# Zwahlen Alexander

Establishing a natural-like fluorescence in zirconia

for restorative dental applications

# Master thesis, Therapeutic Technologies

Principal: Dr. Marc Stephan, Institut Straumann AG Expert: Dr. Gerhard Schreiber, PASS Technologies AG Supervisor: Dr. Michael de Wild, School of Life Sciences FHNW

#### INTRODUCTION

The optical impression of the human tooth is also affected by the fluorescence of the dentine. To imitate the visual appearance of the natural tooth, fully anatomical restorations are shaded based on a color key. If the fluorescence effect is neglected, restorations can optically differ from the natural teeth in sunlight or in light from artificial sources with a high amount of UV radiation (see Fig. 1). Different products for the incorporation of a fluorescence effect are available on the market. In contrast to veneering materials and glassceramics, the results produced in zirconia ceramics are unsatisfactory. The application in dental restorations results in numerous challenging requirements to the used phosphor compounds.



Fig. 1: Restoration of an anterior maxillary tooth under regular (left) and UV (right) light [1]

### CONCEPT

In this project, different approaches for the incorporation of the desired fluorescence effect in zirconia were assessed. Multiple phosphors were chosen from literature which should express appropriate photoluminescence (PL) properties to mimic the fluorescence of the natural human tooth. Different doping methods were used to incorporate the phosphors into the zirconia. Further, the resulting optical, chemical and mechanical properties of the ceramic were investigated. Samples with commercially available products were produced to allow comparisons.

## **RESULTS**

Conventional yttria stabilized zirconia (YSZ) did not show an emission when excited with 365nm (see Fig. 2).

Porous zirconia was infiltrated with a liquid bismuth nitrate solution before sintering. With this approach a whitish-blue luminescence very similar to human tooth could be generated when excited with 365nm light. The luminescence emission intensity could be influenced by the variation of the solution concentration. An excitation was possible in the whole UV spectrum with an excitation maximum at 322nm for the emission wavelength of 460nm.

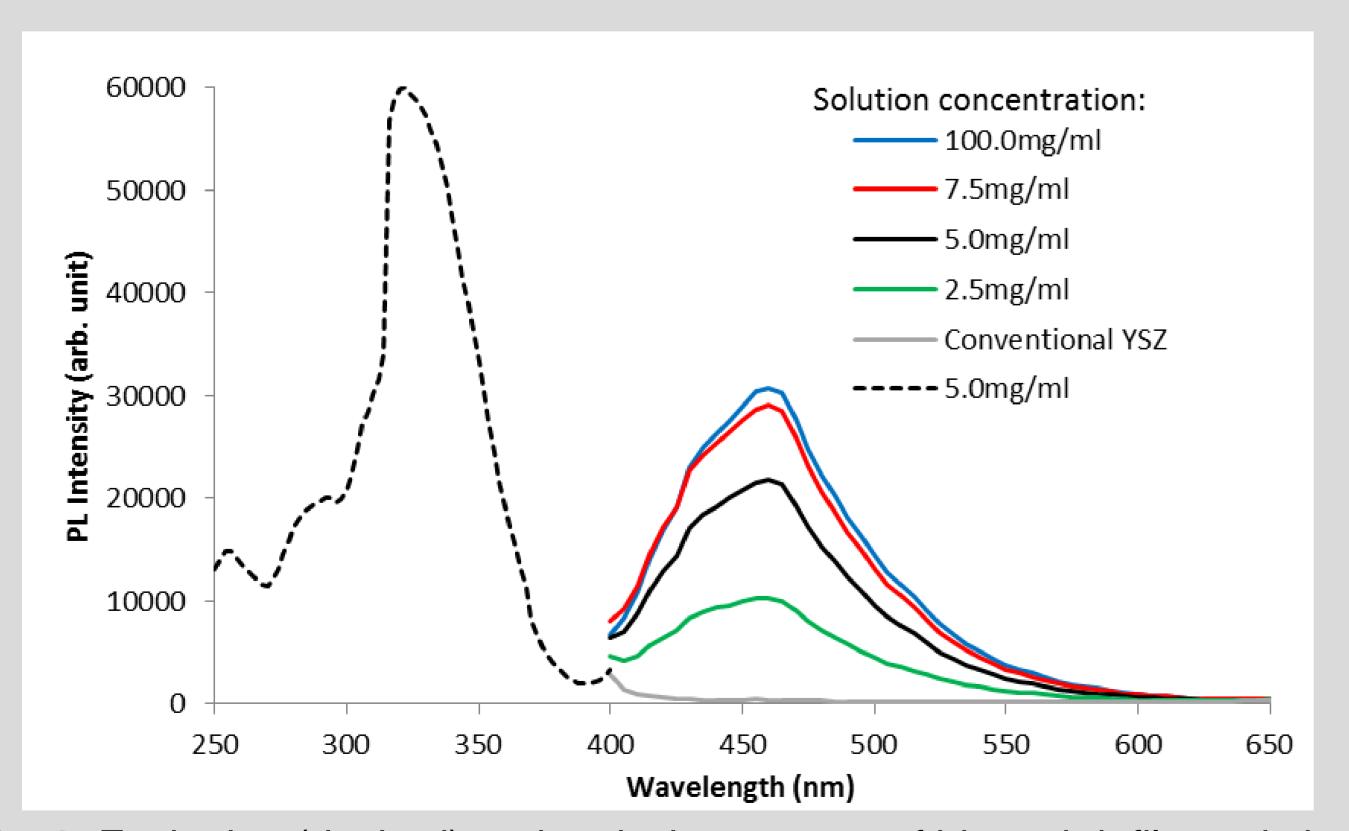


Fig. 2: Excitation (dashed) and emission spectra of bismuth infiltrated zirconia

The same luminescence properties could be generated with a bismuth diffusion doping process. The porous zirconia was sintered in a bismuth dopant atmosphere. The emission intensity could be influenced by the variation of bismuth amount given into the atmosphere (see Fig. 3).

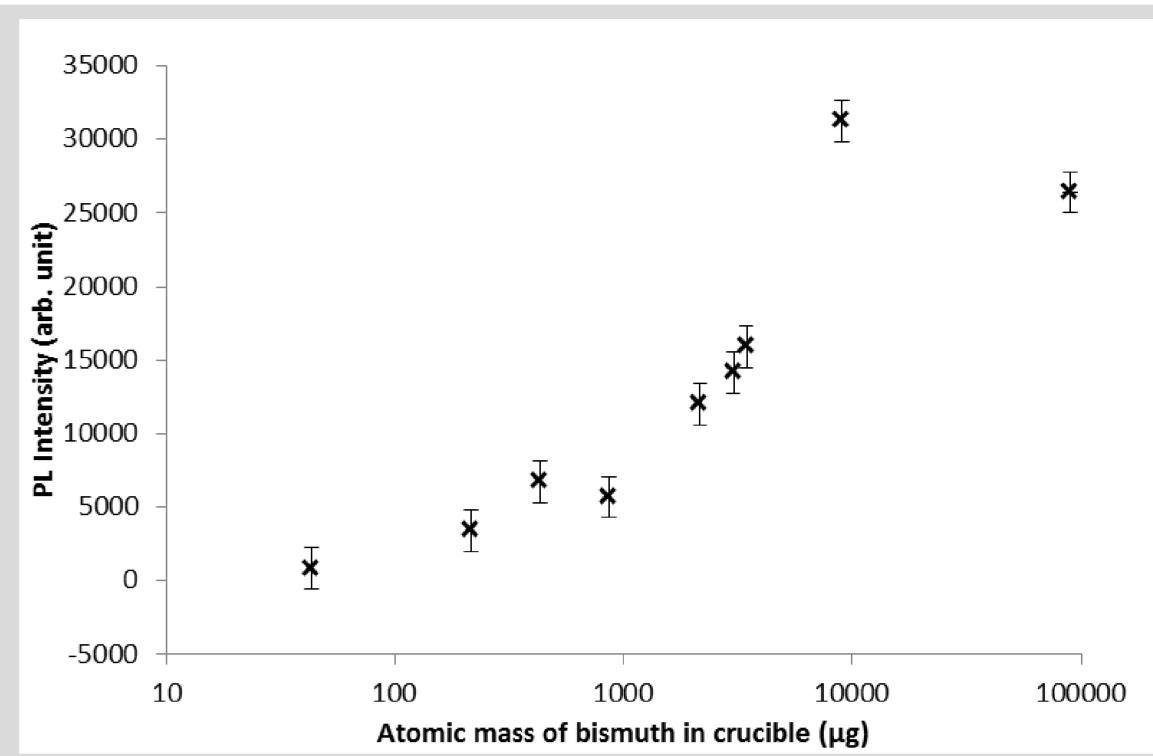


Fig. 3: Emission intensity at 460nm ( $\lambda_{ex}$  = 360nm) of bismuth atmosphere sintered zirconia and atomic mass of bismuth

CAD/CAM milled zirconia crowns were bismuth doped with different doping approaches. A bismuth atmosphere sintered crown (Fig. 4, each left) was compared with a crown which was treated with a commercial bismuth containing product (Fig. 4, each right). Coincident luminescence properties were achieved in this practical application.



Fig. 4: CAD/CAM milled zirconia crowns under regular (left) and UV (right) light

## CONCLUSION

The evaluation of the selected phosphors showed that bismuth doped yttria and zirconia as well as blue phosphor are the most appropriate phosphors to imitate natural tooth fluorescence regarding the luminescence properties. The incorporation of blue phosphor into zirconia is problematic due to the oxidation of the europium in air to an undesired electronic configuration. Therefore only bismuth remains as acceptable fluorescence activator in zirconia. Bismuth diffuses out of the bismuth doped yttria phosphor during sintering, and is doping the yttria stabilized zirconia. The incorporation of bismuth doped yttria into zirconia seems therefore unrealistic. Although the bismuth doped yttria stabilized zirconia shows an undesired yellowish discoloration, this phosphor was considered as the most suitable for the application in dental restorations. Compared to the other assessed phosphors higher emission intensity could be created with bismuth doped yttria stabilized zirconia. This is possible since the mainly contained crystal phase is doped and not only the yttria, for example, which is contained in much lower concentration.

No effect on the microstructure and the mechanical properties by doping with bismuth could be determined.

The infiltration of porous zirconia with a liquid bismuth solution before sintering is the incorporation approach which is used in a commercially available product. A novel doping process for the application in dental restorations was developed with the sintering of porous zirconia in bismuth atmosphere. With this approach, the same luminescence properties could be achieved in zirconia as by the infiltration with liquid bismuth solution. Both approaches allow the tuning of the resulting emission intensity. The sintering of zirconia ceramic in bismuth atmosphere doping process was not previously known for this application and a patent application was filed.

# REFERENCES

[1] Mondelli, R. F. 2012. Challenges of restoring an anterior maxillary tooth: The impact of fluorescence and the mock-up approach. Quintessence International. 2012, Vol. 43, 10.

