was heated under dynamic vacuum; at 130°C deuterium is released and $LiMgAlD_6$ is formed: $LiMg(AlD_4)_3 \rightarrow LiMgAlD_6 + 2Al + 3D_2$. At 180°C $LiMgAlD_6$ decomposes: $LiMgAlD_6 \rightarrow LiD + MgD_2 + Al + 3/2D_2$. The first reaction is endothermic; the second exothermic, indicating that $LiMg(AlD_4)_3$ is not thermodynamic stable. $LiMg(AlD_4)_3$ crystallizes in the monoclinic space group $P2_1/c$ with cell parameters: a = 8.37 Å, b = 8.74 Å, c = 14.30 Å and β = 124.83 °. The structure consists of isolated AlD_4 tetrahedra that are connected by octahedral Mg and Li atoms. $LiMgAlD_6$ crystallizes in the trigonal space group $P321$ with cell parameters: a = 7.98 Å and c = 4.38 Å. The structure consists of isolated AlD_6 octahedra tied together by hexa-coordinated Li and Mg atoms.
A small amount of $TiCl_3$ was added to $LiMg(AlD_4)_3$ and mixed using the ball milling technique. The effect of addition of $TiCl_3$ was also studied for $LiMgAlD_6$.

[1] Bogdanovic, B., Schwickardi, M., *J. Alloys Compd.,* 1997, 253-254, 1.
[2] Grove, H., *et al*., *J. Alloys Compd.* (2007), article in press: doi:10.1016/j.jallcom.2007.01.150.
[3] Grove, H., *et al.* submitted manuscript.

MS17 P11

Structural phase transitions in Sr_2ScReO_6

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Keywords: Re-containing double perovskites, structural phase transition, magnetism of Re^{+5}

In double perovskites A_2MReO_6, where A – an alkaline-earth ion and M – a non-magnetic two – or three-valence cation such as Zn^{2+}, Mg^{2+} or Sc^{3+}, only the Re ion is relevant to the unusual magnetism in these compounds [1, 2]. Structural thermal behaviour of these compounds, which can be connected with magnetic and transport properties, is not yet investigated. In our work, high-temperature structure investigations of Sr_2ScReO_6 were performed at beamline B2 (HASYLAB DESY, Germany) in Debye-Scherrer mode using the on-site readable image-plate detector OBI and a STOE furnace. All diffraction patterns have been analyzed by using the software package WinPLOTR [3]. Two phase transitions with a change of symmetry of the crystal structure from monoclinic (S.G. $P2_1/n$) to tetragonal (S.G. P4/mnc) and then to cubic (Fm-3m) have been detected at elevated temperatures. These phase transitions were also proved by DSC measurements. Low-temperature investigations of Sr_2ScReO_6 are in progress.

[1] H.Kato, T. Okuda, Y. Tomioka *Phys. Rew.* B 69 (2004) 184412.
[2] K. G. Bramnik, H. Ehrenberg, J. K. Dehn, H. Fuess *Solid State Science* 5 (2003) 235-241.
[3] T. Roisnel, J. Rodriguez-Carvajal, *Mater. Sci. Forum* 378-381 (2001) 118-123.

MS17 P12

X-ray Induced Water Order-Disorder Transition in Hydrated Cesium Cobalt Oxide

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Keywords: X-ray Induced, Order-Disorder Transitions, Water Structure

Metal cobalt oxides, A_xCoO_2 (A= Li, Na, K, Rb, Cs), with layered structure have been attracting wide attention for the past two decades. Li_xCoO_2 is one of the most important intercalation compounds for secondary lithium ion batteries. Na_xCoO_2 is recognized to be a potential candidate for thermal electric power materials and non-cuprites superconductors. A_xCoO_2 compounds have a layered structure, with the CoO_2 layers consisting of CoO_6 octahedra sharing common edges and forming a triangular Co–O sublattice. Open and polarizable framework structure makes the compounds adaptable by chemical modification. The superconductivity of hydrated $Na_{0.35}CoO_2{\cdot}1.3H_2O$ oxide was found and immediately targeted by research scientists owing to its unusual bilayer-hydrate (BLH) structure. In the coupling strength of CoO_2 layers might be varied by the replacement of different ionic size alkalis resulting in the change of c-axis lattice constant. The influence of coupling strength between CoO_2 layers on superconductivity, therefore, can be possibly studied when the process of controlling the interlayer spacing is developed. The bilayer-hydrate of $Cs_{0.2}CoO_2{\cdot}0.63H_2O$ with a greatest interlayer spacing d 10.0(2)Å among alkali cobalt oxides has been grown in crystal form. Magnetic susceptibility measurement of $Cs_{0.2}CoO_2{\cdot}0.63H_2O$ displays a paramagnetic behavior down to 1.9 K. We find that X-ray powder diffraction patterns of $Cs_{0.2}CoO_2{\cdot}0.63H_2O$ changed according to various X-ray dosages during the XRD measurement. The water ordering in $Cs_{0.2}CoO_2{\cdot}0.63H_2O$ is sensitive to X-ray irradiation. The relative diffraction intensity vary is strongly dependent on the amount of water contain and the location at interfacial position. We will report the X-ray dosage dependent crystal structure of $Cs_{0.2}CoO_2{\cdot}0.63H_2O$ in the meeting.

MS17 P13

Investigation of $K_xNa_{1-x}NbO_3$ (KNN) near the Morphotropic Phase Boundaries

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Keywords: morphotropic phase boundary, sodium potassium niobate, neutron and X-ray scattering

PZT is commonly regarded as the leading piezoelectric material for a wide range of applications, and one which all others must be assessed against. However, there are growing concerns over the toxicity and environmental issues of lead-based substances , which is why attention has turned to other lead-free piezoelectric materials, one of which is Sodium Potassium Niobate (KNN).

The newer lead-free materials are united with PZT in that they exhibit a region in their phase diagrams where there appears to be a sudden change in crystal structure. This region has been termed the Morphotropic Phase Boundary (MPB) and appears to coincide with the maximum piezo-response of these materials. Of particular interest in $K_xNa_{1-x}NbO_3$ (KNN) is the presence of three morphotropic phase boundaries (MPB) that occur at x ~ 0.18, x ~ 0.35, and x ~ 0.48[1].

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 $K_xNa_{1-x}NbO_3$

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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 be calculated. NMR studies were performed on the sodium, potassium, and niobium nuclei (^{23}Na, ^{39}K and ^{93}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.

[1] M. Demartin Maeder, D Damjanovic, N. Setter, *Journal of Electroceramics* 2004, 13, 385–392.
[2] Saito et al., *Nature* 2004, 432, 84
[3] M. Ahtee, A.M. Glazer, *Acta Cryst.* 1975, A32, 434

MS17 P15

Anisotropic thermal expansion and compressibility in $BaMgF_4$ and $BaZnF_4$

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Keywords: fluorides, multiferroic, high pressure

The compounds BaMF$_4$ (M = 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 = Fe, Co or Ni) [3]. In addition, $BaMnF_4$ has a second-order phase transition to an incommensurate phase at low temperatures (T ~250 K; [4]). Currently, we are interested in the structural behavior of BaMF$_4$ (M = 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 $BaMgF_4$.

[1] J. Lapasset, H.N. Bordallo, R. Almairac, and J. Nouet, *Z. Kristallogr.* NCS 211, 934-935 (1996).
[2] H.G. von Schnering and P. Bleckmann, *Naturwiss.* 55, 342-343 (1968).