NANOSTRUCTURES FORMING DURING THE SYNTHESIS OF PEROVSKITE CaTiO₃ UNDER HYDROTHERMAL CONDITIONS

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Perovskite materials exhibit a variety of properties that have made them interesting for applications in different electronic devices during the past few decades. In the bulk form they have been utilized as high-permittivity capacitor materials, piezoelectric sensors and actuators, dielectric resonators, electrode materials, phase shifters, etc. Lately, these properties have become attractive for the expanding field of nanotechnology, and much effort has been put into the synthesis of various nanostructures that will potentially serve as building blocks in future nano-electronic circuits. Particularly interesting are single-crystalline onedimensional nanostructures, such as nanowires and nanotubes. One of the most promising routes for the synthesis of single-crystalline perovskite nanowires appears to be the hydrothermal method. Several successful syntheses of ferroelectric perovskite nanowires of BaTiO₃, PbTiO₃ and KNbO₃ under hydrothermal conditions have been reported in the literature. There is, however, a lack of insight into the formation mechanisms, which hinders the prediction of the conditions under which such nanostructures form. For this reason we systematically studied the formation of perovskite CaTiO₃ from an organometallic precursor, titanium isopropoxide, and a salt, calcium acetate, in a hydrothermal environment. By applying high-resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy (EELS) and energy-dipersive X-ray spectroscopy (EDS) we found that prior to the formation of perovskite at least two distinct phases appear that differ in composition, morphology and crystal structure. The first of the phases is in the shape of poorly crystalline nanowires with a Ca:Ti ratio of roughly 1:3, whereas the second phase appears in the form of single-crystalline sheets with a Ca:Ti ratio of 0.45. Furthermore, the EEL spectrum reveals differences in the Ti L_{2,3} fine structures, which is most likely connected to the differences in the distortion of the [TiO₆] octahedra between the phases. In combination with X-ray diffraction (XRD) and differential thermal analyses (DTA) we found that the latter phase is structurally closely related to either kassite CaTi₂O₄(OH)₂ or cafetite CaTi₂O₅(H₂O). We believe that by controlling the formation of these intermediate phases the morphology of perovskite CaTiO₃ nanostructures under hydrothermal conditions can be controlled.