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Analytical chemical methods for advanced and environmental materials. — High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GFAAS) microanalytical methods with solid and solution sampling were developed for the determination of Bi additive in lithium niobate ($LiNbO_3$) optical crystals [1]. Atomization transients, pyrolysis and atomization curves and matrix effects (e.g., Figure 1) were studied with various solution media and chemical modifiers, e.g., triammonium citrate (TAC), Pd–Mg. TAC slightly, but Pd–Mg significantly increased the optimal pyrolysis and atomization temperatures, i.e., up to 1300 °C and 2100 °C, respectively. The dissolved $LiNbO_3$ matrix acted as an internal modifier, exhibiting higher optimal pyrolysis and atomization temperatures for Bi. The limit of detection (LOD) was 0.4 µg/g and 0.3 µg/g for solid and solution analysis, respectively. Flame HR-CS-AAS methods were also developed with matrix-matched standards. The analytical results for all methods were in good agreement (mean bias: <12%). The precision of the solid and solution sample methods was at 6-16% and 1-13%, respectively. The Bi content of the doped crystals ranged from 56 to 311 µg/g. The characteristic mass (absolute sensitivity) for solid and solution sampling was 220 pg and 17 pg, respectively. The accuracy of the method was checked against the GBW07407 (laterite soil) certified reference material too. ELCAD-OES methods were developed for increasing sensitivity in water samples (e.g., tap, lake, river) for a couple of elements. A Special Issue on the development/application of low-cost environmental sensors for air quality monitoring was edited and published [2].

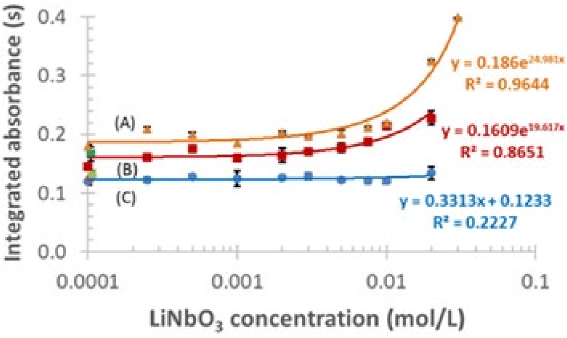

Figure 1. Effects of the $LiNbO_3$ matrix solution on the absorbance of 20 µg/L Bi; (A) with 5 µg Pd+1 µg Mg (as nitrates), (B) without modifier, (C) with 0.05 mol/L TAC, (green data points are matrix-free standards); each data point and error bar represent mean ±SD, n=3.

Intrinsic and extrinsic defects in $LiNbO_3$ nanocrystals. — A series of undoped and Er^{3+} or Yb^{3+} doped congruent $LiNbO_3$ nanocrystals were produced by grinding process under wet conditions in a high-energy ball mill and the structural changes were followed by Raman and absorption spectroscopy, respectively. In the undoped $LiNbO_3$ case the Raman band intensities in the whole spectra decreased, showing a formation of an amorphous, disordered phase due to the mechanical impact. Besides this, the appearance of $LiNb_3O_8$ phase, already at the beginning of the grinding, was pointed out in the Raman spectra. While the intensity of $LiNb_3O_8$ bands also decreased with grinding time, their relative intensity increased compared to the $LiNbO_3$ ones. Using thermal treatments at 300 and 500 °C, the Raman bands reappeared, showing recrystallization of the structure with a stronger presence of the $LiNb_3O_8$

phase. These experimental observations are well explained by the Li_2O out-diffusion during the grinding process [3]. From the change of the absorption spectra of the rare-earth (RE) doped $LiNbO_3$ crystals during the milling process, the out-diffusion of the RE ions from the nano-$LiNbO_3$ particles and the appearance of a broad absorption band belonging to RE ions surrounded by an unordered phase were clearly shown [4]. To interpret the experimental results force−field quantum chemical calculations using the GULP code based on a $Li_{245}Nb_{245}O_{735}$ unit cell was utilized. Two distinct parts were distinguished in the nano-$LiNbO_3$ crystals: a disordered shell and a relatively ordered core region. Additional calculations showed that the optimal energetic location for the Nb_{Li} + 4 V_{Li} defects is in the outer shell, which supports the Li_2O out-diffusion. Finally, calculations on the $LiNb_3O_8$-like defect structure indicated no significant energetic difference compared to the Nb_{Li} + 4 V_{Li} case, supporting its appearance in the lattice in agreement with the experimental findings (see Figure 2) [3]. From the calculations containing one Er^{3+} or Yb^{3+} ion in the unit, the out-diffusion and the appearance of the RE ion in the unordered shell were clearly demonstrated. In the double-doped case, for investigation the possible interaction between the RE ions, only independent incorporation was found [4].

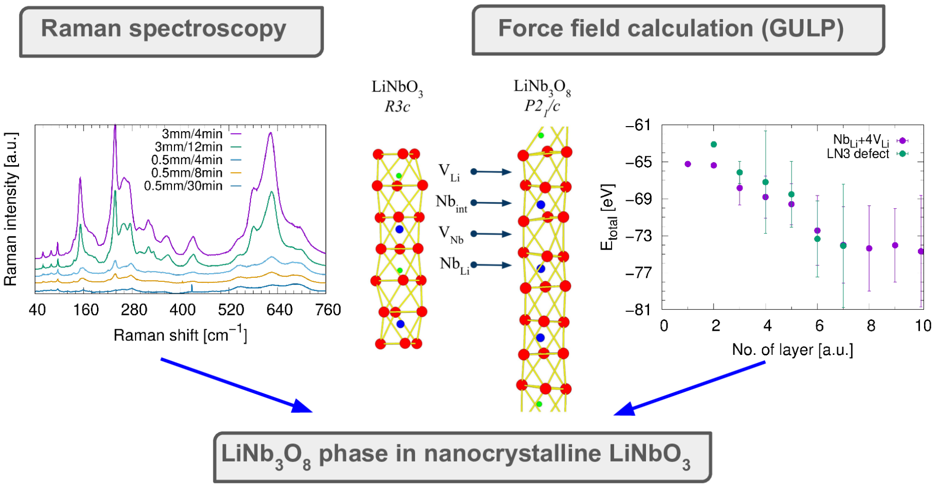

Figure 2. Experimental and quantum chemical evidences for the appearance of $LiNb_3O_8$ phase in nano-$LiNbO_3$ crystals due to milling process.

References:

[1] https://doi.org/10.1021/acsomega.5c05486

[2] https://doi.org/10.3390/books978-3-7258-5656-5

[3] https://doi.org/10.1021/acs.jpcc.5c05506

[4] https://doi.org/10.1002/pssa.202300932