

Several samples of KNN have been produced, with  $x$  ranging from 0.25 to 0.85. Both neutron and X-ray scattering studies were performed at ISIS and Oxford. Rietveld refinement was used to obtain the information about lattice parameters, atom positions and anisotropic displacement parameters as a function of temperature and compositions.

At present, the phase transition occurring approximately at  $x = 0.48$  is being studied. In the region  $0.48 < x < 1$ , orthorhombic phase M is labeled without any tilting of oxygen octahedra. After the phase transition has occurred, phase L appears (space group Pm). The extra peaks indicate that phase L has the  $a^0b^+a^0$  oxygen octahedral tilt system and off-centre cations movements approximately along [110].

High temperature measurements were performed by X-ray diffraction. Lattice parameters were extracted over temperature. The transitions of orthorhombic, tetragonal, and cubic phases were observed in the region  $x > 0.48$  at high temperatures.

[1] M. Ahtee, A.M. Glazer, 1975, *Acta Cryst.* A32, 434.

#### MS17 P14

**Structural studies of the morphotropic phase boundary near  $x=0.3$  in  $K_xNa_{1-x}NbO_3$**  Daniel Baker<sup>a\*</sup>, Pam Thomas<sup>a</sup>, Nan Zhang,<sup>b</sup> Mike Glazer<sup>b</sup> <sup>a</sup>*Department Physics, University of Warwick.* <sup>b</sup>*Department of Physics, Oxford University.* E-mail: [d.w.baker@warwick.ac.uk](mailto:d.w.baker@warwick.ac.uk)

**Keywords:** piezoelectric, mpb, perovskite

Lead zirconium titanate (PZT) is commonly regarded as the leading piezoelectric material for a wide range of applications, and one which all others are assessed against. However, there are growing concerns over the toxicity and environmental issues of lead-based substances [1], which is why attention has turned to other lead-free piezoelectric materials. Sodium potassium niobate (KNN) is of particular interest not only because its piezoelectric properties are comparable to that of PZT [2], but also because the phase diagram contains three morphotropic phase boundaries (MPB), at  $x=0.2$ ,  $x=0.3$  and  $x=0.5$ . An MPB is a phase transition that occurs at a discrete range in composition, as illustrated by vertical lines in the phase diagram. MPBs are a very interesting area of study, since dielectric and piezoelectric properties are enhanced in these regions, and the atomic-level structural mechanisms underlying these transitions are poorly understood. Until now, only the MPB at  $x=0.5$  in KNN has been studied, and no information was available on the other two. Several samples of KNN have been produced with varying composition around the MPB at  $x=0.3$ . Neutron scattering studies of some of the samples were performed at ISIS, UK, whilst high resolution powder X-ray diffraction and NMR analysis was conducted in-house at the University of Warwick. Rietveld refinement was used on the X-ray and neutron data to extract lattice parameters as a function of temperature and establish space groups[3]. Detailed structural analysis of cation displacements and oxygen tilting have also been calculated. NMR studies were performed on the sodium, potassium, and niobium nuclei ( $^{23}\text{Na}$ ,  $^{39}\text{K}$  and  $^{93}\text{Nb}$ ), to gain an insight in to the local structure of the materials. The aim is to not only better understand the physical properties of KNN, but also the underlying structural mechanism of MPBs.

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[2] Saito et al., *Nature* 2004, 432, 84

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#### MS17 P15

**Anisotropic thermal expansion and compressibility in  $BaMgF_4$  and  $BaZnF_4$**  J.M. Posse, K. Friese, A. Grzechnik, *Department of Condensed Matter Physics, University of the Basque Country, Bilbao, Spain.* E-mail: [josemaria@wm.lc.ehu.es](mailto:josemaria@wm.lc.ehu.es)

**Keywords:** fluorides, multiferroic, high pressure

The compounds  $BaMF_4$  ( $M = \text{Co, Fe, Mn, Ni, Zn, or Mg}$ ) crystallize in the same space group,  $Cmc2_1$ . The cation M is surrounded by six fluorine atoms forming an irregular octahedron. Four of the octahedra are connected via common corners with others, generating puckered layers perpendicular to the  $b$ -axis. The neighbouring layers are shifted with respect to each other by a translation of  $a/2$ . The barium atoms are located in the interlayer spaces [1-2].

These compounds are interesting due to the fact that some of them exhibit a multiferroic behavior at ambient conditions ( $M = \text{Fe, Co or Ni}$ ) [3]. In addition,  $BaMnF_4$  has a second-order phase transition to an incommensurate phase at low temperatures ( $T \sim 250 \text{ K}$ ; [4]). Currently, we are interested in the structural behavior of  $BaMF_4$  ( $M = \text{Mg, Zn}$ ) at low temperatures and high pressures.

High resolution powder diffraction experiments were carried out at the beamline ID31 (ESRF, Grenoble), in the temperature range 290-10K. The lattice parameters of both compounds obtained with the Le Bail method show the same characteristics: negative thermal expansion for the  $a$  parameter below 70K and a “bump” in the curve of the  $c$  parameter around 50K. In addition, we performed single crystal diffraction experiments on  $BaMgF_4$  at low temperatures. The results of the structural refinements show that, as temperature decreases, the octahedra rotate around the  $a$  axis. At the same time, the interoctahedral angle of the puckered layers decreases and neighbouring layers approach each other.

We also obtained powder diffraction diagrams under high pressures using a diamond anvil cell at the beamline D3 in HASYLAB (Hamburg). The two compounds show different behaviors: the pressure-induced broadening of the Bragg reflections in  $BaMgF_4$  above ambient pressure might be an evidence for an onset of amorphization or might indicate a lack of periodicity in the layer stacking direction. In the case of  $BaZnF_4$ , a splitting of reflections above 7 GPa was observed, due to a structural phase transition, without noticeable hysteresis. This observation is confirmed by the change of the vibrational modes in the Raman spectra.

Our intention is to perform additional single-crystal diffraction experiments under high pressure to characterize the new phase of  $BaZnF_4$  and to determine the reasons for the broadening of reflections in  $BaMgF_4$ . Rietveld refinements of the low temperature structure of  $BaZnF_4$  will also be carried out and the results will be compared with the ones obtained for  $BaMgF_4$ .

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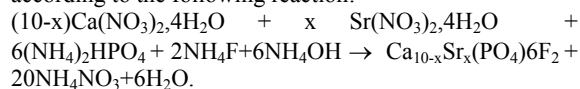
#### MS17 P16

**Substitution effect on the structure of apatite ( $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ ,  $x = 0, 4, 6, 10$ )** Fatima Zahra Boujrhah<sup>a,b</sup>, Bouchra Sghir<sup>b</sup>, Rajaâ Cherkaoui El Moursli<sup>b</sup>, El Kébir Hlil<sup>c</sup>, Abdelaziz Laghizil<sup>d</sup>, <sup>a</sup>Department of Physics, Faculty of Sciences and Technologies, Beni Mellal, Morocco. <sup>b</sup>Laboratory of Nuclear Physic, Faculty of Sciences, Rabat, Morocco, <sup>d</sup>Laboratoire de Chimie-Physique Générale, Faculté des Sciences, Rabat, Maroc, <sup>d</sup>Laboratory Chemistry-Physic, Faculty of Sciences, Rabat, Morocco, <sup>c</sup>Laboratoire de Crystallographie, Grenoble, France. E-mail: [boujrhah@yahoo.fr](mailto:boujrhah@yahoo.fr)

**Keywords:** apatite, pollutants, structure

The apatite is known to be an ideal material for long-term containment pollutants (stables: heavy metals and radioactifs) because of its high sorption capacity for actinides, fission products and heavy metals, low water solubility and high stability to heat treatment and to irradiation. In this work, we study the effect of substitution of the strontium (fission products) on the apatite structure. This stable element is the isotope of the one of product fission

The synthesis of Solid solution  $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$  are synthesized by wet process. This method consists in pouring 0.1 moles of an aqueous solution [(10-x)  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  et x  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] on a soluble phosphate solution (7.92g of  $(\text{NH}_4)_2\text{HPO}_4$ ) added ammonium fluoride (0.5g) in ammoniac medium of such way that the pH of the mixture is higher than 10. The reagents quantities are taken in stoichiometric proportions according to the following reaction:



The mixture is then heated under agitation at 80°C during two hours of precipitation. After maturation, filtration and drying of the precipitate, the obtained powder was heated in a continuous pipe still with at 900°C during three hours before be characterized by various physicochemical. The obtained synthetic apatite are  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ,  $\text{Ca}_6\text{Sr}_4(\text{PO}_4)_6\text{F}_2$ ,  $\text{Ca}_4\text{Sr}_6(\text{PO}_4)_6\text{F}_2$  and  $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$  corresponding for  $x = 0, 4, 6$  and  $10$  successively.

X ray diffraction and Rietveld refinements with FullProf code are used in order to determine a and c cell parameters, atomic positions, site occupancies and thermal parameters for various substitutions.

The results are given with the values of R-factor and the Bragg R-factor.

The analysis of the results gives evidence that the  $\text{Ca}^{2+}$  substitution by  $\text{Sr}^{2+}$  modifies the cell parameters (a and c) which increase with the introduction of Strontium ions, but the group of space is preserved for these compounds.

To help gain understanding the retention properties of apatites ( $\text{Ca}_{10-x}\text{Sr}_x(\text{PO}_4)_6\text{F}_2$ ) we have carried out an electronic structure study. The calculation were performed using CRYSTAL code. Other synthesized apatite with heavy metal are in progress.

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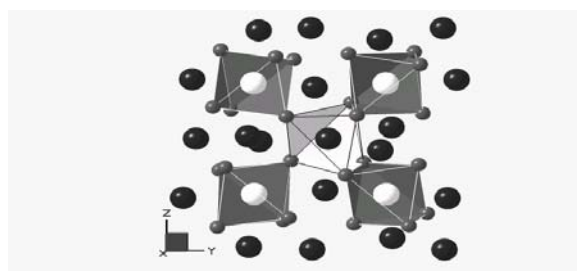
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#### MS17 P17

**Preparation and x-ray characterization of the mixed oxides ( $\text{Gd}_{1-x}\text{RE}_x$ )<sub>2</sub>O<sub>3</sub>; (RE=Ho, Yb and Y) as powder and thin films buffer layers for YBCO coated conductors** Z.K. heiba<sup>a</sup>, L. Arda<sup>b</sup>, <sup>a</sup>Physics Department, Faculty of science, Ain Shams University, Cairo, Egypt. <sup>b</sup>Bahcesehir University, Faculty of Arts and Science, Besiktas Campus, 34349 Istanbul, Turkey . E-mail: [zein\\_kh@yahoo.com](mailto:zein_kh@yahoo.com)

**Keywords:** buffer layers, mixed rare earth oxide, microstructure.

Buffer layers from mixed rare-earth oxides ( $\text{Gd}_{1-x}\text{RE}_x$ )<sub>2</sub>O<sub>3</sub>; (RE=Ho, Yb and Y) with 100% lattice match with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) were prepared applying a simple sol-gel process and dip-coating method. X-ray diffraction structural analysis of the sol-gel derived powders were performed using Rietveld refinement method and the value of mixing parameter x which eliminate the lattice mismatch with YBCO was determined. The cationic distribution over the two non-equivalent sites 8b and 24d, figure 1, of the space group *Ia-3* is investigated. The analysis showed anisotropic variation of crystallite size and microstrain along different crystallographic directions. Microstructural investigations were carried out for ( $\text{Gd}_{1-x}\text{RE}_x$ )<sub>2</sub>O<sub>3</sub> films, with appropriate value of x, epitaxially grown on cube textured Ni (100) substrates by sol-gel dip coating process. X-ray diffraction of the films showed strong out-of-plane orientation on Ni tape. The ( $\text{Gd}_{1-x}\text{RE}_x$ )<sub>2</sub>O<sub>3</sub> (222) pole figure indicated a single cube-on-cube textured structure. The full-width-at-half-maximum (FWHM) values of omega and Phi scans of the films revealed good out-of-plane and in-plane alignments. ESEM and AFM micrographs of the film revealed pinhole-free, crack-free, smooth and dense microstructures.



**Figure 1.** Oxygen octahedra in the cubic rare earth bixbyite structure *Ia-3*. For clarity, only one half of the unit cell is shown, in the X direction. Large balls (dark 24d, white 8b) represent rare earth atoms and small ones represent oxygen.