Metastable structures in Rb-doped $\text{K}_2\text{ZnCl}_2$: New phase transitions due to memory effects

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Crystals of the A$_2$BX$_4$-family typically exhibit a phase sequence from the high temperature orthorhombic via an incommensurably modulated structure (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 described 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 $\text{K}_2\text{ZnCl}_4$ single crystals doped with different amounts of Rb (from 0.4 % to 8 %) was grown from aqueous solution. High-resolution $\gamma$-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 obtained 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 proceeds on a timescale of days to months and in mechanistic agreement with a strongly retarded anti-stipple 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. Subsequently, 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 $\text{K}_2\text{ZnCl}_4$ [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 given time to gradually relax the discommensuration lattice. Therefore, this non-equilibrium lattice instability is presumably caused by the annihilation/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 additional 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 incommensurately 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. &


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