Poster Presentations

[MS14-P08] Metastable structures in Rb-doped K_2ZnCl_2: New phase transitions due to memory effects Karsten Behrendt, Jeannis Leist, Holger Gibhardt, Götz Eckold

Institut für Physikalische Chemie, Georg-August- Universität Göttingen, Tammannstraße 6, 37077 Göttingen, Germany
E-mail: kbehren@gwdg.de

Crystals of the A_2BX_4-family typically exhibit a phase sequence from the high temperature ortho- rhombic via an incommensurably modulated struc- ture (INC) to a commensurate ferroelectric phase (C), followed by a low temperature monoclinic structure. Close to the INC to C lock-in transition, the modulation waveform changes from sinusoidal to square-like. The structure can therefore be de- scribed as an ordered sequence of commensurate nanodomains of alternating polarization [1].
The discommensuration density generally decreases on cooling via the nucleation of topological defects, known as anti-stripples. This motion of domain walls and hence the transition into the ferroelectric phase is strongly influenced by pinning at lattice defects like impurities. As a consequence the lock- in transition of mixed crystals is observed at lower temperatures than in pure samples [2].
In order to study this influence systematically, a series of high-quality K_2ZnCl_4 single crystals doped with different amounts of Rb (from 0.4 % to 8 %) was grown from aqueous solution. High-resolution γ-ray diffraction was used to study the temperature- dependent variation of satellite reflections (from 1st to 5th order) characterizing the modulated structure. Complementary information about the dielectric properties, reflecting domain behaviour, was ob- tained by in-situ impedance spectroscopy.
As we have shown recently, the major effect of impurity doping is kinetic hindrance of the lock-in transition rather than changing the thermodynamic phase stability. Thus, introducing higher amounts of Rb (> 1%) results in an INC-phase metastable down to temperatures far below the actual transition point into the C-phase at 400 K. The transformation pro- ceeds on a timescale of days to months and in mechanistic agreement with a strongly retarded anti-stripple nucleation [3].
In a crystal containing 0.4% Rb, however, the INC- phase was found to be metastable only within a certain temperature interval. Below approx. 350 K the discommensuration lattice seems to collapse and the C-phase is formed instantaneously. Subse- quently, an additional anomaly in the dielectric constant is observed around 240 K on cooling as well as heating. This signal might correspond to a similar effect reported in a sample of nominally pure K_2ZnCl_4 [4]. So far, no structural change could be found at this point. In fact, this behaviour is only observed in quenched crystals which were not giv- en time to gradually relax the discommensuration lattice. Therefore, this non-equilibrium lattice insta- bility is presumably caused by the annihila- tion/formation of non-coherent domain walls. Another remarkable observation was made on a sample with 1% Rb. When the quenched crystal is cooled into the monoclinic phase, the INC-satellites vanish. Heating up again, the orthorhombic C-phase forms directly; above 200 K however, far below the lock-in temperature, the metastable INC-phase is restored gradually.
Altogether, we demonstrated the existence of addi- tional metastable phases in slightly doped crystals. Three non-equilibrium transitions were observed, of which the C-phase formation has to be distinct from the common stripple mechanism. It can be concluded that defects do not only play an important role in the transition kinetics of incom- mensurately modulated structures. Moreover, memory effects leading to phase transitions into metastable structures can only be explained by a structural rearrangement of defects and thereby stabilization of the discommensuration lattice.

[1] Leist, J., Gibhardt, H., Hradil, K. &

Eckold, G. (2008). *J. Phys.: Condens. Matter* **20**, 415209.
[2] Hamano, K., Ema, K. & Hirotsu, S. (1981).*Ferroelectrics* **36**, 343 346.
[3] Mashiyama, H. & Kasatani, H.(1987). *J. Phys. Soc. Jpn.* **56**, 3347-3353.
[4] Ahn, H. Y. & Jeong, S. Y. (2001). *Europhys. Lett.* **54**, 361-365.

Keywords: disordered incommensurate modu- lated structures, nonequilibrium phase change, dielectric properties