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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