

powder diffraction, structure-properties relationship

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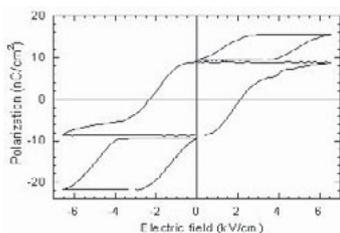
Discovery of polarization flop and ferrielectric character of multiferroic RMn_2O_5

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Rare-earth (R) manganese oxides of the form RMn_2O_5 are known as multiferroic materials which exhibit colossal magnetoelectric effects because of magnetic frustration and dielectric properties strongly coupling with magnetic ordering. However, the origin of the ferroelectricity of RMn_2O_5 is not yet clear. We have studied the relationship between dielectric properties and magnetic ordering of RMn_2O_5 especially by simultaneous measurements of the electric polarization and permittivity under neutron diffraction, and discovered several new facts. It is believed that the ferroelectricity of RMn_2O_5 appears only along the *b*-axis. But we discovered that the polarization of TmMn_2O_5 flops from the *b*-axis to the *a*-axis below about 5 K, which is attributed to a magnetic phase transition in an incommensurate magnetic phase. According to a structure analysis, RMn_2O_5 may be ferrielectric.

Actually both ferroelectric and antiferroelectric hysteresis loops of ErMn_2O_5 are observed as the figure at 35.4 K, in a commensurate magnetic phase. These loops can be obtained by a Sawyer-Tower circuit with a new technique, the double-wave method.



Keywords: ferroelectrics, magnetic frustration, neutron diffraction

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Structure and magnetic property of one-dim. chain complex: $\text{M}^{\text{II}}(\mu\text{-bpt})(\mu\text{-COOC}_5\text{H}_4\text{N})\cdot\text{H}_2\text{O}$ (M=Mn, Fe)

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The one dimensional chain complex, $\text{M}^{\text{II}}(\mu\text{-bpt})(\mu\text{-COOC}_5\text{H}_4\text{N})\cdot\text{H}_2\text{O}$ (M=Mn, Fe), with the metal centers connected each other with bpt and isonicotinic acid forms an infinite chain along a screw axis 4₁. It is synthesized by solvo-thermal synthesis and the structure is characterized by single crystal x-ray diffraction. The complex is crystallized in tetragonal space group *I*4₁/*a* with cell parameters of *a* = *b* = 21.5910(2), *c* = 15.2330(3) Å. It is iso-structure for both metal ions. Fe(II) is octahedrally coordinated by four nitrogen of bpt and two oxygen of isonicotinic acid, $[\text{FeN}_4\text{O}_2]$. The bond lengths of Fe-N are 2.331(1) Å, 2.130(1) Å, 2.233(1) Å, 2.126(1) Å and of

Fe-O are 2.057(1) Å, 2.093(1) Å at 300 K; which are typical bond lengths of FeII at its high spin state. However, this Fe chain complex displays distinct ferromagnetic interaction between the FeII centers. The hydrogen bonds between water molecules and the ligands may play important role on the inter-chain interactions. On the contrary, the Mn(II) complex shows typical paramagnetic character with antiferromagnetic interaction at low temperature, even the structure is exactly the same as that of Fe chain complex. The detail structure of the chain complexes and the comparison on the magnetic property of the two metal chain complexes will be presented.

Keywords: inorganic materials, one-dimensional structures, magnetic properties

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Structural change of cordierite by substitution Ni for Mg bringing high *Q* on millimeterwave ceramics

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Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) is a candidate for millimeterwave dielectrics because of the low dielectric constant of 6.19. This study has been focused on the affects of substitution Ni for Mg in octahedron. In the case of octahedron substitution, the quality factor *Q* of the Ni-substituted analogy with single phase was improved from 39900 to 90600 GHz. The origin of improvement of *Q* comes from changing to the high symmetry which is from orthorhombic to hexagonal. Here, cordierite with orthorhombic system *Cccm* (No.66) transforms to indiarite with hexagonal system *P6/mcc* (No.192). It is confirmed based on the crystal structure obtained by Rietveld method that configuration of $\text{Si}_4\text{Al}_2\text{O}_{18}$ ring changes to hexagonal ring from distorted ring according to the substitution Ni for Mg. The volumes and covalencies of SiO_4 and AlO_4 tetrahedra also change to same size according the substitution. The crystal structure tends to become higher symmetry hexagonal ring with accompanying Si-Al disordering. In this case, contribution of high symmetry for *Q* might be greater than that of ordering.

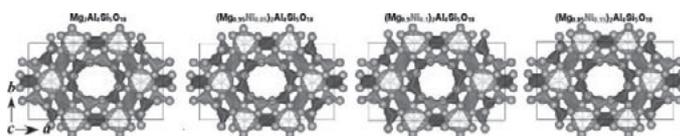


Fig. 1 Structural change on cordierite substituted Ni for Mg.

Keywords: microwave materials, indiarite, order-disorder structure

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On-line symmetry-mode analysis of any ferroic structure

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We report the addition to the Bilbao Crystallographic Server (www.cryst.ehu.es) of a new tool that can perform the symmetry

mode analysis of any ferroic structure. As input only the ferroic distorted structure and the (real or virtual) non-distorted one of higher symmetry is required. With this information the program AMPLIMODES identifies the displacive distortion present in the structure and decomposes it in terms of modes of different symmetries associated with irreducible representations of the high-symmetry space group. The decomposition of the structure in collective symmetry-adapted distortion modes is given in terms of global amplitudes and normalized polarization vectors for each of the modes present. The importance and character of each of the allowed symmetry modes can be extracted from a comparison of their amplitudes and the internal structure of their polarization vectors. The polarization vector of each frozen mode is presented in a crystallographic way, as a list of relative atomic displacements within an asymmetric unit. This allows a straightforward construction of virtual structures corresponding to the sole presence with arbitrary amplitudes of any of the relevant modes. This type of analysis allows to distinguish and isolate the correlated atomic displacements that correspond to the structural instabilities at the origin of the ferroic distortion, i.e. the so-called primary modes. In this way, secondary weaker induced distortions of marginal relevance are separated. The Bilbao Crystallographic Server, where this tool can be used on-line, is a free web site with many other crystallographic databases and programs [1,2].

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Keywords: ferroic materials, structural phase transitions, symmetry modes

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New organic conductors based on cobaltacarborane anion and its derivatives

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Just a few conducting radical cation salts containing metallacarborane anions have been described so far [1,2]. No radical cation salt derived from the cobalt bis(dicarbollide) anion $[3,3^{\prime}\text{-Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ or its halogen derivatives was reported. First molecular conductors with cobalt bis(dicarbollide) anion and its iodine and bromine derivatives were electrochemically synthesized and investigated by X-ray study [3-5]: (TMTSF)₂[3,3[′]-Co(1,2-C₂B₉H₁₁)₂] (1), (TTF)[3,3[′]-Co(1,2-C₂B₉H₁₁)₂] (2), (ET)[3,3[′]-Co(1,2-C₂B₉H₁₁)₂] (3), (ET)₂[3,3[′]-Co(1,2-C₂B₉H₁₁)₂] (4), (ET)₂[8-I-3,3[′]-Co(1,2-C₂B₉H₁₀)(1[′],2[′]-C₂B₉H₁₁)] (5), (BMDT)[3,3[′]-Co(1,2-C₂B₉H₁₁)₂] (6), (ET)₂[3,3[′]-Co(8-Br-1,2-C₂B₉H₁₀)₂] (7), (BMDT)₄[3,3[′]-Co(8-Br-1,2-C₂B₉H₁₀)₂] (8), and ET[3,3[′]-Co(8-BrC₂B₉H₁₀)₂] (9). Salt (1) is a semiconductor with activation energy $E_a=0.03$ eV, conductivity $S(293) = 15 \text{ Ohm}^{-1}\text{cm}^{-1}$, that is the maximum value of conductivity for all metallacarborane radical cation salts studied before [1,2].

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[5] O.N.Kazheva, et al., *JSSS*, 2008, in press

Keywords: organic conductors, carboranes, X-ray crystal structure analysis

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Phase and glass forming diagrams in the gallium borate and ternary barium gallium borate systems

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The revealing of new stoichiometric compositions still actual problem for new acentric or non-centrosymmetric solids (single crystals, ceramics) development. The glass ceramic (GC) technology combines flexibility, simplicity and cheapness of glass technology with possibility to form crystal structures of the reference sizes and compositions through controlled and oriented crystallization. Alkaline earth binary borates and alkaline-earth ternary borates are the good candidate for this purpose, because they combine nonlinear characteristics with good glass forming ability. This was a motivation for study and construction both phase and glass forming diagrams in the binary gallium borate and ternary barium gallium borate systems. The glasses were melted from chemically pure^o grade chemicals in platinum crucibles in air at 1300-1600 °C in electrical furnace.

Keywords: barium gallium borates, phase diagram, glass forming diagram

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SAXS investigation of SBA-15 vacuum calcination process

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Ordered mesoporous silica (OMS) is a new alternative material for many technologies, ranging from microelectronics to medical applications. In this work, in situ analysis of the calcination process of SBA-15 was carried out in vacuum at the SAXS2 beamline of LNLS, Brazil. The as-synthesized powder was submitted to a heat treatment procedure at a pressure of about $1 \cdot 10^{-3}$ torr, from room temperature up to 540 °C, at a constant temperature increase of around $2^\circ\text{C} \cdot \text{min}^{-1}$. The sample was kept at this temperature for 6 hours. At around 300 °C the polymer starts to decompose and the lattice parameter decreases from $a=12.8\text{nm}$ to $a=12.4\text{nm}$, until the temperature reaches 540 °C, when the polymer decomposes. The lattice parameter reaches a final value of 12.3nm, remaining at this constant figure until the final cooling process. The peak areas do not change up to 300 °C. A strong and subtle increase of peak areas is observed at this temperature. During the isothermal calcination process, part of the ordered structure is destroyed, as indicated by the decrease of the diffracted intensities. A sample previously calcined in nitrogen and air showed a larger shrinkage effect, resulting in $a=11.8\text{nm}$. Also, the SAXS curve of this sample presented a larger background when compared to that registered in the measurements of the vacuum heat treated sample. This result is attributed to the presence of disordered pores, with maximum gyration radius of 7nm, to micropores and/or to inter-grain scattering. Ex-situ SAXS analysis of a similar sample submitted to vacuum heat treatments at 300 °C, 400 °C and 540 °C was also carried