

FA2-MS17-P01

High pressure effects on the crystal and magnetic structure of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Deleg Sangaa^a, Denis P. Kozlenko^a, Sergey E. Kichanov^a, Tuan A. Tran^a, Zdenek Jiráček^b, Boris N. Savenko^a. ^aFrank Laboratory of Neutron Physics, JINR, 141980 Dubna Moscow Reg., Russia. ^bInstitute of Physics, Academy of Sciences, 16253 Prague, Czech Republic.
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A crystal and magnetic structure of manganite $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ has been studied by means of powder neutron diffraction at pressures up to 5 GPa in the temperature range 10–300 K. Under high pressure, a suppression of the initial pseudo-CE type antiferromagnetic (AFM) state and an appearance of A-type AFM state was observed. An anisotropic compression of the lattice was found which leads to the apical compression of MnO_6 octahedra. Possible mechanisms of the observed magnetic phase transition are discussed.

Keywords: Pressure; Magnetic Structure; Manganites

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High pressure structural studies of selected dicarbides. I. Efthimiopoulos^a, G. V. Vajenine^{a,b}, E. Stavrou^a, K. Syassen^a, St. Liebig^c, U. Ruschewitz^c, M. Hanfland^d. ^aMPI-FKF, Stuttgart, Germany. ^bInstitut für Anorganische Chemie, Universität Stuttgart, Germany. ^cDepartment für Chemie, Universität zu Köln, Germany. ^dESRF, Grenoble, France.
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Carbides of electropositive metals have attracted attention due to their physical properties such as superconductivity in layered MC_6 carbides with $M = \text{Y}$ or Ca [1]. The MC_6 compounds are formed by metal atom intercalation into graphite. Carbides with the MC_2 composition, featuring isolated C_2 dumbbells, have been characterized for all alkaline-earth and most rare-earth metals. For divalent metals these dicarbides are insulators or semiconductors. They can be viewed as acetylides featuring a triple carbon-carbon bond in the C_2^{2-} units. Interestingly, different valence electron counts might also lead to superconductivity such as in YC_2 [2]. Dicarbides of alkaline-earth metals crystallize with NaCl-related structures at ambient pressure. They are interesting candidates for in-situ high-pressure structural and spectroscopic investigations. On the one hand, changes in the local coordination in the course of structural phase transitions are of interest. On the other hand, possible polymerization of the C_2 dumbbells might lead to extended carbon networks. We have investigated the structural and vibrational properties of BaC_2 and CaC_2 under pressure by means of synchrotron-based X-ray diffraction and Raman spectroscopy. The ambient-pressure tetragonal $I4/mmm$ phase of CaC_2 [3] was found to be stable up to ~30 GPa, while the monoclinic C2/c phase fully converts into the tetragonal one below 7 GPa. When pressure exceeds 30 GPa, irreversible amorphization is observed, accompanied by a loss of the C_2 Raman signal. In contrast, the ambient-pressure tetragonal $I4/mmm$ phase of BaC_2 [4] undergoes a reversible phase transition at 4 GPa, accompanied by an increase of local coordination numbers. Similar to CaC_2 , BaC_2 becomes amorphous above 30 GPa. Simulations of the phase stability of CaC_2 and BaC_2 by first-principles calculations will be reported.

[1] Weller T. E., Ellerby M., Saxena S. S., Smith R. P., Skipper N. T., *Nat. Phys.*, 2005, 1, 39. [2] Giorgi A. L., Szklarz E. G., Krupka M. C., Wallace T. C., Krikora N. H., *J. Less-Common Met.*, 1968, 14, 247. [3] Knapp M., Ruschewitz U., *Chem. Eur. J.*, 2001, 7, 874. [4] V. Vohn V., W. Kockelmann W., Ruschewitz U., *J. Alloys Compd.*, 1999, 284, 132.

Keywords: BaC_2 , CaC_2 , high-pressure phase transitions

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Metastable Bi_2O_3 Polymorphs obtained by High Pressure and High Temperature. T. Locherer^a, S. Ghedia^a, A. Senyshyn^{b,c}, D. L. V. K. Prasad^a, R. Dinnebier^a, M. Jansen^a. ^aMax Planck Institute for Solid State Research, Stuttgart, Germany. ^bInst. For Materials Science, TU Darmstadt, Germany. ^cFRM II, Garching, Germany.
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Although being well known for the high ionic conductivity of its high temperature modifications, only little is known about the high pressure behavior of Bi_2O_3 . Previous reports contradict each other to a certain degree and do not present structures of high pressure modifications [1], [2]. Using a large volume multi anvil type device we were able to identify two new metastable (quenched to ambient conditions) polymorphs of Bi_2O_3 by means of X-ray and neutron powder diffraction. Structural analysis shows that in one of these modifications Bi_2O_3 crystallizes in an entirely new structure type within the non centrosymmetric space group $P31c$. The structure determining lone pairs for $\text{Bi}^{(III)}$ compounds are less pronounced on the $2b$ site and exhibit a highly polar orientation. These structural properties are giving raise to the assumption that the high pressure phase of Bi_2O_3 is a potential ferroelectric. Upon annealing it relaxes to a second new modification at about 106 °C, before at about 310 °C the transformation towards the stable ambient α -modification is completed. This “relaxed” phase can be considered as an intermediate polymorph similar to the ambient. In contrast to the former it exhibits a two dimensional channel network with the lone electron pairs pointing into these channels. A weak ionic conduction was determined for this modification.

[1] C. Chouinard, S. Desgreniers, *Solid State Commun.* 113 (2000) 125–129. [2] T. Atou *et al.*, *Mater. Res. Bull.* 33 No. 2 (1998) 289–292.

Keywords: High Pressure Phase Transformations, Lone Pairs, Neutron and X-ray diffraction

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Texture determination of ferroelectrics from *in situ* X-ray diffraction. Manuel Hinterstein^a, Michael Knapp^b, Hartmut Fuess^c, Helmut Ehrenberg^b. ^aComplex Materials, IFW Dresden, D-01069 Dresden, Germany. ^bCELLS, P.O.B 68, 08193 Barcelona, Spain. ^cMaterials Science, Technical University Darmstadt, Germany.
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Piezoelectric ceramics such as lead zirconate titanate (PZT) or bismuth sodium titanate (BNT) with perovskite structure can be found in a multitude of applications. Most of these applications require electric poling, i.e. there must be a

preferred orientation of the ferroelectric domains accompanied by a macroscopic polarization.

In PZT highest piezoelectric response is found at the morphotropic phase boundary (MPB), separating a rhombohedral structure, in which the polarization is along the $[111]_c$ direction, from a tetragonal structure, in which the polarization lies along the $[001]_c$ direction[1]. The subscript "c" denotes the pseudocubic perovskite unit cell. A similar MPB with a rhombohedral and a tetragonal phase can be found in BNT doped with barium titanate (BT)[2].

In situ high resolution X-ray diffraction experiments with a specially developed sample environment for applied electric fields[3] were conducted at the MS beamline at the SLS[4]. The experiments were focused on texture analysis and revealed the microstructural reactions during poling and fatiguing of BNT and PZT based materials.

The results indicate that poling and fatiguing of morphotropic ferroelectrics results in a combination of reversible phase transitions and complex texture formations. Reconstructed and inverse pole figures contribute additional informations to the interpretation of the complex microstructural processes during the application of an electric field.

Texture analysis was performed using the program MAUD[5], which is especially designed for texture and structure analysis.

[1] B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*, (Academic Press, London, 1971). [2] T. Takenaka, K. Maruyama and K. Sakata, *Jpn. J. Appl. Phys.*, Part 1 30, 2236 (1991). [3] K. A. Schoenau, M. Knapp, H. Kungl, M. J. Hoffmann, and H. Fuess, *Phys. Rev. B* 76, 144112 (2007). [4] L. Lutterotti, S. Matthies, H.-R. Wenk, A. S. Schultz and J. W. Jr Richardson, *J. Appl. Phys.* 594–600 81 (1997).

Keywords: ferroelectrics, X-ray diffraction, texture analysis

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Synthesis, crystal structure and thermal behavior of Sr3B2SiO8. Krzhizhanovskaya Maria

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FA2-MS17-P07

Metastable Bi₂O₃ Polymorphs obtained by High Pressure and High Temperature. T. Locherer^a, S.

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Although being well known for the high ionic conductivity of its high temperature modifications, only little is known about the high pressure behavior of Bi₂O₃. Previous reports contradict each other to a certain degree and do not present structures of high pressure modifications [1], [2]. Using a large volume multi anvil type device we were able to identify two new metastable (quenched to ambient conditions) polymorphs of Bi₂O₃ by means of X-ray and neutron powder diffraction. Structural analysis shows that in one of these modifications Bi₂O₃ crystallizes in an entirely new structure type within the non centrosymmetric space group $P31c$. The structure determining lone pairs for Bi^(III) compounds are less pronounced on the **2b** site and exhibit a highly polar

orientation. These structural properties are giving raise to the assumption that the high pressure phase of Bi₂O₃ is a potential ferroelectric. Upon annealing it relaxes to a second new modification at about 106 °C, before at about 310 °C the transformation towards the stable ambient α -modification is completed. This "relaxed" phase can be considered as an intermediate polymorph similar to the ambient. In contrast to the former it exhibits a two dimensional channel network with the lone electron pairs pointing into these channels. A weak ionic conduction was determined for this modification.

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Keywords: High Pressure Phase Transformations, Lone Pairs, Neutron and X-ray diffraction

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High-pressure single-crystal structure investigations of sillenites. Leonore Wiehl, Alexandra Friedrich, Eiken Haussühl, Wolfgang Morgenroth, Björn Winkler.

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Sillenites, Bi₁₂MO₂₀ ($M = \text{Si, Ge, Ti}$), crystallize in the cubic non-centrosymmetric space group $I23$. They are piezoelectric and optically active, they exhibit electro-optic effects and high photoconductivity, leading to applications using the photo-refractive effect [1]. It is assumed that these properties are correlated with the stereochemical activity of the 6s² lone electron pair of Bi³⁺. The lone electron pairs are hosted within large cavities, which are built up from four distorted BiO₅ pyramids and two regular MO₄ tetrahedra. These cavities have a large potential to be considerably compressed at high pressure, accompanied by a reduction of the stereochemical activity of the lone electron pair. Strong pressure-induced changes of the Bi coordination were observed for example in Bi₂Ga₄O₉ [2] and Bi₂S₃ [3]. The aim of our single-crystal X-ray diffraction experiments was to investigate the effect of pressure on the stereochemical activity of the Bi³⁺ lone electron pair within the sillenite structure.

The crystal structures of Bi₁₂SiO₂₀ (BSO), Bi₁₂GeO₂₀ (BGO) and Bi₁₂TiO₂₀ (BTO) were determined at high pressures in diamond anvil cells. Single-crystal X-ray intensity data were collected at ambient conditions in house and at pressures up to 16.8(3) GPa with synchrotron radiation at HASYLAB (D3). Lattice parameters were determined up to 23.0(3) GPa. All data sets could be refined to R1 values below 4% and wR2 below 9%. The cubic symmetry is preserved at least up to 16.8 GPa in BSO and 8.6 GPa in BGO with no indication of a phase transition. The unit cell volumes of BSO and BGO as function of pressure were fitted with a 3rd-order Birch-Murnaghan equation of state. We found the largest compression of interatomic distances (Bi – Bi, Bi – O) along the lone pair directions, but nearly as large Bi – Bi compressions in directions perpendicular to this. Despite of some tilts the cavities are compressed nearly isotropically. The eccentricity of the Bi coordination is reduced considerably, but less than in Bi₂Ga₄O₉ [2]. A complete collapse of the cavities seems to be prevented by the high symmetry of the crystals. Changes of the Bi^{[5+2]O₇} polyhedra will be discussed. The results are supported by complementary data from X-ray