

The high crystal quality of the as-grown crystals as well as the efficiency of the substitution was pointed out by room-temperature single-crystal X-Ray Diffraction (XRD) data. The evolution of the structural distortion with the rise of substitution rate from ambient temperature to high temperature (near 1050°C) was followed by powder X-Ray Diffraction and Raman scattering analyses. Both electrical and optical twins were refined using Shelxl 97 software. The substitution rate and its distribution homogeneity along different crystal were carefully examined by Energy Dispersive X-ray analyses.

Keywords: quartz, solid-solution, X-ray

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Crystallographic and kinetic study of octa-coordinated hafnium(IV) complexes

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Zirconium and hafnium show extremely similar chemical properties and occur together in nature. Zirconium ore (*a.k.a.* Zircon – ZrSiO₄) is found to always contain hafnium as an impurity (1-5%), and separation of these two metals is very difficult due to their near identical chemical properties.

The aim of this study was to investigate the chelating behaviour of tetrachlorido hafnium(IV) (HfCl₄) with different organic bidentate ligands e.g. trifluoroacetylacetone (tfaaH), hexa-fluoroacetylacetone (hfaaH) and 8-hydroxyquinoline derivatives (OxH) and the characterization of the new compounds obtained from this by means of single crystal X-ray crystallography and UV/Vis spectroscopy. Optimal reaction conditions was found for different substituted L,L'-bidentate halido-hafnium complexes. Any small differences in solution behaviour, whether it being reaction mechanism, solubility, coordination modes, equilibrium behaviour, etc., could possibly be exploited in developing novel separation techniques for the two metals. The structures of six new complexes, namely the [Hf(tfaa)₄] [1], [Hf(OH)(hfaa)₃] [2], Hf(dbm)₄ [3], [Hf(Ox)₄] [4] [5], [Hf(5,7-diMe(Ox))₄], [Hf(5,7-diBr(Ox))₄], [Hf(5,7-diCl(Ox))₄] were determined. This enabled the identification of products for kinetic studies and increased the available pool of these rare compounds in literature. The crystallographic characterization of all these complexes will be presented.

As part of the preliminary kinetic investigation the formation of the above complexes, i.e., the stepwise reactions between HfCl₄ and OxH ligands were followed by means of stopped-flow and UV/Vis spectroscopy. A total of five reactions were observed for the stepwise coordination of OxH to the HfCl₄ complex.

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Anion order in perovskite RTa(O,N)₃ and pyrochlore

R₂Ta₂(O,N)₇ where R = La, Ce, Pr

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Anion order in RTaON₂ perovskites and R₂Ta₂O₅N₂ pyrochlores is closely tied to physical properties, particularly the dielectric properties. Reports on alkaline-earth ATaO₂N perovskites vary from fully ordered to completely disordered. [1], [2], [3], [4], [5], [6]. Recent studies of SrTaO₂N using variable temperature NPD provide the most compelling evidence to date of local cis-ordered TaO₄N₂ units connecting to make zig-zag chains.[7] Does this phenomena persist when the oxide anions are in minority (local TaO₂N₄ units) such as the case with perovskite CeTaON₂ and PrTaON₂?

The symmetry of ATaO₂N and RTaON₂ oxynitride perovskites can be lowered from the cubic aristotype by {a} octahedral tilting, {b} anion ordering, and/or {c} out-of-center displacements of Ta(V) ions. Various combinations of these distortions lead to a large number of possible structures. Differentiating these structures using X-ray diffraction can be challenging as the distortions are subtle and the anion order is not necessarily complete. In this presentation we use symmetry analysis, computational modeling (total energy minimization), and Raman spectroscopy to augment diffraction studies of structural distortions in these compounds.

Oxynitrides that crystallize with structures that possess chemically distinct anion sites often show considerable chemical order of the oxide and nitride ions. One structure type that offers this possibility is the pyrochlore structure. Oxynitride pyrochlores R₂Ta₂O₅N₂ where R = La, Pr, Ce have been prepared for the first time using a unique, selective-oxidation precursor, BaO₂. Synthesis and characterization of these compounds will be presented, including a discussion of site ordering preferences of the anions.

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Diffuse scattering in substitutionally disordered perovskites

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Perovskites ABO₃ are the subject of an enormous material engineering effort. This reflects the fact that a wide range of physical properties can be gained with different compositions, where both cation sites can be occupied by two or more different species. One of the most prominent examples is that of ferroelectric relaxors, for which mixing cations greatly enhances electromechanical qualities. The variety of properties in these compounds is a derivative of atomic scale phenomena. Therefore, some local probe experiment is an essential part of any structure-property investigation. Diffuse scattering (DS) can be a method of choice for such studies as it contains information about atomic correlations and thus essentially any type of collective phenomena.

The morphology of DS effects in perovskites can be, in most of the cases, related to the symmetry of the most prominent phonon modes.

More detailed analysis reveals, however, how compositional disorder sets up a local strain field and couples to soft modes preventing their condensation into a low symmetry phase. We study, by means of DS experiments and atomistic modelling different ferroelectric compounds that exhibit this type of behaviour [1]. In the case of $\text{KNb}_{1-x}\text{Ta}_x\text{O}_3$ substituting ferroelectrically active Nb atoms with Ta (up to high values of x) does not alter significantly the tendency for the system to host polar BO_6 chains. It does however constrain the transverse correlation of chains (the fact observed experimentally for similar, BaTiO_3 -related compounds [2]). For $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ molecular dynamics simulations for different realizations of B-site partial disorder enables extraction of the conditions necessary for the existence of polar order. At the same time it is shown that the DS observed for this compound is not directly related to so-called polar nano-regions. $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ are among the other materials being analyzed.

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Keywords: ferroelectrics, diffuse scattering, atomistic modelling

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Orbital Ordering of Co^{3+} Intermediate-Spin State in RT ferromagnet $\text{Sr}_3\text{YCo}_4\text{O}_{10.5}$

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$\text{Sr}_{1-x}\text{R}_x\text{Co}_4\text{O}_{10.5}$ ($R = \text{Y}$ and lanthanide, $0.2 < x < 0.25$) has been found recently as a room temperature ferromagnet with $T_C \sim 340$ K, which is the highest T_C among perovskite Co oxides [1]. The crystal structure is formed with the CoO_6 octahedral layers and the $\text{CoO}_{4.25}$ layers, which stack along c axis alternatively. By powder x-ray diffraction, the orbital state of Co^{3+} ($3d^6$) was evaluated from the anisotropy of the CoO_6 octahedron in the ferromagnetic phase, and the e_g orbital ordering of intermediate spin (IS) state was proposed as an origin of the ferromagnetism [2]. Therefore, the orbital ordering and spin-state of Co^{3+} have been investigated using a resonant x-ray scattering technique [3].

A resonating signal with a $\sigma \rightarrow \pi$ scattering component was observed at $(h\ 0\ 0)$, where $h=2n+1$ (n : integer), near the $1s \rightarrow e_g$ transition energy of Co. This provides direct evidence of not only e_g orbital ordering but also the existence of the IS state. Moreover, we suggest that the ferrimagnetism is induced by the e_g orbital ordering of the IS state of Co^{3+} . The peculiar e_g orbital, spin-state, and magnetic orderings are also discussed.

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Keywords: orbital ordering, spin-state ordering, resonant X-ray scattering

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Total neutron scattering in the α -quartz type materials for piezoelectric applications.

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Quartz type materials belong to the $P3_121$ or $P3_221$ space group with formula $A^{\text{IV}}\text{O}_2$ or $A^{\text{III}}B^{\text{V}}\text{O}_4$. The structure consists of a helical chain of tetrahedra along the z -axis. In the quartz family of materials, the thermal stability of the α -phase is linked to the tilt of the tetrahedra around a two-fold axis, which is the mechanism of the α - β phase transition. This behaviour depends on the nature of the cations at the center of the tetrahedra. Thermal stability in the α -quartz type materials was studied by total neutron scattering on the GEM diffractometer at the ISIS spallation neutron source. Average structures have been refined and atomic pair distributions have been generated. Analysis by reverse Monte Carlo modelling of our total scattering experiments in this group of materials show that the degree of disorder in the instantaneous structure increases well before the phase transition for materials exhibiting an α - β phase transition. This dynamic disorder in the oxygen sub-lattice is at the origin of the rapid decrease of the piezoelectric properties at high temperature. This occurs for example at close to 500K in α -quartz, well below the α - β transition at 846K. We show that the chemical nature of the cations (size, number of electrons) in the tetrahedra can be used to improve the thermal stability of these materials [1], [2]. In the case of GaAsO_4 , which contains the largest cations and is the most distorted in this group of materials, the degree of dynamic disorder is limited even at temperatures up to the decomposition of the material around 1300K.

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News on mullite and mullite-type compounds

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Synthetic forms of the mineral mullite represent one of the most important constituents of high-temperature ceramics. It can be synthesized in a solid-solution series with general composition $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ where x ranges between 0.18 and 0.88 [1]. Within this compositional range, there are two thermodynamically stable compounds with $x = 0.25$ (3:2-mullite, $3\text{Al}_2\text{O}_3 : 2\text{SiO}_2$, $\text{Al}_{4.5}\text{Si}_{1.5}\text{O}_{9.75}$, so-called sinter-mullite) and $x = 0.4$ (2:1 mullite, $2\text{Al}_2\text{O}_3 : 1\text{SiO}_2$, $\text{Al}_{4.8}\text{Si}_{1.2}\text{O}_{9.6}$, so-called fused-mullites). Sinter-mullites are usually produced by solid-state reactions and fused-mullites by melting or crystal-growth techniques. About six years ago, Fischer and Schneider [2] did the first attempt to define the mullite-type family of crystal structures for a class of compounds having the same arrangement of