EUROPEAN SYNCHROTRON RADIATION FACILITY

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Application for beam time at ESRF – Experimental Method

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Aims of the experiment and scientific background

Perovskite-type oxides ABO_3 are intriguing materials with versatile structure that find applications in thermoelectrics, emission control, catalysis and fuel cells. Treatment with NH_3 at > 400°C produces perovskite oxynitrides $AB(O,N)_3$ (A – typically La, Ca, Sr, Ba; B – transition element, Ta Nb, Mo; up to 30-40% of nitrogen), which have been found to be promising photocatalysts for water splitting under visible light [1]. When heated in synthetic air, $AB(O,N)_3$ structures undergo re-oxidation. The thermogravimetric trace of this process shows the unexpected formation of an intermediate phase $(ABO_{3\div3.5}(N_2)_x)$ [2] which is characterized by a partially or completely amorphous structure and by the presence of N≡N-entities, as revealed by *ex situ* XRD, XPS and Raman spectroscopy [2,3]. Moreover, this phase possesses a remarkable thermal stability (depending on the starting formulation, some intermediates are stable at $T > 1273$ K under synthetic air) [4], which can be tuned by A– and B– site substitution [4,5].

A detailed *in situ* study on the formation process, the structure, the bonding and the chemical activity of the re-oxidation intermediate is required to unravel possible catalytic applications.

Therefore, our experiments aim to investigate the formation of the intermediate by re-oxidation of the oxynitride and their reactivity under flowing H_2 using *in situ* X-ray absorption spectroscopy (XAS), and X-ray diffraction (XRD). Additionally, the coupling with the newly installed Raman spectrometer at SNBL is of great interest owing to the Raman active N≡N-entities and to the perovskite structure. The goal of the temperature programmed reduction (TPR) study is to clarify whether the re-oxidation intermediate is able to exchange/replace the N≡N-entities, which process may exhibit interesting catalytic properties (ammonia synthesis, ammoxidation).

The high brilliance of synchrotron radiation is required to reduce the data collection time thus enabling the monitoring of the chosen processes with high time resolution. XRD will be used to monitor changes in the long-range order during the re-oxidation, thus allowing the detection of the formation and the decomposition of the intermediate(s). XAS will be measured around the Ta- and Nb-K edges to detect changes in the oxidation state and coordination of the B-site cation during the re-oxidation and the TPR test.

Moreover, the availability of *in situ* Raman spectroscopy at ESRF enables monitoring the formation of the N≡N-entities, their bonding to the intermediate matrix and the changes they undergo when the intermediate is reacted with the H_2.

Experimental method

The re-oxidation experiment of the oxynitride-perovskite (for example, $LaTa(O,N)_3$ and $La_{1-x}Ca_xTa(O,N)_3$ and the corresponding Nb-containing materials) will be carried out in flowing synthetic air or 20 vol.% O_2/He to follow formation of the stable intermediate. The TPR experiments will be carried out from room temperature to ca. 800°C in flowing 5 vol.% H_2/He on the native perovskite ($ABO_{3\div3.5}$), the oxynitride-perovskite ($AB(O,N)_3$) and the N≡N-intermediate phase ($ABO_{3\div3.5}(N_2)$) isolated at the home institution. Non-perovskitic TaON and NbON will be used as possible reference materials.

The experimental setup requires the use of gases (He, 5 vol.% H_2 and O_2 or air). The *in situ* capillary transmission/fluorescence reactor-cell [6] can be attached to gas lines including mass-flow controllers and to a mass spectrometer for on-line analysis of gases exiting the cell as done in previous studies. Gas sensors will be installed to ensure security during measurement. All this equipment can be provided by Empa and ETH. The beam-time (4-5 days) will be organized as follows: 1 day for equipment set up, 1 day for ex situ samples and reference materials, 3-4 days measurements.

Results expected

The detailed *in situ* investigation of the change in the crystal structure (XRD), the coordination and the oxidation state of the transition element (Nb, Ta, Mo) (XAS), the formation of the N≡N-entities and their bonding to the oxide matrix (Raman spectroscopy) is crucial for a complete understanding of the structure and the re-oxidation process of the oxynitride. The data will allow us to propose a detailed mechanism of the formation of the stable intermediate(s) and to investigate its structure and bonding.

The results of the TPR tests will be crucial to demonstrate the potential of the N≡N-intermediate to exchange N-atoms with the environment [7]. Such experiments are intended as *in situ* catalytic activity tests for the N≡N-intermediate as novel catalytic material. Therefore, we expect to gather important structure-activity relationships needed to develop such a catalyst.

References

[1] K. Maeda and K. Domen, J. Phys. Chem. B 111 (2007) 7851.
[2] L. Le Gendre, R. Marchand and Y. Laurent, J. Eur. Chem. Soc. 17 (1997) 1813.
[3] L. Le Gendre, R. Marchand and B. Piriou, Eur. J. Solid State Inorg. Chem. 34 (1997)973-982; A. Rachel, S.G. Ebbinghaus, M. Güngerich, P.J. Klar, J. Hanss, A. Weidenkaff, and A. Reller, Thermochim. Acta 438 (2005) 134.
[4] F. Tessier, L. Le Gendre, F. Chevire, R. Marchand, and A. Navrotsky, Chem. Mater. 17 (2005) 3570; D. Logvinovich, A. Börger, M. Döbeli, S.G. Ebbinghaus, A. Reller and A. Weidenkaff. Progr. Solid State Chem. (2007) in print.
[5] S.J. Clarke, C.W. Michie, and M.J. Rosseinsky, J. Solid State Chem. 146 (1999) 399.
[6] J.D. Grunwaldt, M. Caravati, S. Hannemann and A. Baiker PCCP 11 (2004) 3037.
[7] M. Olea, M. Florea, I. Sack, R.P. Silvy, E.M. Gaigneaux, G.B. Marin, P. Grange, J. Catal. 232 (2005) 152.