Lead-free alternative for memory or piezoelectric applications

Structure-property relations in the $Na_{1-x}K_xNbO_3$ lead-free piezoelectric materials

***D. Fritsch*[1,2]**, [1] *Helmholtz-Zentrum Berlin für Materialien und Energie,* [2] *Institute of Physics and Astronomy, University of Potsdam*

In Short

- motivation: identify lead-free alternatives to most commonly used piezoelectric ceramic lead zirconate titanate (PZT)
- promising candidates $NaNbO_3$ and $KNbO_3$ show range of phase transitions and possible polymorphs
- employ *special quasirandom structures* to investigate $Na_{1-x}K_xNbO_3$ solid solution
- contribute to in-depth material understanding and their potential as key materials in future memory or piezoelectric applications

Over the last decade, a large proportion of materials science investigations has been devoted to identify more environmentally friendly materials for several applications. This led to a surge in investigations for indium free photovoltaic devices, as well as identifying lead-free alternatives for the industry standard lead zirconate titanate (PZT) for piezoelectric applications [1,2]. The latter case is at the centre of the proposed project, and has already seen the identification of $NaNbO_3$, $KNbO_3$, and their solid solution $Na_{1-x}K_xO_3$ as promising replacement candidates.

Experimental research efforts employing a plethora of growth techniques, tools for structural characterisation, and subsequent analyses into electronic and optical properties, allowed for a much improved understanding of material properties in general. On the theoretical side, the development of ever more capable exchange and correlation functionals to be employed in density functional theory (DFT) calculations, and the wide-spread availability of high-performance computing facilities, led to an in-depth understanding of structure-property relations in a wide range of material classes.

Here, we're concerned with $NaNbO_3$ and $KNbO_3$ piezoelectric materials, occurring in a variety of structural polymorphs and showing several phase transitions [3,4]. We will perform first principles calculations based on density functional theory (DFT) to shed some light on the intricate balance of the underlying crystal structure on the electronic and optical properties, as well as subsequent quasiparticle calculations for a better description of the optical properties.

We employ two different parameterisation of the density functional, namely the newly introduced SCAN functional [5], and the more accurate hybrid functional HSE06 [6]. While the SCAN functional satisfies all known possible exact constraints for the exact density functional and has been claimed to match or improve on the accuracy of computationally more demanding hybrid functionals [7], calculations based on hybrid functionals have been shown to yield improved structural and electronic properties compared to standard parametrisations [8]. The electronic band structure of $Pbcm$ $NaNbO_3$ is exemplarily shown in Fig. [1]. In order to get a better grasp of the optical properties, additional quasiparticle calculations based on the GW method introduced by Hedin [9] will be performed as well.

Once the structural, electronic, and optical properties of the structural polymorphs (see Fig. [2] for low temperature polymorphs of $NaNbO_3$ [4]) have been obtained, additional calculations will investigate the solid solution $Na_{1-x}K_xNbO_3$. Here, we will make use of so-called *special quasirandom structures*, introduced by Zunger *et al.* [10], to sample the whole composition range within the solid solutions. Thereby, the concept of *special quasirandom structures* allows to identify only symmetry-inequivalent cation distributions within the solid solutions, ulti-

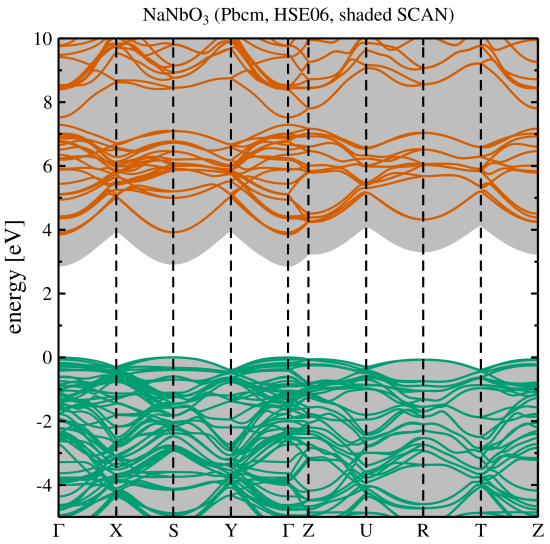

Figure 1: *Electronic band structure of $NaNbO_3$ crystallising in the orthorhombic P phase ($Pbcm$) at room temperature. Shown are the valence (green) and conduction (orange) bands, calculated by means of a more accurate hybrid functional approach (shaded semi-local functional).*

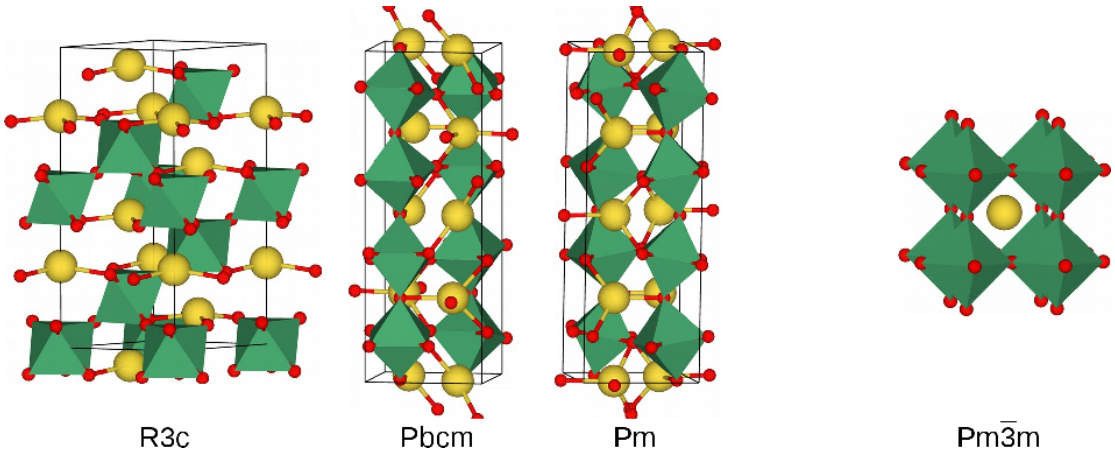

Figure 2: *Crystalline phases of $NaNbO_3$ at room temperature and below in comparison to the cubic perovskite phase ($Pm\bar{3}m$, SG 221) (right). From left: rhombohedral $R3c$ phase (SG 161), orthorhombic $Pbcm$ phase (SG 57), and monoclinic Pm phase (SG 6) [4].*

mately leading to an efficient use of provided computational resources. Here we rely on the supercell program of Okhotnikov *et al.* [11].

Once the structural, electronic, and optical properties of the structural polymorphs (see Fig. [2] for low temperature polymorphs of $NaNbO_3$ [4]) have been obtained, additional calculations will investigate the solid solution $Na_{1-x}K_xNbO_3$. Here, we will make use of so-called *special quasirandom structures*, introduced by Zunger *et al.* [10], to sample the whole composition range within the solid solutions. Thereby, the concept of *special quasirandom structures* allows to identify only symmetry-inequivalent cation distributions within the solid solutions, ultimately leading to an efficient use of provided computational resources.

The results obtained in this project will contribute to an atomic scale insight into structural, electronic, and optical properties of piezoelectric materials, and will allow for the identification of prospective lead-free materials to replace PZT.

WWW

https://www.helmholtz-berlin.de

More Information

[1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, *Nature* **432**, 84 (2004). doi:10.1038/nature03028.

[2] X. Tan, C. Ma, J. Frederick, S. Beckman, and S. G. Webber, *J. Am. Ceram. Soc.* **94**, 4091 (2011). doi:10.1111/j.1551-2916.2011.04917.x

[3] H. D. Megaw, *Ferroelectrics* **7**, 87 (1974). doi:10.1080/00150197408237956

[4] D. Fritsch, *Advances in Materials Science and Engineering* **volume 2018, article ID 6416057** (2018). doi:10.1155/2018/6416057

[5] J. Sun, R. C. Remsing, Y. Zhang, Z. Sun, A. Ruzsinszky, H. Peng, Z. Yang, A. Paul, U. Waghmare, X. Wu, M. L. Klein, and J. P. Perdew, *Nature Chem.* **8**, 831 (2016). doi:10.1038/NCHEM.2535

[6] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **124**, 219906 (2006). doi:10.1063/1.2204597

[7] M. Bokdam, J. Lahnsteiner, B. Ramberger, T. Schäfer, and G. Kresse, *Phys. Rev. Lett.* **119**, 145501 (2017). doi:10.1103/PhysRevLett.119.145501

[8] D. Fritsch, B. J. Morgan and A. Walsh, *Nanoscale Research Lett.* **12**, 19 (2017). doi:10.1186/s11671-016-1779-9

[9] L. Hedin, *Phys. Rev.* **139**, A796 (1965). doi:10.1103/PhysRev.139.A796

[10] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, *Phys. Rev. Lett.* **65**, 353 (1990). doi:10.1103/PhysRevLett.65.353

[11] K. Okhotnikov, T. Charpentier, and S. Cadars, *J. Cheminform.* **8**, 17 (2016). doi:10.1186/s13321-016-0129-3