

PS10.06.07 GIANT MAGNETORESISTANCE EFFECT IN THE LAYERED PEROVSKITES $(\text{Ca},\text{La})_4\text{Mn}_3\text{O}_{10}$ F.J.Lincoln, Research Centre for Advanced Mineral and Materials Processing, University of Western Australia, Nedlands, W.A. Australia 6907, P. Goodman, and N. S. Witte, School of Physics, University of Melbourne, Parkville, Australia 3052, R.H. March, Physics Department, Dalhousie University, Halifax, Canada B3H3J5

Recent observations of giant magnetoresistance (GMR) in ABO_3 perovskites where B is $\text{Mn}^{3+}/\text{Mn}^{4+}$ and A is a rare earth/alkaline earth mix¹, and more recently, of similar observations within the family $\text{La}_n\text{SrMn}_n\text{O}_{3n+1}$, for $n = 1, 2$ & 3 , has encouraged us to re-examine data collected recently³ on a different but related series. In above series², the compounds start with Mn in the Mn^{3+} state and achieve a finite Mn^{4+} population by Sr doping. Our approach was the reverse: we start from an initial Mn^{4+} compound and introduce an Mn^{3+} population by La^{3+} doping of the Ca^{2+} site. Using a combination of AC susceptibility, resistivity and neutron diffraction observations we examined three phases $\text{Ca}_{(n+1-x)}\text{La}_x\text{Mn}_n\text{O}_{3n+1}$, with $n=3$, and x values 0, 0.01 & 0.1.

With increasing doping we find a drop in peak resistivity of 10⁷ Although all three samples have semiconducting character following the thermal activation law above 100K, between 77K and 100K this law cannot account for our data. Also we find antiferromagnetic ordering, present in the undoped sample, disappearing in the doping interval 0.01 to 0.1. We predict that with higher La^{3+} doping a paramagnetic metallic phase will emerge, and that at this phase boundary the system will exhibit Giant Magnetoresistance.

1. Raveau, Maignan, & Caignaert (1995), *J. Sol. State. Chem.* **117**, 424.
2. Moritomo, Asamitsu, Kuwahara & Tokura (1996) *Nature* **380**, 141.
3. Rossell, Goodman, Bulcock, March, Kennedy, White, Lincoln & Murray (1996), *Australian J. of Chemistry* **49**, 205-217.

Materials VII Optic/Electronic Materials

MS10.07.01 OPTIMIZING THE SEARCH FOR NEW FERROELECTRIC/FERROELASTIC OPTICS. S. C. Abrahams, Physics Department, Southern Oregon State College, Ashland, OR 97520, USA

The application of crystallographic principles to structural studies published in the literature provides an accelerated path toward new materials with desirable properties. Nonlinear optics differ from classical optics in having both a strong dependence on light intensity and a capacity for coherent light generation at combination frequencies. The impetus for increasing the number of known nonlinear optics arises from the demand for a range of devices dependent upon these unique properties, including second and third harmonic generation, parametric oscillation and optical bistability. Uses include high speed signal switching in all-optical systems and information storage at high densities. Nonlinear optic properties imply noncentrosymmetry. The magnitude of higher order optical susceptibilities is generally larger in ferroelectric crystals than in simple piezoelectrics and such materials are hence in greatest demand. The rate-determining step along the discovery path is the prediction of new ferroelectrics, or new ferroelectric/ferroelastics, using similar principles. Following verification of the predicted property additional criteria must be met, including transparency in the required spectral range, superior optic figures of merit and the growth of optical quality single crystals, before a material becomes a new nonlinear optic of value. Systematic application of established principles to all structures listed in several polar point groups within the inorganic database has led to the prediction of many new ferroelectrics; the eventual treatment of all polar point groups will substantially enlarge this number. In the meantime, new ferroelectrics have also been predicted from the current literature. Newly predicted ferroelectric/ferroelastic nonlinear optics will be discussed. This work has been supported by NSF grant DMR-9310461.

MS10.07.02 PERIODIC DOMAIN INVERSION IN CRYSTALS: "DESIGNER" OPTICAL MATERIALS. P.A. Thomas, Department of Physics, University of Warwick, Coventry CV4 7AL, UK.

Periodic domain inversion (PDI) refers to the deliberate introduction of an array of domains of alternating structural polarity into a polar, usually ferroelectric, crystal. The crystals which have been the subject of PDI thus far are nonlinear optical materials such as LiNbO_3 , LiTaO_3 and KTiOPO_4 , all of which show ferroelectric behaviour at room temperature. The purpose of PDI is to confer tailor-made nonlinear optical properties to the resulting materials.

The most stringent requirement of crystals to be used effectively for nonlinear optical applications such as second-harmonic generation (frequency-doubling), is that the crystal should be phase-matchable, *i.e.* that the input wave at the fundamental frequency, ω , and the output wave at the second-harmonic, 2ω , should propagate in phase-synchronization. In terms of the refractive indices, n_{ω} and $n_{2\omega}$, of the crystal, this requirement is most simply expressed by $n_{\omega} = n_{2\omega}$. This condition is met fortuitously in a very few crystals through a combination of birefringence and dispersion: however, for meeting the vast range of new applications of optical materials, it would be preferable to find a method of "designing-in" phase-matching properties to existing materials. Periodic domain inversion is one such technique.

In this talk, the principles and practice of PDI will be described. The technique will be viewed in the context of the crystal structures and ferroelectric properties of crystals which have been successfully domain-inverted so far. The potential for the extension of the technique to new materials will then be evaluated. Finally, methods for examining the arrays of inversion domains established in the crystals will be considered with particular emphasis on our recent work using high-resolution x-ray topography and diffraction [1]-[2].

References

- [1] Z. W. Hu, P. A. Thomas, M. C. Gupta & W. P. Risk. *Appl. Phys. Lett.* (1995) **66**(1), 13-15.
- [2] Z. W. Hu, P. A. Thomas & J. Webjorn. *J. Phys. D: Appl. Phys.* (1995) **28**, A189-194.

MS10.07.03 STRUCTURAL STUDIES OF THE NONLINEAR OPTICAL, FERROELECTRIC, AND IONIC-CONDUCTING PROPERTIES OF NEW MEMBERS OF THE KTiOPO_4 FAMILY. E.L. Belokoneva, B.V. Mill, Moscow State University, Russia. S.Yu. Stephanovich, Karpov Inst. of Physical Chemistry, Russia. K.S. Knight, W.I.F. David, Rutherford Appleton Laboratory, UK.

New compounds with KTiOPO_4 (KTP) structure - AMOXO_4 : A-Na, K, Rb, Tl, Ag; M-Sb, Ta; X-Ge, Si - have been prepared that are analogous to the more familiar phosphates and arsenates. Their crystal structures have been investigated using X-ray single crystal and neutron high resolution powder diffraction data at high and low temperatures.

Nonlinear optical properties (SHG measurements on powder samples) indicate that all compounds are, like KTP, ferroelectrics with Curie points between 272K (TiSbOGeO_4) and 1200K. The lower transition temperatures and associated smaller SHG signals of these new compounds compared with the phosphates and arsenates results from a higher degree of pseudosymmetry and regularity of crystal structures. Importantly, substitution of highly polarisable Nb in $\text{KSb}_{1-x}\text{Nb}_x\text{GeO}_5$ and $\text{KTa}_{1-x}\text{Nb}_x\text{GeO}_5$ systems increases the SHG signal. Indeed in the latter solid solution, the SHG signal approaches that of KTP.

The loss of polarity (and concomitant loss of ferroelectric and nonlinear optical properties) occurs at a second-order phase transition which exhibits both order-disorder and displacive behaviour. The dominant displacements and disordering are associated with the A-cations and agree with the Abrahams-Jamieson-Kurtz (AGK) criteria.

The most important property of AgSbOSiO_4 is cationic conductivity. Ion exchange channels, marked by Ag-atoms, are described and the anisotropy of conductivity in the KTP structure is explained. The behaviour of A-cations determines the ionic-conducting and ferroelectric properties; M-octahedra together with A-cations make a considerable contribution to the non-linear optical properties.