TEMPERATURE DRIVEN PHASE TRANSITIONS OF PEROVSKITES WITH THE CHEMICAL COMPOSITION $Ca(Fe,Mn,Ti)O_{3-\delta}$

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Perovskites (ABX_3) have numerous physical, magnetic and electronic properties and offer a wide range of technological applications due to their chemical and structural variability. Most of the perovskites do not exhibit the ideal cubic aristotype structure at ambient conditions but a distorted one of lower symmetry; e.g. the mineral perovskite $CaTiO_3$ is orthorhombic at ambient conditions but undergoes structural transitions to the cubic *Pm-3m* structure at elevated temperatures. A correct determination of these phase transitions as well as a detailed knowledge of the structural development with regard to internal and external parameter variation is essential for technological applications and has therefore been in the focus of research for several decades. The objective of this study is to investigate the structural development of $Ca(Fe,Mn,Ti)O_{3-\delta}$ perovskites as a function of temperature and composition with a special focus on the intra-orthorhombic *Pbnm* to *Cmcm* transition (HOWARD & STOKES, 2005), which has been discussed controversially in the past for several perovskite-type oxides. The crystal structures of $CaFe_xTi_{(1-x)/2}Mn_{(1-x)/2}O_{3-\delta}$.($0.08 \leq x \leq 0.31$) perovskites were therefore refined applying the Rietveld method from high resolution powder X-ray diffraction data collected in-situ from 296 to 1273 K in capillary transmission geometry at a Panalytical Empyran Diffractometer equipped with a Galipix detector and a focussing mirror for Mo radiation. The samples exhibit a series of *Pbnm* → *Cmcm* → *I4/mcm* → *Pm-3m* transitions with increasing temperature (ALEKSANDROV, 1976; GLAZER, 1972). The phase transitions as well as the structural development is characterized by the complex interaction between cell distortion, octahedral tilting and -distortion in dependence of temperature, chemical composition and oxygen vacancies. A method to determine the *Pbnm* to *Cmcm* transition in $Ca(Fe,Mn,Ti)O_{3-\delta}$ perovskites, that depends not solely on the visual inspection of weak peak splittings or R factor comparisons, has been derived by formulating a suitable phase boundary condition for the stability field of *Pbnm* (tilt system $a^-a^-c^+$) based on group-subgroup and unit cell relationships in comparison to the cubic aristotype.

HOWARD, C.J., STOKES, T. (2005): Acta Crystallogr., A61, 93–111.
ALEKSANDROV, K.S. (1976): Ferroelectrics, 14, 801-805.
GLAZER, A. (1972): Acta Crystallogr., B28, 3384-3392.