Polar oxide nanomaterials - an emerging playground in ultrafast photophysics

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Introduction

Volume single crystals of the niobate or tantalate family are established as central workhorses in the research field of photorefraction from its very beginning. A proper control of the initial photogeneration processes yielding a directed photogalvanic current density requires homogeneous, i.e. cluster-free doping with impurity atoms (such as $\mathrm{Fe}_{\mathrm{Li}}^{2+/3+}$) within the entire volume. The dimensions of the photorefractive crystal on the mm-length scale have strong impact on key photophysical quantities, such as the efficiency, angular and/or wavelength sensitivity of recorded mixed gratings in holographic applications, but also on experimental parameters (such as the intersection angle of reference and signal beams to adjust for the grating vector of the incident light intensity pattern) or the experimental access - be it in the context of the optical detection of transmitting beams in multiwave mixing or for the electrical tapping of surface charges. Some of the early applications (e.g. holographic data storage) inevitably required large scale, homogeneous crystalline materials. Accordingly, research on single crystal growth, preparation and characterization of polar oxide crystals with high bulk homogeneity (doping, composition) and quality, commonly associated with a lack of grain boundaries, cracks, unwanted defect centers, but also a high optical quality of the surfaces ($< \lambda/20$) is closely related to the research and application field of photorefraction.

In the era of nanotechnology, the establishment of top-down material processing methods, such as micro-mechanical drilling or ion beam enhanced etching, has significantly expanded the possibilities to tailor niobate and tantalate single crystals for new type of applications, particularly in the domain of micro- and nanophotonics. Examples include whispering gallery mode resonators with sub-mm diameters enabling impressive quality factors for sensing (by the Buse group, Freiburg, Germany), free-standing ultrathin lithium niobate membranes with layer thickness down to 200 nm for integrated photonic chips (by the Tünnermann group, Jena, Germany) or niobate layer systems, e.g. lithium niobate on silicon oxide (insulator) on silicon (substrate) with lithium niobate film layers down to 300 nm for optoelectronic devices ('LNOI' by nanoLN inc., Japan). As a consequence of the reduced length scale, the requirements for single crystal homogeneities and qualities changed, and the optical properties profited from the nanostructuring rather than from doping.

These developments directed our attention to photophysical processes in nanoscaled niobates on a microsopic level. For instance, the question about the existence of the photogalvanic effect in doped niobate nanomaterials with dimensions in the sub-20-nm region is still not answered. While the persistence of the spontaneous polarization down to the sub-5 nm length scales has been validated in several representatives of the perovskite-like polar oxidic nanocrystals (such as BaTiO_3), information about the charge transport including small polaron hopping, but also about the build-up of space-charge fields in crystals with dimensions much below the space-charge limitation length (both in the bulk and on the surface), are missing completely in literature. Besides the availability of proper nanomaterials, it is also due to missing experimental techniques for investigations.

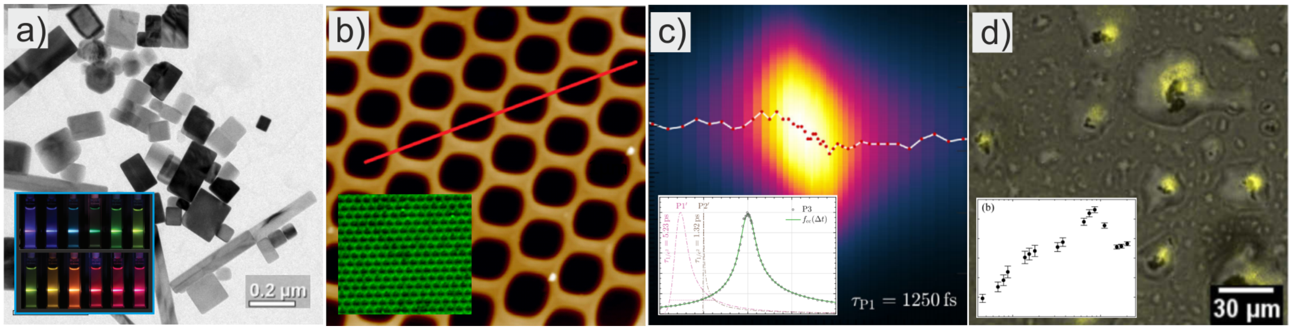

Figure 1: (a) Electron microscopy image of potassium niobate nanocrystals [1], (b) atomic force microscopic image of stamped lithium niobate metamaterials [2], (c) pulse stretching effect in nanoparticle powder pellets [3], (d) second-harmonic emission of lithium niobate nanocrystals [4]

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This contribution gives insight to the first steps of research on nanoscale niobate crystals at Osnabrück University profiting from newly established synthesis routes for the bottom-up synthesis of nanoniobate crystals [1], stamped niobate metamaterials [2], the development of novel experimental tools based on nonlinear ultrafast spectroscopy & microscopy and reproducible preparation routes for nanoparticle powder pellets [5]. Challenges in modelling the experimental data using combined analytical and numerical tools are adressed and reveal first examples of discovered nonlinear optical phenomena directly assigned to the nanosized properties [3], but also opens the path to evaluate the impact of nanoniobates for new applications.

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