

STRUCTURAL PHASE TRANSITIONS IN CsInF₄A. L. Thompson¹ A. E. Goeta¹ C. C. Wilson² A. Ayala³ C.W.A. Paschoal³ I Guedes³ J-Y Gesland⁴¹University of Durham. Department of Chemistry, Science Laboratories, South Road, DURHAM DH1 3LE UK ²ISIS, Rutherford Appleton Laboratory, Didcot, Oxon, UK. ³Departamento de Física, Universidade Federal do Ceara, CP 6030, 60455-760 Fortaleza (CE) Brasil. ⁴Universite du Maine - Cristallogene, 72025 - Le Mans CEDEX 09 - France

In the past 20 years many studies have been devoted to the structural characterization of cubic perovskite compounds, of the form ABX₃. This has been mainly due to the wide variety of potentially important technological properties shown by these materials, e.g. Ferroelectricity, ionic conductivity, superconductivity, etc. Phase transitions on these materials are thought to be caused by tilts of rigid BX₆ octahedra, even in the case of large tilt angles. If rigid BX₆ octahedra are so important for understanding the behavior of these materials, it is clear that the study of systems involving phase transitions with rigid octahedra forming only a 2-dimensional array, could provide additional insight on the theory of phase transitions. Moreover, it will help towards understanding issues like the displacive character of ferroelastic transitions, as it simplifies the problem. 2-Dimensional arrays of octahedra like the one mentioned previously are found, for example, in tetrafluoroaluminates MAIF₄ (M=Ti, Rb,K,NH₄), where several phase transitions are observed. In this communication we will be introducing CsInF₄, a new material of the ABX₄ family. CsInF₄ appears to have a number of temperature dependent phase transitions based on the tilting of the InF₆ octahedra. Dielectric measurements clearly show the presence of four distinct phases with transitions at 280 K, 380 K and 415 K. In addition, the transitions have been verified and further characterized by Differential Scanning Calorimetry (DSC), variable temperature X-ray powder diffraction and single crystal neutron diffraction experiments. Results and conclusions drawn from these experiments will be presented.

Keywords: CSINF4 PEROVSKITES (2 DIMENSIONAL) ABX₄**CRYSTAL AND MAGNETIC STRUCTURE OF TbBaMn₂O₆**A.J. Williams J.P. Attfield
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The first example of an A cation ordered manganese oxide perovskite was the oxygen deficient YBaMn₂O₅ reported by Chapman et al.[1], in which double pyramidal manganese layers containing Ba²⁺ cations were interleaved with oxygen-free yttrium layers. More recently, Millange et al.[2] have synthesised the analogous LaBaMn₂O₅, and by careful reoxidation, a form of LaBaMn₂O₆ in which the La/Ba cations are ordered along the c axis. We have investigated the Tb analogue TbBaMn₂O₆. The 300 K powder neutron pattern of this phase is fitted by a monoclinic model (*P*₂₁/*m*, *a* = 5.56036(6), *b* = 5.56051(6), *c* = 7.63694(6) Å, β = 90.230(1)°) containing two distinct Mn sites, consistent with Mn³⁺/Mn⁴⁺ charge order. The two Mn sites exhibit large distortions from octahedral symmetry, with average Mn-O bond distances equal to 1.93 Å for Mn⁴⁺ and 1.99 Å for Mn³⁺. There is evidence for orbital ordering at the latter site. The charge order in TbBaMn₂O₆ is of the rocksalt type, and not the striped arrangement as observed in materials with disordered A cations such as (La_{0.5}Ca_{0.5})MnO₃[3]. Susceptibility measurements show an antiferromagnetic ordering below 20 K and this is confirmed by low temperature powder neutron diffraction patterns, which show a magnetic supercell with *a* = 2*a*, *c* = 2*c*.

References

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Perovskite materials (La,Mn)-doped PbTiO₃ have been prepared by solid state reaction method. X-ray diffraction (XRD) data were collected by SIEMENS D5000 diffractometer in two regimes and Rietveld refinement of the XRD data was used to determine the crystal structure and oxygen content for a series of samples. The first regime concerns room temperature. For *x* = 0 the crystal structure of Pb_{1-x}La_xTiO₃^{-δ} (PLT) has tetragonal symmetry belonging to space group P4/mmm (123) with the unit cell parameter ratio *c/a* = 1.063. When *x* increases, the parameter *a* increases but *c* decreases leading to a gradual reduce of the *c/a* ratio which reaches 1 at *x* = 0.15. There thus occurs a tetragonal-to-cubic phase transition. As for Pb_{1-x}La_xTi_{0.98}Mn_{0.02}O₃^{-δ} (PLTM) a similar transition occurs but with a quicker rate and, as a result, in the cubic phase the unit cell of PLTM is bigger than that of PLT. In the second regime *x* is fixed to be 0.08 but the temperature is increased from the room one to 630°C and then decreased back to the room temperature. For most of the samples experimented the tetragonal symmetry changes and the cubic phase is formed starting from about 500°C up to 630°C. The reverse cubic-to-tetragonal transition however takes place at about 575°C when the temperature decreases from 630°C down to the room temperature displaying a kind of hysteresis. It is also observed that the oxygen non-stoichiometry depends on *x* in a non-monotonic manner and physical properties such as piezoelectric are quite sensitive to the addition of La.

Keywords: X-RAY POWDER DIFFRACTION, PEROVSKITE MATERIALS, RIETVELD REFINEMENT**INVESTIGATION OF THE STRUCTURE AND PHASES IN PEROVSKITE-TYPE LEAD MAGNESIUM NIOBATE TITANATE (PMN-PT).**D. Zekria A. M. Glazer
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Lead magnesium niobate titanate, [1-x]Pb(Mg_{1/3}Nb_{2/3})O₃:[x]PbTiO₃ (PMN-PT), has the perovskite structure, with general formula ABO₃. PMN-PT is currently attracting interest for its high piezoactivity, reaching about ten times the value of that for the commonly used material lead zirconate titanate (PZT)[1]. As well as ceramics[2], our own work suggests that, unlike PZT, it is possible to grow PMN-PT in single crystal form across the entire composition range from *x* = 0 to *x* = 1. Thus, the material has great potential for industrial applications. In PZT, it is known that the increase in piezoactivity is accompanied by a sudden change in crystal structure from a rhombohedral phase to a tetragonal phase at the so-called morphotropic phase boundary (MPB). It is believed that PMN-PT exhibits an analogous rhombohedral-tetragonal MPB at about *x* = 0.35. By using a method of birefringence imaging employing a rotating polarizer technique[3], the positions of the phase transitions of a single crystal can be mapped out against temperature. By combining data from crystals of a range of compositions, the complete phase diagram for PMN-PT may be established. The rhombohedral phase of PMN-PT differs from cubic by only very slight distortions, making its parameters difficult to measure by any but the most sensitive techniques. By taking x-ray back-reflection photographs, the rhombohedral splitting of some spots can be detected. The lattice parameters and rhombohedral angle may be calculated by measuring the positions and splitting of these spots.

References

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[3] A. M. Glazer, J. G. Lewis and W. Kaminsky, *Proc. R. Soc. Lond., A* (1996) 452, 2751-2763**Keywords: PEROVSKITE FERROELECTRIC PHASE TRANSITION**