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Ferroelectricity and Modulated Phases in Mixed Crystals of the A_2BX_4-Compounds

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Incommensurately modulated structures may frequently be regarded as an ordered sequence of nanodomains. In ferroelectric systems, these domains exhibit alternating anti-parallel orientations of their polarisation. Impurities or other topological defects are known to have a strong influence on the domain structure. The systems K_2ZnCl_4, Rb_2ZnCl_4, K_2ZnBr_4, Rb_2ZnBr_4 were used to study the influence of the substitution of alkali metals or halides on the incommensurate phase and the ferroelectric lock-in transition by high-resolution gamma-ray diffraction, neutron and Raman scattering.

While doping of Rb_2ZnCl_4 with potassium shifts the stability regime of the incommensurate phase towards higher temperatures, the opposite effect is observed if chlorine is replaced by bromine [1,2]. Moreover, the usual variation of the modulation wavelength with temperature is suppressed by introducing chemical defects. This finding is a clear indication of very strong pinning effects. In addition, even the ferroelectric lock-in transition is effectively suppressed. The particular effect of halide substitution may be explained by the associated reduction of the local symmetry along with a variation of the moment of inertia of halide tetrahedra since the collective tilting of these tetrahedra is responsible for the modulation to evolve.

Using γ-ray diffraction as well as neutron scattering, the doping behaviour of Rb_2ZnCl_4 was investigated in detail for the first time in various single crystals containing bromine as well as potassium as dopants. Care has been taken to grow high quality crystals, as reflected by a mosaicity of less than 0.04° in all samples, even when adding more than 10% of bromine and potassium each. In order to characterise the defect distribution, the content of halides in the crystals was determined via Raman scattering. Apart from enabling an analysis of the quantitative halide composition, the spectra yielded information about the distribution within the tetrahedra. There is clear evidence that bromine impurities are statistically distributed among the sites without any significant correlation. The Rb-K ratio, on the other hand, could be determined very precisely via scintillation analysis of the characteristic radiation from the radioactive isotopes ^{40}K and ^{87}Rb.

It was found that the coherence length of the modulation decreases significantly on increasing the overall amount of dopant. The stability regime of the incommensurate phase proved to be influenced independently by the two types of dopants. This allows one to vary the temperature of the transition to the normal phase over a range of more than 300 K just by varying the concentration of cation and anion impurities. The incommensurate phase remains stable at least down to temperatures of 20 K in all those crystals. Even if the ferroelectric phase is obviously suppressed, third-order diffraction satellites were observed on cooling. This is a clear evidence for the existence of the well-defined polarised nanodomain structure, which is usually observed only close to a ferroelectric lock-in transition [3]. Hence, the formation of this characteristic distortion of the modulation is not prevented by the particularly strong pinning centers present in those doped crystals.

Only for potassium concentrations well below 1 % the lock-in transition of Rb_2ZnCl_4 is preserved. Thermal hysteresis, however, is strongly enhanced and a large interval of phase coexistence could be observed in an example containing 0.2 % of potassium, only. This indicates the presence of various pinning centers of different strength, which however do not inhibit the lock-in transition completely. Application of an external electric field parallel to the polar axis stabilises the ferroelectric phase in the same degree as in the pure substances. The entire coexistence range thus is shifted to higher temperatures by 0.35 K/(kV cm^{-1}).

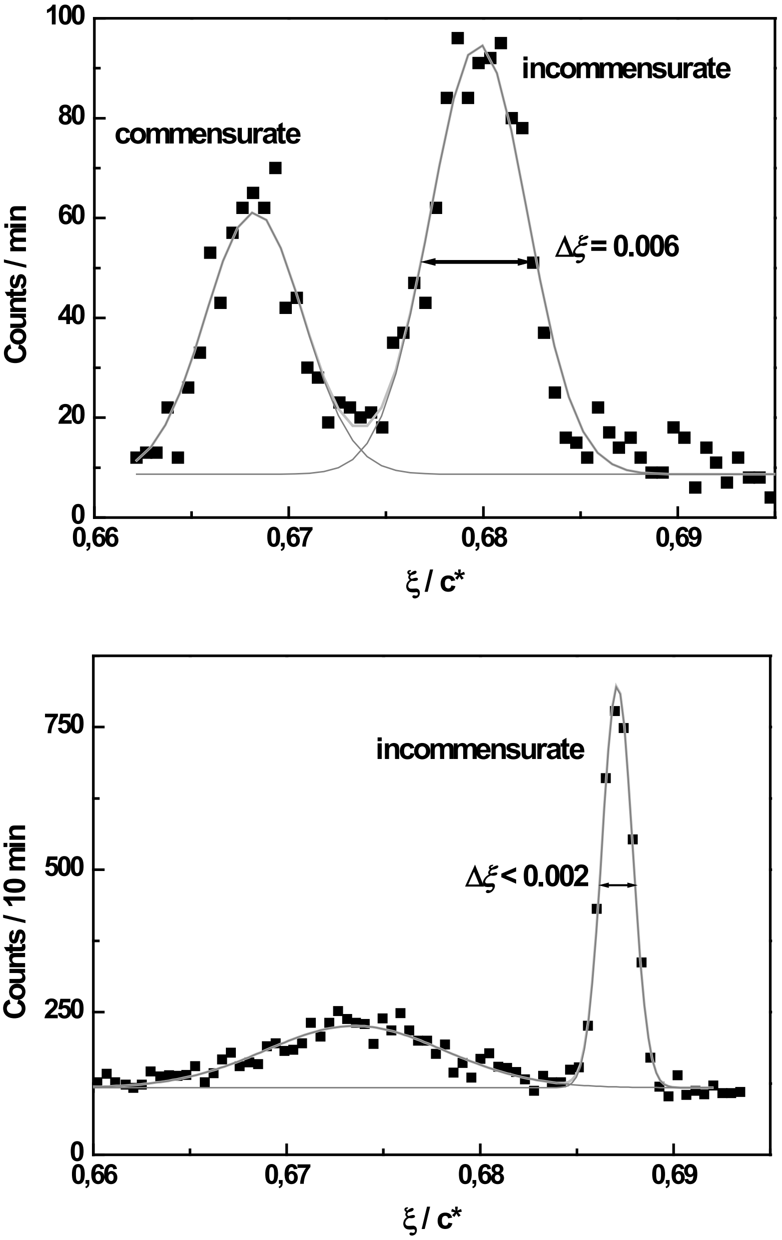

Fig. 1 First order satellite reflections at room temperature before (left) and after (right) a temperature cycle.

Investigation of a K_2ZnCl_4 crystal containing 8 % of rubidium revealed the coexistence of both, a commensurate and an incommensurate phase even at ambient temperature (Fig.1, left). Third- as well as higher-order satellites were clearly observed within the latter phase. Both phases remained pinned even down to at least 100 K. On heating this sample above 430 K, the commensurate phase vanished and was not recovered on cooling. Rather, the pure incommensurate phase with strong third order satellites persist even at room temperature. The modulation coherency turned out to be remarkably larger after performing the temperature cycle, as reflected by a reduced width of the reflection satellites (Fig.1, the FWHM of 0.002 c* represents the instrumental resolution). This finding leads to the assumption that the mixed modulation created during crystal growth can be rearranged at elevated temperatures. Due to the strong pinning effects, however, the ordered ferroelectric phase is suppressed on cooling. Hence, in this system a very well-defined nanodomain structure is present already around room temperature.

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