Anionic Substitutions in Perovskites

R. Aguiar [1], S. G. Ebbinghaus [1], D. Logvinovich [2], A. Reller [1], and A. Weidenkaff [2]

1) Universität Augsburg Lehrstuhl für Festkörperchemie
Universitätsstrasse 1
D-86159 Augsburg

2) Empa Festkörperchemie und -analytik
Überlandstrasse 129
CH-8600 Dübendorf

EMPA Materials Science & Technology

Oxynitride Perovskites: Basic Concepts

ABO_3 e.g. $SrTiO_3$

$O^{2-} \rightarrow N^{3-}$

charge compensation

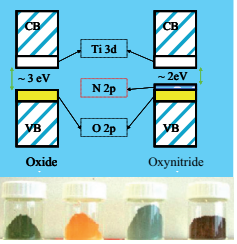
$A_{1-y}A'_yB_{1-z}B'_zO_{3-x}N_x$ e.g. $Sr_{1-x}La_xTiO_{3-x}N_x$

$ABO_{3-3x/2}N_x$ $3O_O^x \rightarrow 2N'_O + V_O^{\cdot\cdot}$ e.g. $SrTiO_{3-3x/2}N_x$

Substitution $O^{2-} \rightarrow N^{3-}$:

-Creates donor level between valence and conduction bands, which decreases the band gap, resulting in semi-conducting compounds.

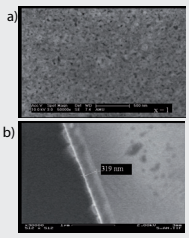
- Causes absorption in the visible light range (400nm - 800nm) resulting in coloured materials.



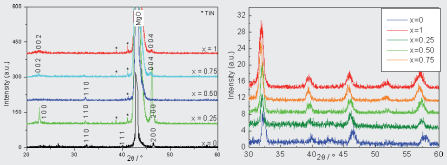
Nitridation of thin films

-Thin films of $La_xSr_{(1-x)}TiO_{3+x/2}$ were grown by laser ablation on STO and MgO substrates.

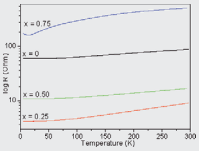
-The films were reacted with NH_3 at 950°C for 3h.



SEM images of the oxynitride thin film, with x=1 ($LaTiO_2N$) (a) and cross section of x= 0.5 (b).



XRD pattern of the oxynitride films grown by laser ablation on MgO substrate (left) and by spin coating on STO (right).

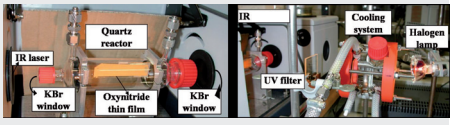


-The laser ablated films are denser than the spin coated ones.

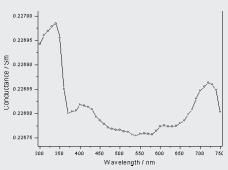
-The electrical sheet resistance of the laser ablated films varies from 9Ω to 600Ω at 300K, and the resistance of the spin coated films varies from 100Ω to 20KΩ.

-The laser ablated films grow almost epitaxial with (100) direction, while the spin coated films have a random orientation.

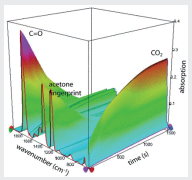
-Photocatalytic power and Photoconductivity of the oxynitrides are currently studied.



IR system used to measure the photocatalytic power of the oxynitrides.



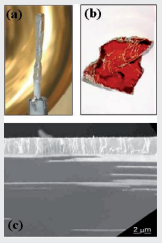
Conductivity as function of wavelength of the spin coated film of $La_{0.25}Sr_{0.75}Ti(O,N)_3$.



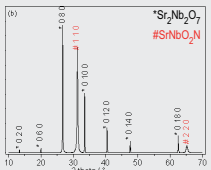
Typical graph for acetone decomposition, using P25 a common photocatalytic.

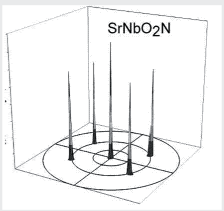
-Single crystals of oxide perovskites ($La_2Ti_2O_7$ and $Sr_2Nb_2O_7$) were grown by the floating zone technique.

-Slices of these crystals were reacted with ammonia, resulting in a well oriented epitactical oxynitride layer on the crystal surface.

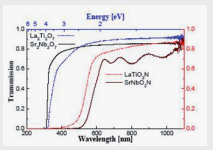


(a) Oxide single crystal,
(b) slice of the crystal after ammonolysis
(c) cross section SEM image of the crystal surface.





XRD pattern of $Sr_2Nb_2O_7$ single crystal slice after ammonolysis (left) and the p ole figure showing the epitactical relationship between the ammono lysed layer and the crystal (right).



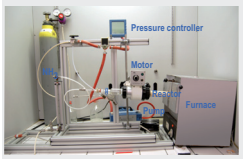
UV-Vis spectrum of $LaTiO_2N$ and $SrNbO_2N$ in comparison to the corresponding oxides.

-Oxynitride perovskite layers were epitactically grown by nitridation of the oxide single crystals.

-After ammonolysis the absorption edge shifts to ca. 450-500nm, resulting in red-brown colours.

-Next stage is the preparation of new single crystalline oxynitride films by the ammonolysis of single crystals e.g. $LaTaO_4$, $CaNbO_{3.5}$ or $SrTaO_{3.5}$ and measuring their electrical (Hall effect measurements in coop. with H.von Wenckstern) and optical properties.

Nitridation of powders by thermal ammonolysis



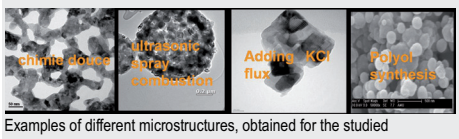
-Rotating cavity reactor for the thermal ammonolysis

-Further innovative reactor concepts, e.g. fluidized bed, plasma reactors are currently developed

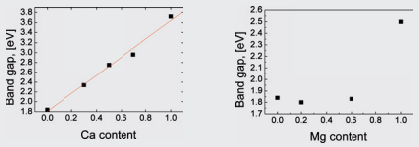
-(La,Ca,Ba)(Ti,Mg,Co)O_xN_y e.g. $La_xCa_{1-x}TiO_{2+x}N_x$ (x= 0,0.3, 0.5, 0.7, 0.1), $La_2Ti_{1-x}Mg_xO_{4+2x}N_{2-2x}$ (x= 0,0.2, 0.6, 1.0) systems were successfully synthesized from the corresponding oxide precursors, produced by soft-chemistry methods.

-The nitrogen content, crystal structure, microstructure, optical, transport and thermal properties of the obtained materials were investigated by XRD, ND, TGA-DTA-MS, XPS, Hotgas extraction, RBS,TEM, SEM, PPMS Impedance spectroscopy.

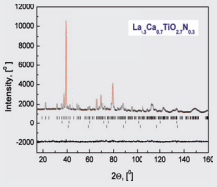
-$AMo(O,N)_3$, $AW(O,N)_3$, $AV(O,N)_3$ (A = Ba, Sr, La) will be synthesized and characterized

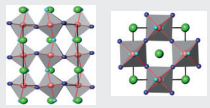


Examples of different microstructures, obtained for the studied oxynitrides.



Band gap width dependence from Ca and Mg content for $La_xCa_{1-x}TiO_{2+x}N_x$, and $La_2Ti_{1-x}Mg_xO_{4+2x}N_{2-2x}$ oxynitride perovskites correspondingly.





Rietveld Plot and room temperature crystal structure of $La_{0.3}Ca_{0.7}TiO_{2.7}N_{0.3}$ (*Pnma*-space group)

-Room temperature crystal structure of $La_xCa_{1-x}TiO_{3-x}N_x$ oxynitrides was studied using Neutron diffraction

-At room temperature all materials crystallize in *Pnma* space group.

-No significant O/N ordering was detected

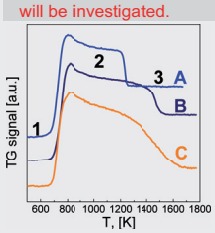
-Photocatalytic activity and Transport properties of the obtained materials will be investigated.

-Thermal reoxidation of oxynitrides proceeds via an intermediate phase formation.

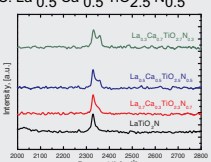
-The phase keeps the crystal structure of the parent oxynitride and contains nitrogen in form of dinitrogen species, detected by Raman spectroscopy.

-Ca doping is leading to the appearance of an additional signal in the Raman spectra of the intermediate and enhancement of its kinetic stability .

- Intermediates structure will be studied (coop. AK Heitjans, NMR)

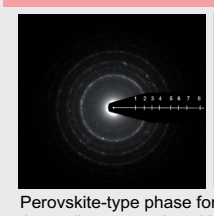


TGA of thermal reoxidation of:
A. $LaTiO_2N$,
B. $La_{0.7}Ca_{0.3}TiO_{2.3}N_{0.7}$
C. $La_{0.5}Ca_{0.5}TiO_{2.5}N_{0.5}$



Raman spectra of the reoxidation intermediates of Ca doped $LaTiO_2N$.

Study of the late transition metals incorporation (Fe,Cr,Co,Mn) into Ti sites



-10% Co substituted $LaTiO_2N$ was synthesized.

-The obtained material crystallizes in the perovskite type structure.

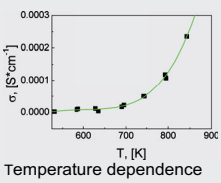
-Temperature dependence of its total conductivity follows polaronic behaviour

Perovskite-type phase formation for the thermally ammonolysed $LaTi_{0.9}Co_{0.1}O_3$

-Higher level of Co substitution is currently under the investigation

-Mn, Fe, Cr substitution studies are planned

-Electronic, crystallographic and photocatalytic properties, Seebeck coefficient, thermal conductivity will be tested



Temperature dependence of conductivity of $LaTi_{0.9}Co_{0.1}(O,N)_3$

References

- Rachel A, Ebbinghaus S.G, Güngerich M, Klar P.J, Hanss J, Weidenkaff A, Reller A,Thermochim. Acta. 438 (2005) 134.
- Ebbinghaus S.G., Weidenkaff A., Rachel A., Reller A., Acta Crystal. 60 (2005) 91.
- Ebbinghaus S.G., Kalytta A., Kopf J., Weidenkaff A., Reller A., Z. Kristallogr. 220 (2005) 269.
- Logvinovich, D., Börger, A., Döbeli, M., Ebbinghaus,S.G., Reller, A., and Weidenkaff., A. Progr. in Solid State Chem., submitted
- Aguiar, R., Weidenkaff, A., Schneider, C.W., Reller, A., Ebbinghaus, S., Progr. in Solid State Chem., submitted.