Mechanochemical preparation of black TiO_2 and black Nb_2O_5 in 10 min

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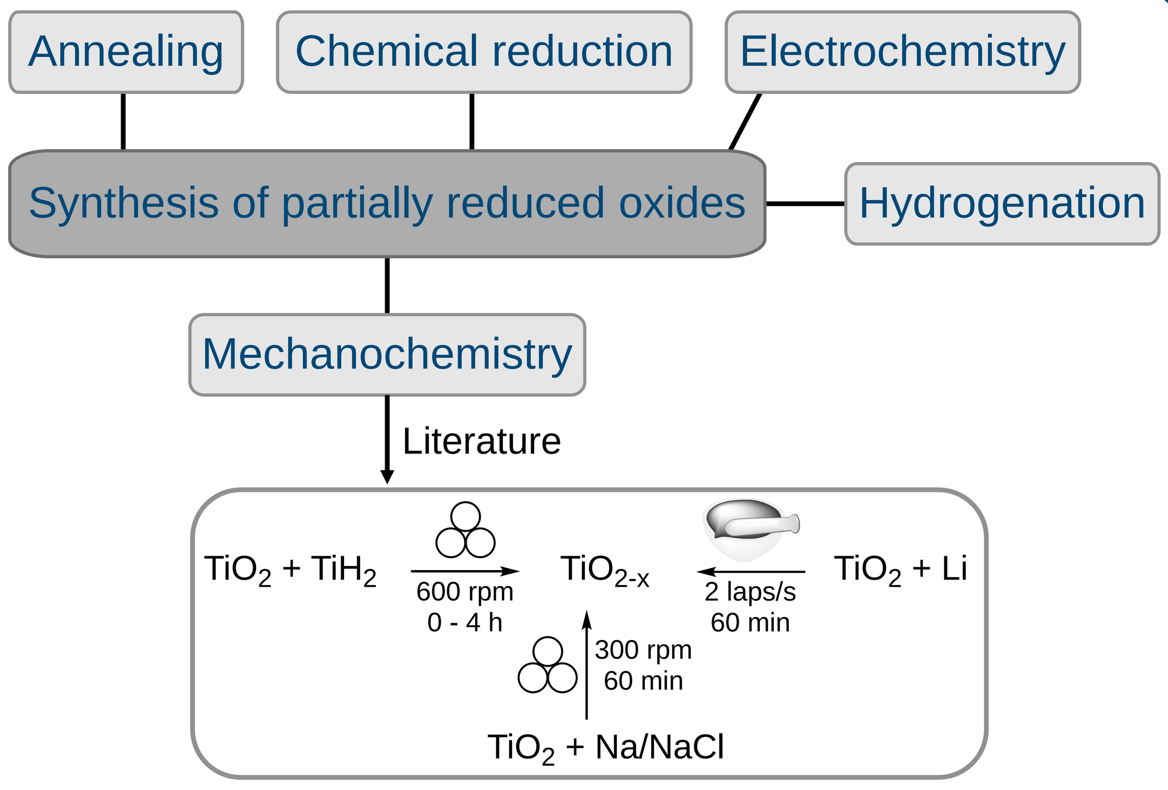
Introduction: Preparation of black metal oxides and their applications

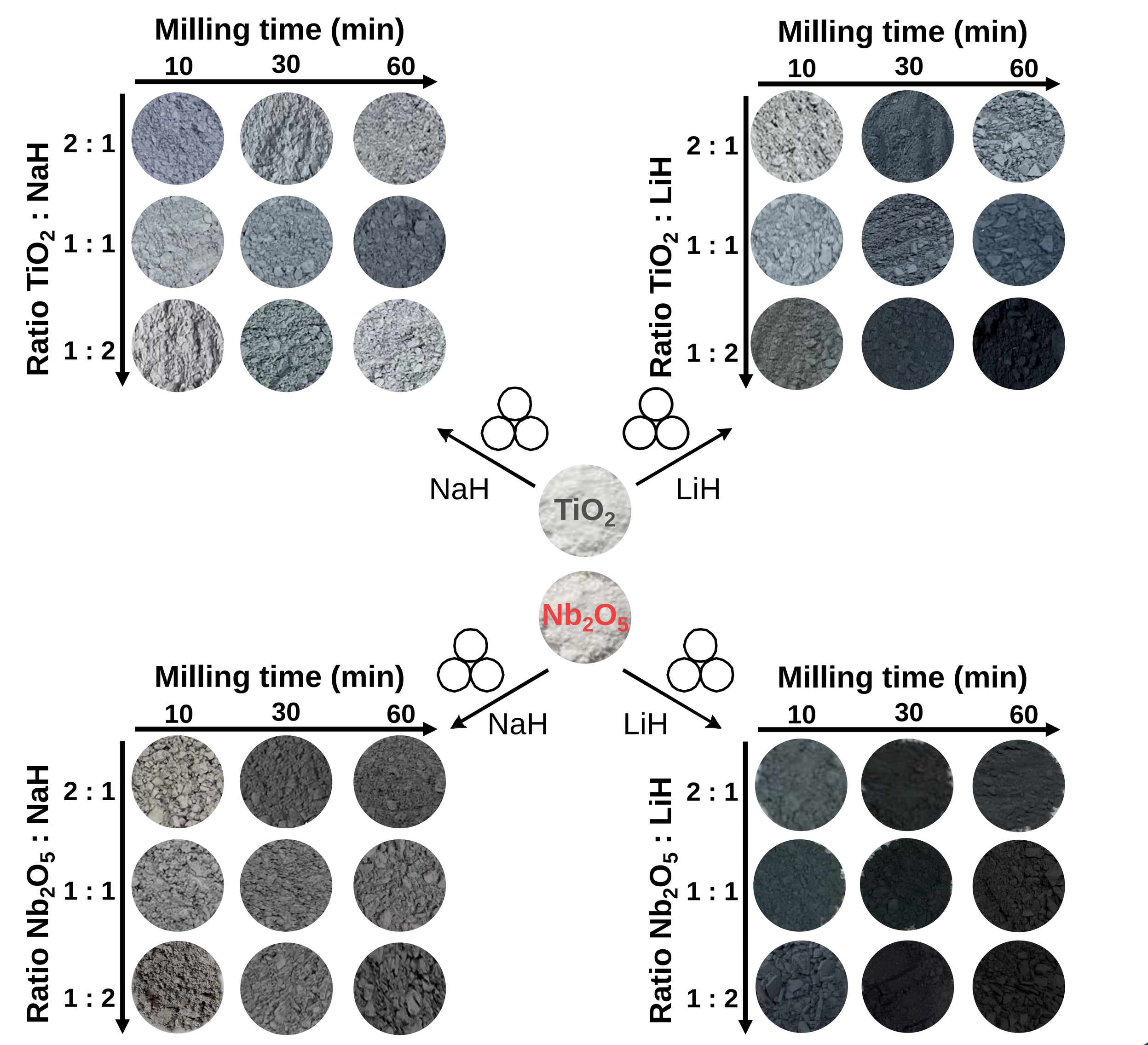
The introduction of defects can greatly influence the properties of the material. The term "black titania" was introduced by Chen *et al.* when they synthesized defective-rich TiO_2 with a black color, an ordered/disordered core-shell structure and enhanced photocatalytic activities after hydrogenation of TiO_2 for 5 days at 20 bar.[1] Since then, the formation of defects such as oxygen vacancies or reduced metal species has been applied to other transition metal oxides and nowadays black Nb_2O_5,[2] ZrO_2,[3] WO_3[4] and V_2O_5[5] are also known in the literature. Due to the changed electronic properties, e.g., decrease of the band gap and additional mid-gap states, the defect-rich oxides usually exhibit light absorption in the visible region, enhanced photocatalytic, and photoelectrochemical (PEC) activity as well as a better electrochemical behavior than the pristine oxides. Besides hydrogenation, defective oxides are also prepared via annealing at high temperature under vacuum or inert gas, via chemical reductions at high temperatures, electrochemically or in solutions, e.g., with metals (Mg, Al) or metal hydrides ($NaBH_4$, NaH).[6, 7] However, only few mechanochemical approaches are known in the literature, for example using highly reactive alkaline metals, such as Na[8] or Li[9] or non-conventional hydrides such as TiH_2.[10]

In this study, LiH and NaH were studied as readily available hydrides in the powerful and fast mechanochemical reduction of TiO_2, the most studied oxide for photocatalysis and defect engineering, and Nb_2O_5, an interesting alternative for TiO_2 due to similar properties, but also many possible application areas. The influence of the type and amount of reducing agent as well as the milling on the final properties of the materials were systematically studied.

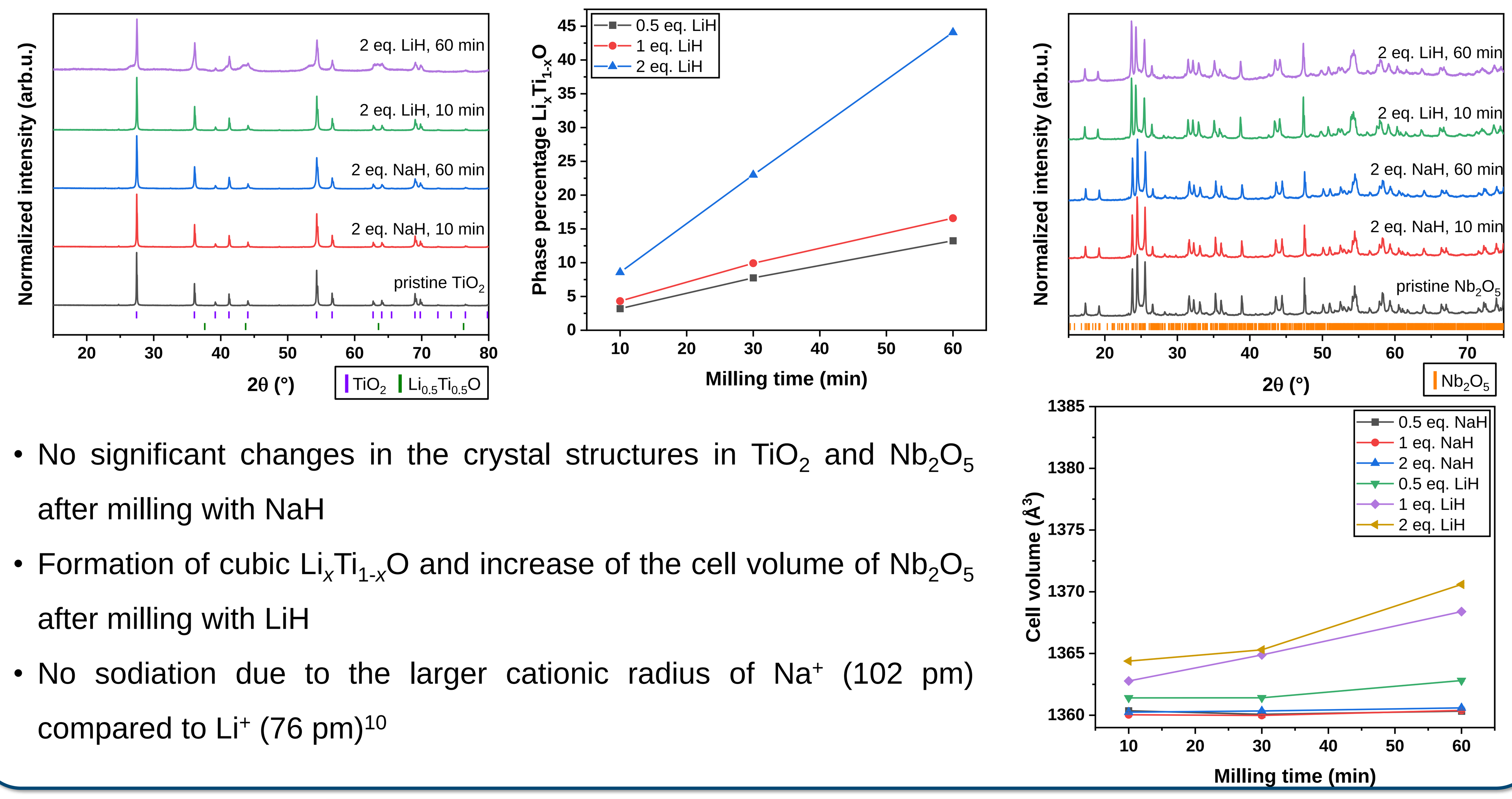


Results and Discussion

Color change during ball milling

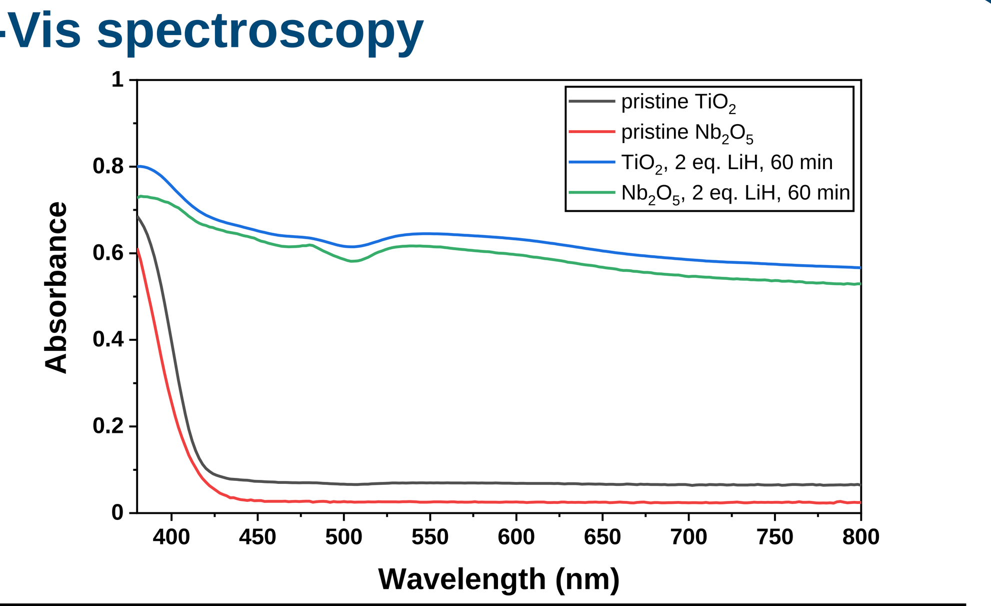


X-Ray Diffraction (XRD) measurements and Rietveld refinement



- No significant changes in the crystal structures in TiO_2 and Nb_2O_5 after milling with NaH
- Formation of cubic $Li_xTi_{1-x}O$ and increase of the cell volume of Nb_2O_5 after milling with LiH
- No sodiation due to the larger cationic radius of Na^+ (102 pm) compared to Li^+ (76 pm)[10]

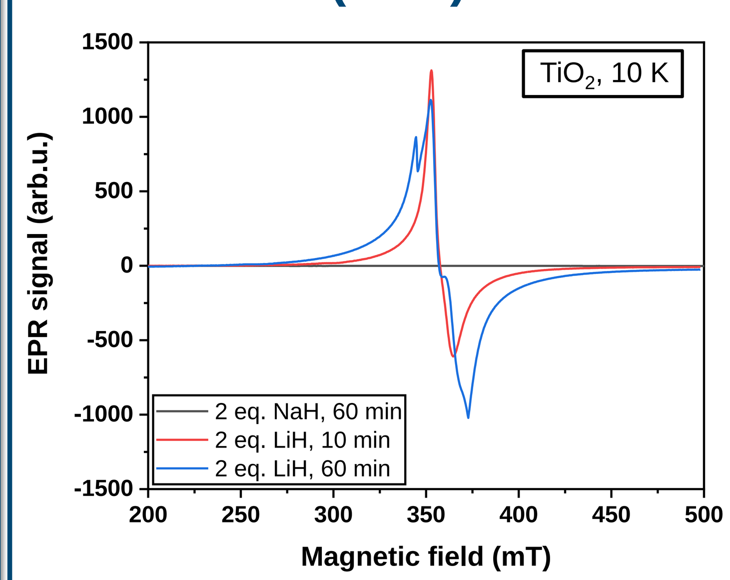
UV-Vis spectroscopy



Oxide	Reducing agent	Milling time (min)	E_g (direct) (eV)
TiO_2	-	0	3.11
TiO_2	0.5 eq. NaH	60	3.11
TiO_2	2 eq. NaH	60	3.11
TiO_2	2 eq. LiH	10	3.08
TiO_2	2 eq. LiH	60	2.89
Nb_2O_5	-	0	3.17
Nb_2O_5	0.5 eq. NaH	60	2.99
Nb_2O_5	2 eq. NaH	60	3.03
Nb_2O_5	2 eq. LiH	10	3.01
Nb_2O_5	2 eq. LiH	60	2.81

➢ Increased absorption of visible light and decrease of the band gap, the darker the samples are

Electron paramagnetic resonance (EPR)

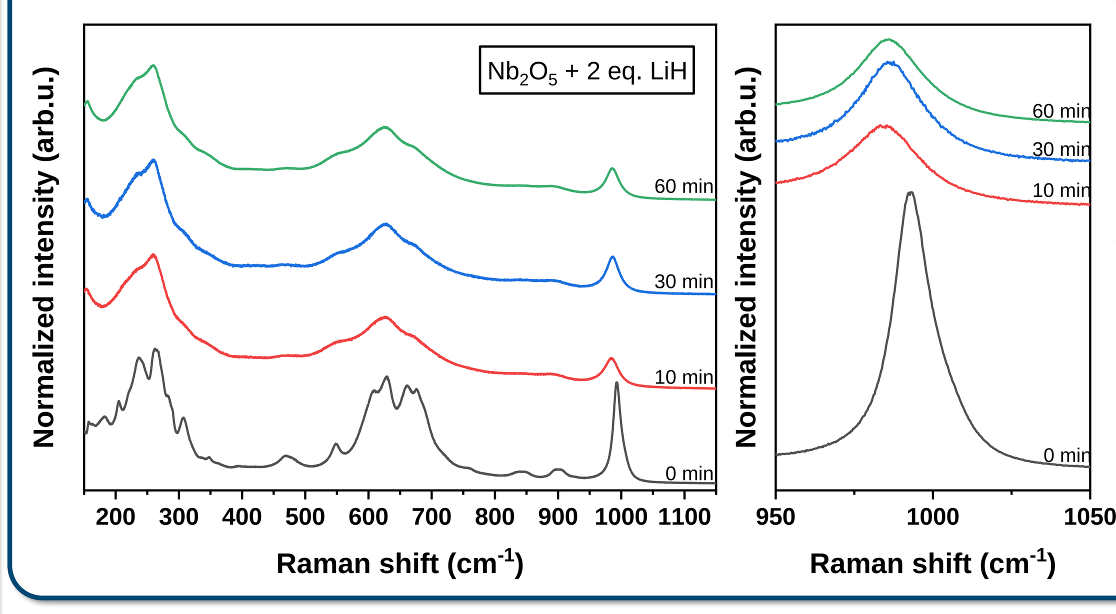


- Only significant number of unpaired electrons in LiH reduced samples

→ Lower degree of reduction with NaH than with LiH

- g = 1.96 → located on Ti^{3+} [10]
- Higher degree of reduction the longer the milling time

Raman spectroscopy



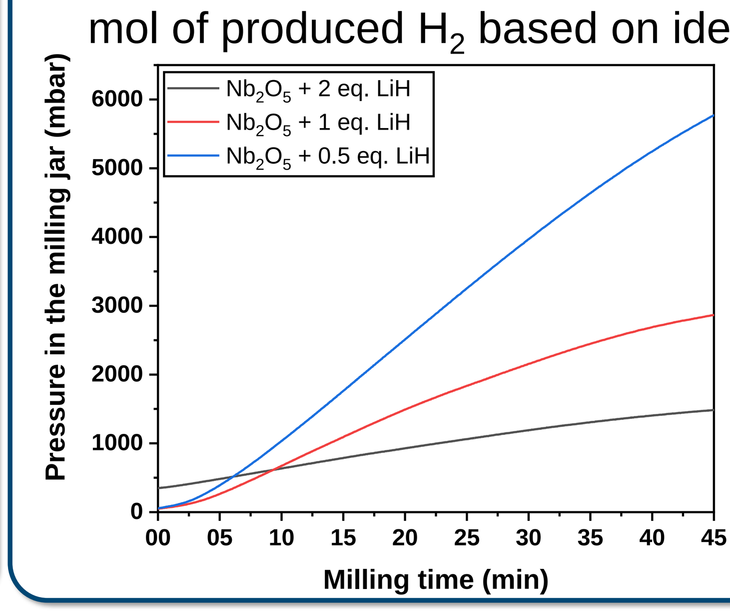
- LO mode of NbO_6 edge-shared octahedra: red shift from 993 cm^{-1} to 985 cm^{-1}
- Significant decrease of the Raman intensity and broadening

→ Successful introduction of defects[2]

Pressure increase during ball milling

- Continuous increase of the pressure during ball milling → calculation of the number of mol of produced H_2 based on ideal gas behavior

$$TiO_2 + 2x\,MH \longrightarrow TiO_{2-x} + x\,M_2O + x\,H_2$$



Sample	$T_{initial}$ [°C]	$p_{initial}$ [mbar]	T_{final} [°C]	p_{final} [mbar]	$n_{formed\ gas}$ [mmol]
NL_2:1_60	26.8	0.351	34.8	1.498	1.41
NL_1:1_60	23.7	0.049	34.2	2.895	3.57
NL_1:2_60	24.5	0.057	35.2	5.863	7.28
TL_1:2_45	23.4	0.040	33.0	1.230	1.45
TN_1:2_45	25.0	0.060	34.0	0.370	0.35

Conclusions

A simple and rapid room temperature mechanochemical reduction process was developed for the reduction of TiO_2 and Nb_2O_5 with alkali metal hydrides. Generally, longer milling times and higher concentrations of reducing agent resulted in a darker sample color, a higher degree of reduction of the metals and thus the formation of more oxygen vacancies. After the reduction, only a partial lithiation was observed by XRD measurements due to the smaller radius of Li^+ compared to Na^+. Raman and EPR spectroscopy consistently showed an increase of defects with prolonged milling. Hereby more defects are introduced with LiH as it can be seen by the darker color of the reduced oxides.

References

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