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ELECTRICAL FIELD EFFECTS IN SPARK PLASMA SINTERING OF HYPERSTOICHIOMETRIC UO_2

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Recent research in the field assisted sintering of actinide oxides and nitrides has shown the great potential of the technique, but has also evidenced the need for a better understanding of the behavior of such class of materials during processing with current/fields [1-3]. Uranium dioxide, due to its multiple oxidation states and semiconductor characteristic, represents a good model material to investigate some of the peculiar effects of the electric field in the processing of materials. The stoichiometry of UO_2 is of paramount importance, since it governs its fundamental properties, such as the thermal and electrical conductivity, the diffusion coefficients and thus also the sintering and grain growth kinetics.
Here we report the densification behavior of hyperstoichiometric UO_{2+x} in spark plasma sintering. The O/U ratio of the sintered pellets was studied by XRD, X-ray absorption spectroscopy (XAS) and Raman spectroscopy, while finite element methods (FEM) was used to assess the temperature distribution during processing. It is found that powders with an original stoichiometry of $UO_{2.16}$ are gradually reduced to perfectly stoichiometric $UO_{2.00}$ as a function of the sintering temperature and time. Most interestingly, a gradient in the oxidation state in the axial direction was observed for pellets sintered in intermediate conditions (Fig. 1). This gradient depends unequivocally on the direction of the current. Microstructural analysis confirmed the field/current effect in the sintered material. The reasons for the gradient in stoichiometry will be discussed and the implications for the electric field processing of UO_2 and non-stoichiometric oxides in general will be addressed.

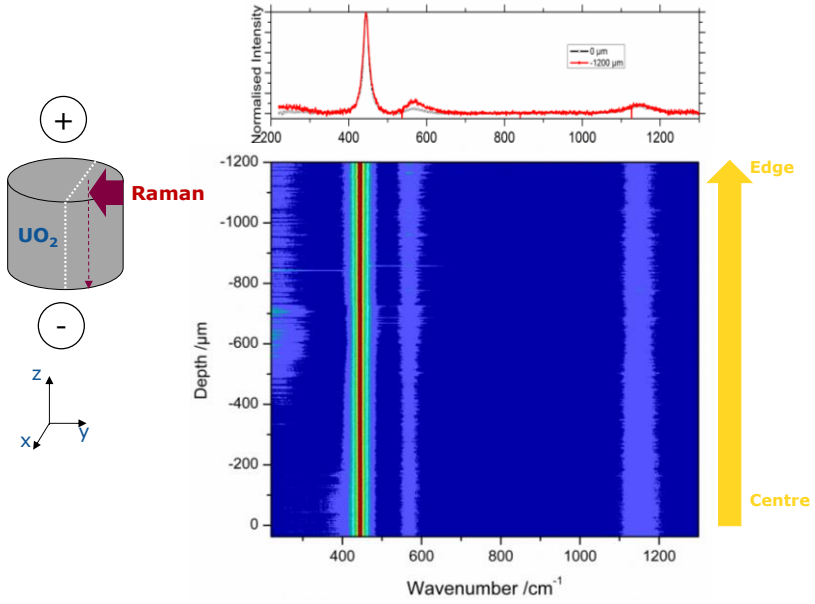

Figure 1 – Raman mapping of UO_2 pellet made by SPS indicating a gradient in the oxidation state.

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