

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  $\text{BO}_6$  chains. It does however constrain the transverse correlation of chains (the fact observed experimentally for similar,  $\text{BaTiO}_3$ -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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## MS81.P05

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

Hironori Nakao,<sup>a</sup> Tetsuya Murata,<sup>b</sup> Daisuke Bizen,<sup>b</sup> Youichi Murakami,<sup>a</sup> Kenji Ohoyama,<sup>c</sup> Kazuyoshi Yamada,<sup>c</sup> Shintaro Ishiwata,<sup>d</sup> Wataru Kobayashi,<sup>e</sup> Ichiro Terasaki,<sup>f</sup> <sup>a</sup>Condensed Matter Research Center and Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801. <sup>b</sup>Department of Physics, Tohoku University, Sendai 980-8578. <sup>c</sup>Institute for Materials Research, Tohoku University, Sendai 980-8577. <sup>d</sup>Department of Applied Physics and Quantum-Phase Electronics Center (QPEC), University of Tokyo, Hongo 113-8656. <sup>e</sup>Graduate school of pure and applied sciences, University of Tsukuba, Tsukuba 305-8571. <sup>f</sup>Department of Physics, Nagoya University, Nagoya 464-8602. E-mail: hironori.nakao@kek.jp

$\text{Sr}_{1-x}\text{R}_x\text{Co}_4\text{O}_{10.5}$  ( $R = \text{Y}$  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  $\text{CoO}_6$  octahedral layers and the  $\text{CoO}_{4.25}$  layers, which stack along  $c$  axis alternatively. By powder x-ray diffraction, the orbital state of  $\text{Co}^{3+}$  ( $3d^6$ ) was evaluated from the anisotropy of the  $\text{CoO}_6$  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  $\text{Co}^{3+}$  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  $\text{Co}^{3+}$ . 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 $\alpha$ -quartz type materials for piezoelectric applications.

Olivier Cambon,<sup>a</sup> Gopalkrishna Bhalerao,<sup>a</sup> Julien Haines,<sup>a</sup> Dave Keen,<sup>b</sup> Matt Tucker,<sup>b</sup> <sup>a</sup>Institut Charles Gerhardt, UMR-CNRS-UM2 5253, C2M, Place E.Bataillon, 34095 Montpellier, (France). <sup>b</sup>ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, (United Kingdom). E-mail: ocambon@ipmc.unic-montp2.fr

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  $\alpha$ -phase is linked to the tilt of the tetrahedra around a two-fold axis, which is the mechanism of the  $\alpha$ - $\beta$  phase transition. This behaviour depends on the nature of the cations at the center of the tetrahedra. Thermal stability in the  $\alpha$ -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  $\alpha$ - $\beta$  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  $\alpha$ -quartz, well below the  $\alpha$ - $\beta$  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  $\text{GaAsO}_4$ , 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

Reinhard X. Fischer, Johannes Birkenstock, Andrea Gaede-Köhler, Hartmut Schneider, *Kristallographie, Universität Bremen, Klagenfurter Straße, D-28359 Bremen (Germany)*. E-mail: rfischer@uni-bremen.de

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

edge-sharing  $\text{MO}_6$  ( $M =$  octahedrally coordinated cations) octahedra forming parallel  $\text{MO}_4$  chains. The crystal structures of all compounds in this family are derived from an aristotype structure in space group  $P4/mbm$  following a hierarchical scheme of subgroup relationships. Meanwhile, several compounds are added to this family, also extending the Bärnighausen tree representing all branches and cross-relationships of the symmetry derivations. Mullite itself is an aluminosilicate with an incommensurately modulated structure [3] reinvestigated here by single-crystal neutron-diffraction analysis of a high-quality 2:1 mullite. Its average crystal structure can be derived from the sillimanite structure by a disordered arrangement of  $(\text{Al,Si})\text{O}_4$  tetrahedra linking the octahedral chains according to the substitution scheme  $2\text{Si}^{4+} + \text{O}^{2-} \rightarrow 2\text{Al}^{3+} + \text{vacancy}$ . The reaction involves removal of oxygen atoms from the structure and the formation of oxygen vacancies. Replacing Si by Al yields the oxygen vacancies and causes a migration of undersaturated Al to the so-called T\* sites (red tetrahedra linking to bridging oxygen forming the  $\text{T}_3\text{O}$  clusters).

We have performed statistical calculations in a  $2 \times 2 \times 2$  and a  $3 \times 3 \times 2$  supercell to find the maximum number of symmetrically independent oxygen-vacancy configurations assuming one to four vacancies in the  $2 \times 2 \times 2$  case and up to seven vacancies in the  $3 \times 3 \times 2$  supercell. The total number of combinations is given just by the binomial coefficient

$$\binom{n}{k} = \frac{n!}{k!(n-k)!}$$

with  $k$  representing the number of vacancies and  $n$  being the site multiplicity of the vacancy positions. As an example, the number of combinations for  $k = 2$  vacancies distributed over  $n = 8$  sites in the  $2 \times 2 \times 2$  supercell (corresponding to mullite with  $x = 0.25$ ) is 28 as calculated from the binomial coefficient. Out of this number, only 20 combinations are crystal-chemically possible, and among these combinations, there are only 6 which are symmetrically independent. We are representing here the full ordering scheme of possible and independent oxygen vacancy distributions as a basis for the interpretation of the incommensurate modulation scheme of mullite.

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### Polymorphism in the quasi-1D quantum magnet, $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$

Saul H. Lapidus,<sup>a</sup> Jamie L. Manson,<sup>b</sup> Kimberly E. Carreiro,<sup>b</sup> Peter W. Stephens,<sup>a</sup> <sup>a</sup>*Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY, (USA)*. <sup>b</sup>*Department of Chemistry, Eastern Washington University, Washington, (USA)*. E-mail: slapidus@gmail.com

While there are many examples of polymorphism in molecules, polymorphism in 3D coordination networks relatively rare. In this work, we will present one instance of this type of polymorphism and the related magnetic behavior of the different polymorphs.

The crystal structures of two polymorphs of  $[\text{Ni}(\text{HF}_2)(\text{pyz})_2]\text{PF}_6$  were determined by synchrotron X-ray powder diffraction. The two polymorphs are a monoclinic ( $C2/c$ ;  $a=9.9481(3)$  Å,  $b=9.9421(3)$  Å,  $c=12.5953(4)$  Å,  $\beta=81.610(3)^\circ$ ) and tetragonal phase ( $P4/nmm$ ;  $a=9.9187(3)$  Å,  $c=6.3497(2)$  Å). Both consist of one-dimensional Ni-

FHF-Ni chains which are connected by pyrazines to create a three-dimensional framework, with a  $\text{PF}_6^-$  counter ion occupying the voids in this network. The main difference between these two polymorphs is that in the monoclinic phase the Ni-FHF-chains are buckled, while in the tetragonal phase the chains are linear. The influence of these structural differences on the magnetic properties will be discussed.

**Keywords:** polymorphism, coordination polymers, magnetism

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### Predicting switchable multi-ferroic ruddlesden-popper phases & phase transitions

Christopher Howard,<sup>a</sup> Michael Carpenter,<sup>b</sup> Erich Kisi,<sup>a</sup> <sup>a</sup>*School of Engineering, The University of Newcastle, Callaghan NSW 2308 (Australia)*. <sup>b</sup>*Department of Earth Sciences, The University of Cambridge, (UK)*. E-mail: chris.howard@newcastle.edu.au

The  $n=2$  Ruddlesden-Popper compound  $\text{Ca}_3\text{Mn}_2\text{O}_7$  forms a structure in polar space group  $Ccm2_1$  at room temperature [1], [2], and is therefore potentially ferroelectric. The structure can be considered derived from a higher symmetry parent, in  $I4/mmm$ , through the combined ‘tilting’ and ‘rotation’ of the Mn-centred octahedra. It is known to order magnetically below about 110 K, the ordering being predominantly antiferromagnetic but with a small ferromagnetic component [3]. It can therefore be classified as multiferroic. It has recently been pointed out [4] that the coupling of the polarisation to magnetisation in  $\text{Ca}_3\text{Mn}_2\text{O}_7$  might allow switching of the magnetisation by reversing the polarisation, or vice versa. This has motivated a group theoretical analysis of the potential for this coupling and the phase transitions expected as temperature is increased.

The octahedral ‘tilt’ is associated with irreducible representation (irrep)  $X3^-$  of the parent space group  $I4/mmm$ , whereas the ‘rotation’ is associated with irrep  $X2^+$ . Polarisation is carried by the mode associated with  $GM5^-$ , which is a secondary distortion produced when  $X2^+$  and  $X3^-$  act together. The antiferromagnetic structure below 110 K, as reported [3], appears to be associated with irrep  $mX1^-$ . This distortion acting along with the tilting ( $X3^-$ ) leads to a ferromagnetic component  $mGM5^+$ . The Brigham Young software [5] shows that we have a fourth degree invariant of the form  $X2^+ * GM5^- * mX1^- * mGM5^+$ , and it is this term that indicates the possibility of reversing the magnetisation ( $mGM5^+$ ) by reversing the polarisation ( $GM5^-$ ) and vice versa.

In the related phase  $\text{Ca}_3\text{Ti}_2\text{O}_7$ , mode amplitudes calculated from the room temperature structure [1], are found to be 0.84 and 1.04 for  $X2^+$  and  $X3^-$  respectively. This suggests that  $X2^+$  would vanish first upon heating giving a path to  $I4/mmm$  via an intermediate in  $Cmcm$ . Mode amplitudes for  $\text{Ca}_3\text{Mn}_2\text{O}_7$  however, are 0.73 and 0.67 for  $X2^+$  and  $X3^-$ , so there must be some possibility that  $X2^+$  will disappear first giving a path via a structure in  $Cmca$  as intermediate. Comparison with structures calculated *ab initio* [4], [6] show that the polarisation determined from the room temperature structure of  $\text{Ca}_3\text{Mn}_2\text{O}_7$  [2] is in reasonable agreement with that from *ab initio* calculations [4], but for  $\text{Ca}_3\text{Ti}_2\text{O}_7$  the polarisation from the analysis above is less than from *ab initio* by a factor five.

These analyses will be developed more fully to demonstrate the utility of the analysis for predicting potentially useful material characteristics.

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