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Strontium incorporation in mullite-type $Bi_2M_4O_9$

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$Bi_2M_4O_9$ compounds (M = Al, Ga, Fe) are described to have potential as electrolytes in solid oxide fuel cells (SOFC) [1]. The conducting properties could be related to an increased number of oxygen vacancies due to the requirement of charge neutrality with the substitution of Bi^{3+} by Sr^{2+} [2].

The samples were synthesized using the glycerine nitrate [3] as well as EDTA/citric acid [4] methods, and washed with nitric acid. Whereas small amounts of Bi_2O_3 and strontium metallates were always found in the as synthesized samples no indication for these impurities were detected after washing. Thermal expansion and thermal stability were investigated using high-temperature powder X-ray measurements evaluated by Rietveld refinements and TG/DTA, respectively. The incorporation of strontium into a mullite-type aluminate sample ($Bi_{2-x}Sr_xAl_4O_9$ with a reactant stoichiometry of x = 0.2) was investigated by HRTEM. Suitable crystallites were analyzed by EDX in a scanning TEM mode. Several particles were evaluated showing strontium contents of x around 0.05 with a homogeneous distribution. This strontium incorporation prevail two possibilities for charge balance: firstly, oxygen deficiency with vacant oxygen positions and secondly, oxidation of Bi^{3+} to Bi^{5+}. To check the latter possibility XPS investigations were carried out on two samples with an initial x = 0.2 and x = 0 (i.e., $Bi_2Al_4O_9$) as references. The same samples were used for NMR spectroscopic investigations to check for tri-cluster formation as a possible result of an oxygen deficiency on the tetrahedral bridging oxygen position.

$Bi_2M_4O_9$ phases show thermal-expansion behavior without any discontinuities for the pure as well as for compounds with mixed metal (M) position occupations. However, a clear discontinuity has been observed in the lattice-parameter expansion of the investigated strontium-doped materials between 1050 K and 1150 K. This discontinuity leads to smaller parameters for the lattice and cell volume in the case of the aluminate phase. In the corresponding gallate compound the *a* lattice parameter was found longer than it was before the heating cycle. XPS investigations on strontium-doped and -undoped aluminates clearly show the existence of only Bi^{+3} in the samples synthesized using the glycerine nitrate method. Evaluation of the ^{27}Al MAS NMR spectroscopic data shows the conventional AlO_4 species at 67.2 ppm. A signal observed at 46.8 ppm can be interpreted with Al^*O_4 units belonging to a tri-cluster. A peak at 16.2 ppm has been assigned to the AlO_6 octahedral chains.

These results clearly show that strontium can be incorporated in the mullite-type $Bi_2M_4O_9$ phases up to approx. 5 mol-% with a thermal stability up to ~1200 K. Tri-cluster formation for these compounds show an oxygen deficiency mainly on the double tetrahedra bridging position.

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Family of molecule-based magnets with M^{II} μ_4-TCNE sheets.

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We have studied a number of magnets which share the common structural motif of wrinkled sheets of M^{II} μ_4-TCNE, (M = Mn, Fe; TCNE = $C_2(CN)_4$), with various units axially bonded to the metal sites. None could be obtained as single crystals, but four members of the family have all been solved from powder diffraction. The sheets are two dimensional ferrimagnets, with $S=1/2$ $TCNE^{\bullet-}$ coupled antiferromagnetically to the transition metals.

The materials display disparate bulk magnetic phenomena. A compound originally thought to be $Fe(TCNE)_2 \bullet y$(solvent), which displays hysteresis and remnant magnetization below 97K, turned out to be $M^{II}(TCNE^{\bullet-})(C_4(CN)_8{}^{2-})_{1/2} \bullet y$(solvent).[1] The Mn analog is an antiferromagnet with susceptibility maximum at 72K. In both of those materials, the aforementioned M^{II} μ_4-TCNE sheets are separated by diamagnetic $(C_4(CN)_8)^{2-}$. A material of composition $FeCl_2(NCMe)(TCNE)_{1/2}$ unexpectedly turned out to be $[Fe^{II}(TCNE^{\bullet-})(NCMe)_2]^+[Fe^{III}Cl_4]^-$, displaying remnant magnetization below 90K.[2] That material has no covalent bonds between the magnetic sheets.

In contrast, $Mn(TCNE)_{3/2}(I_3)_{1/2} \bullet y$(solvent) is thought to owe its much higher magnetic ordering temperature of 171K to a three-dimensional network of magnetically active TCNE links between layers.[3] But this cannot be the whole story, because recently discovered $Mn(TCNE)I(OH_2)$, has no bonds between adjacent layers, and has the same 171K transition temperature [4].

The structures give some insights to the various magnetic phenomena observed, but equally raise questions about the effect of bonding geometry on the magnetic coupling between the TCNE radical ion and transition metals.

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Magnetoelastic effects in multiferroic YMnO3 and HoMnO3

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The coupling between spin and lattice degrees of freedom is one

of the interesting topics of condensed matter research. It has drawn renewed interest in connection with the potentially useful electronic materials such as colossal magnetoresistive and multiferroic materials. One of the dominant effects of this coupling is the spontaneous exchange striction associated with the magnetic ordering at lower temperatures. We have investigated magnetoelastic effects in multiferroic YMnO3 and HoMnO**3** below antiferromagnetic phase transition by neutron powder diffraction. YMnO3 and HoMnO3 belong to the family of hexagonal manganites RMnO3 (R = Sc, Y, Er, Ho, Tm, Yb, Lu) that show multiferroic behaviour. These hexagonal manganites are paraelectric at high temperatures with centrosymmetric space group *P63/mmc*. Below about 1000 K they undergo paraelectric-to-ferroelectric transition to the non-centrosymmetric structure with the space group *P63cm*. At further lower temperatures of the order of about 100 K the magnetic hexagonal manganites order with a non-collinear antiferromagnetic structure with the propagation vector k = 0. We have done neutron powder diffraction experiments on YMnO3 and HoMnO3 on a high-intensity powder diffractometer. The lattice parameter *a* of the hexagonal unit cell of YMnO3 decrease in an usual way at lower temperatures and then shows abrupt anomalous contraction below *TN = 70* K whereas the lattice parameter *c* increases continuously with lowering temperaure and then shows abrupt anomalous increase below *TN*. The unit cell volume *V* also undergoes abrupt contraction below *TN*. By fitting the background thermal expansion of a nonmagnetic lattice with Einstein-Grueneisen equation we determined the lattice strains □a, □c and □V due to the magnetoelastic effects as functions of temperature. We have determined the temperature variation of the ordered magnetic moment of Mn ion by fitting the measured Bragg intensities of the nuclear and magnetic reflections with the known crystal and magnetic structure models and have established that the lattice strains due to the magnetoelastic effect in YMnO3 couples with the square of the ordered magnetic moment or the square of the ordered parameter of the antiferromagnetic phase transition. We have determined the small structural modifications at the antiferromagnetic phase transition due to the magnetostriction effects and related these with the ferroelectric polarisation. Similar results have been obtained for multiferroic HoMnO3. We have compared the present results with those obtained by us [1], [3] in parent compounds LaMnO3 and NdMnO3 of the colossal magnetoresistive (CMR) manganites and also in the whole series of model insulating antiferromagnets MF2 (M = Cr, Mn, Fe, Co, Ni, Cu). This has led us to conclude that the compounds with magnetic ions having considerable unquenched orbital moments behave anomalously compared to those with spin-only moments.

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Keywords: antiferromagnetism, ferroelectricity, neutron diffraction

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Symmetry-mode analysis of the alumina phase diagram

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The oxides and oxyhydroxides of aluminum present a notoriously complex structural family with at least 13 different structural phases. Of particular interest and importance are the phase sequences involving the boehmite, γ, and α phases due to their industrial and technological applications. Much time and effort have been spent mapping out the myriad transition sequences that have been observed within this family, which can vary substantially with only slight changes in the synthetic conditions, initial crystallite size, and/or hydrothermal history. Yet, the detailed transformation mechanisms that relate them are not well understood. Using symmetry principles as a guide, we have uncovered candidate mechanisms that help to explain a variety of transitional phases observed along common phase pathways leading to α alumina.

Keywords: alumina, phase transformation mechanism, symmetry-mode analysis

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Atomic scale description of the macroscopic piezo-ferroelectric properties of high performance lead zirconate titanate (PZT)

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Materials science can be defined as an interdisciplinary field involving the properties of matter and its applications. This scientific field investigates the relationship between the structure of materials and their macroscopic properties. In this framework the "in situ" atomic-scale structural description of the origin of the ferroelectric properties as a function of the applied electric field E, i.e. switching of the spontaneous polarization P_S with an electric field, corresponds to a perfect example of such a goal. Piezoelectricity is inherent to ferroelectricity and the structural investigations of such a material as a function of an applied electric field will create a strong piezoelectric strain ($d_{ij} = \frac{\partial \eta_{ij}}{\partial E_k}$, where d_{kij} is the piezoelectric coefficient, η_{ij} is the strain and E_k is the applied electric field) which unfortunately makes structural determination difficult due to the existence of an associated strong texturing. In this contribution, a 45°-scattering geometry was used to average the preferred orientation and solve "in-situ" the crystal structure as a function of the applied electric field. Note that this set-up could be used in other studies, involving homogeneous strains as a function of other intrinsic physical parameters, i.e. stress, magnetic field, etc. Hence, we were able to describe microscopically the macroscopic physical properties of the most widely used ferroelectric material, lead zirconate titanate (PZT), which is intensively used for technological applications (sensors and actuators, MEMS systems and high frequency devices). As we will show it is possible to directly correlate structural with macroscopic ferro-piezoelectric properties as a function of the electric field and thus elucidate the structural origin of such properties. Polarization flipping of polar lead atoms for example could unambiguously be characterized by a maximum in the disorder parameter of lead, i.e. $Biso$ (Pb) linked to the maximum of the entropy, for the positive-negative value of the coercive field in the P_S-E hysteresis cylce [1].These results will be useful for the design and optimization of higher performance materials.

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