

FORMATION MECHANISMS OF LiNbO₃ NANOCRYSTALS UNDER SOLVOTHERMAL CONDITIONS FROM ALKOXIDE PRECURSORS

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ABSTRACT:

Recent detailed investigations of the formation mechanisms of centrosymmetric metal oxide nanoparticles such as TiO₂ and Zr_xTi_{1-x}O₂ have evidenced the appearance of oxo-alkoxy clusters that further aggregate into amorphous nuclei at low hydrolysis rates of alkoxide precursors [1–3]. In this work, a mixture of LiOEt and Nb₂(OC₂H₅)₁₀ diluted in alcohols and glycols of different chain lengths has been used to produce non-centrosymmetric LiNbO₃ nanocrystals. Upon hydrolysis of the initial precursor solutions kept under magnetic stirring, DLS measurements demonstrate the rapid formation of ~2.7nm oxo-clusters for each solvent after ligand exchange with the initial ethoxide groups. After 24h at room temperature and formation of a viscous, non-transparent light-scattering gel, SAXS measurements confirm the presence of amorphous nuclei of average diameter ~4nm. The subsequent solvothermal treatment at 235°C for 24h then results in the formation of LiNbO₃ nanocrystals whose average crystallite size can be varied between 15 and 70 nm according to the co-solvent chain length. Extensive time- and temperature-dependent experiments first demonstrate the presence of surface-passivated crystalline intermediates of 4-6 nm whose aggregation leads, after rearrangement of the surface ligands [4], to easily re-dispersible LiNbO₃ nanocrystals. Finally, colloidal suspensions of Er-doped and Er-Yb co-doped nanocrystals also evidence scattering of several nonlinear optical (SHG, THG and SFG) and up-conversion (UC) signals.

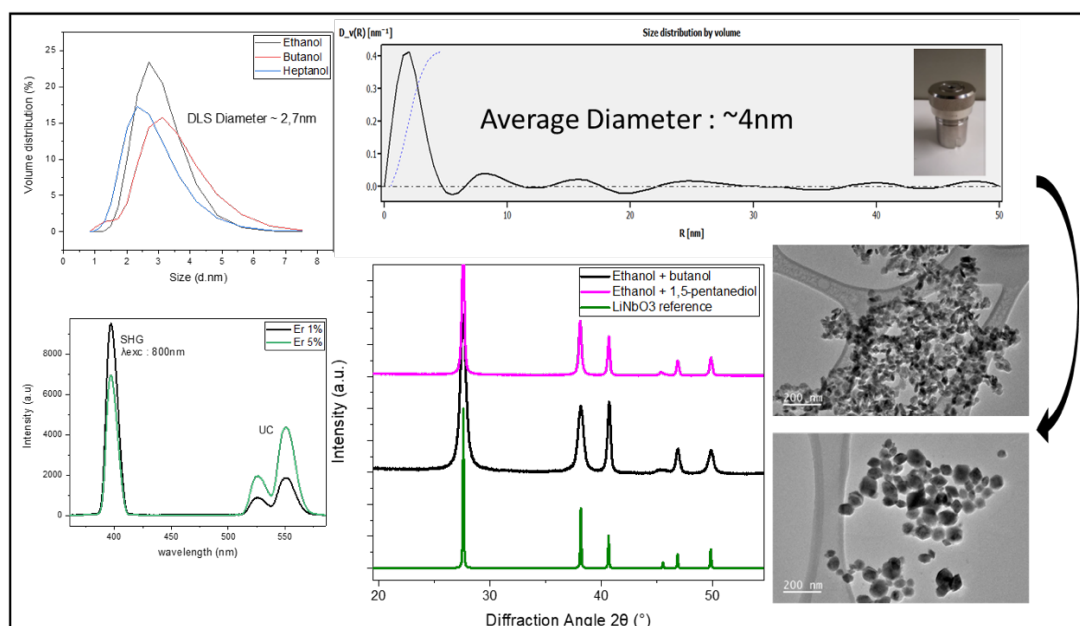


Figure 1: See text above for details

References

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