling for study of melts. We report the first x-ray characterization of metastable forms of benzamide, para-azoxyanisole and 8OCB; we show how it is possible to achieve time resolutions of the order of seconds at low mass fractions, we show how small angle particle scattering precedes diffraction during nucleation and we demonstrate how the orientation of crystals in a fluid flow may be determined.

Keywords: CRYSTALLISATION IN SITU NUCLEATION

USE OF ATR-FTIR FOR CONTROL OF BATCH CRYSTALLIZATION

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Batch crystallization is a challenge for real time control due to the difficulty in measurement and control of supersaturation. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy provides a unique opportunity for supersaturation measurement because the presence of crystals in a slurry does not interfere with the solution phase measurement. When coupled with an automated laboratory reactor such as the LABMAX, it is possible to control batch crystallization without the use of kinetic models. Examples for pH swing and cooling batch crystallizations will be presented.

Keywords: FTIR CRYSTALLIZER CONTROL

**EXPLORING THE MAGNETIC, ELECTRICAL AND STRUCTURAL
PROPERTIES OF TRANSITION-METAL OXIDE PEROVSKITES**

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The remarkable magnetoresistive properties of the manganese based perovskites, LnAMnO₃, stem in part from the simultaneous presence of both localized and itinerant d-electrons. We have been interested in studying structure-property-composition relationships in other transition metal oxides where this condition may be met. Using variable temperature synchrotron and neutron powder diffraction, electrical resistivity and magnetic susceptibility measurements we have characterized the electrical, magnetic and structural properties of two different classes of perovskite based compounds. The double-cell perovskites, SrAMnMoO₆, SrAMnRuO₆ (A = Sr, La) and Sr₂VMoO₆, provide an opportunity to explore how the electronic, magnetic and structural properties are impacted by changes in the electron count and covalency of the transition metal-oxygen bond. These compounds show a wide variety of electrical and magnetic behavior, ranging from Pauli paramagnetic conductors, to spin glass behavior, through half-metallic electronic conductivity, to Mott-Hubbard insulators. The phase transitions and physical properties of the double perovskites, REBaMO_{5+w} (RE = Nd, Sm, Tb, Y; M = Fe, Co), are ideal for exploring the impact of subtle changes in the crystal structure on the magnetic and electrical transport properties. The driving forces behind charge, orbital and magnetic order are revealed by investigating the structure-property relationships in these materials.

Keywords: PEROVSKITES, TRANSITION METAL OXIDES, POWDER DIFFRACTION