



	<b>Experiment title:</b> Dopant sites in novel proton conducting ceramic oxides	<b>Experiment number:</b> HS-1350
<b>Beamline:</b> BM29	<b>Date of experiment:</b> from: 17/11/2000 to: 20/11/2000	<b>Date of report:</b> 04/04/2001
<b>Shifts:</b> 12	<b>Local contact(s):</b> S. Ansell	<i>Received at ESRF:</i>
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### Report:

Several ceramic oxides with the  $ABO_3$  perovskite structure have been shown to exhibit proton conduction and have excited great interest as potential electrolytes for fuel cells [1-3]. The materials are prepared by doping with aliovalent cations, usually rare earths, introducing charge-compensating oxygen ion vacancies, which are filled by hydroxyl ions in the presence of water vapour. Typical examples are rare earth doped  $CaZrO_3$ ,  $BaCeO_3$  and  $SrCeO_3$ . We have an EPSRC grant (GR/L66212) to study these materials. Computer modelling, using energy minimisation and molecular dynamics, is being employed to predict the local environment of the dopants and the migration mechanisms of protons. EXAFS experiments are being used to probe the dopant environment. A detailed comparison of the results from both techniques can identify precise atomic arrangements and diffusion pathways. The work on the  $CaZrO_3$  has been extremely successful [4,5]. The calculations predicted a dependence of the rare earth site on ionic radius (moving from A to B site with decreasing size) which was borne out by rare earth LIII edge EXAFS measurements. Similar calculations have been performed for the cerates, which are the more promising technological materials, but the EXAFS were hampered by overlap of edges. To overcome this problem experiments on the rare earth K edges were conducted on BM29.

Transmission EXAFS spectra were collected in a liquid helium cryostat for seven samples:-

1. *Er K edge of Er doped  $CaZrO_3$ ;*
2. *Nd K edge of Nd doped  $SrCeO_3$ ;*
3. *Sm K edge of Sm doped  $SrCeO_3$ .*
4. *La K edge of La doped  $BaCeO_3$ ;*
5. *Nd K edge of Nd doped  $BaCeO_3$ ;*
6. *Sm K edge of Sm doped  $BaCeO_3$ ;*
7. *Er K edge of Er doped  $BaCeO_3$ .*

The Er doped  $\text{CaZrO}_3$  sample was run as a calibration for comparison with previous data that we had collected for this sample at the Er LIII edge. The K edge data was consistent with the dopant occupying the Zr site, in agreement with the LIII edge data [5].

The spectrum for the Nd doped  $\text{SrCeO}_3$  was distinctly different from that for Sm doped  $\text{SrCeO}_3$ . We have good LIII data for Sm doped  $\text{SrCeO}_3$  and for several of the rare earths beyond Sm, e.g. Er and Yb. A model in which the rare earth occupies the Ce site fits all of these data. This is consistent with computer simulations of the dopant solution energies of these systems [5,6]. The energy for doping on the Ce site is much more favourable than for doping on the Sr site for the smaller rare earths. However, the energies converge as the rare earth size increases, and overlap around La. Thus there is the possibility of Nd occupying the Sr site and this is supported by the K edge data. At this stage it is not possible to estimate the fraction of Nd occupancy on the Sr site, however a detailed analysis is currently in progress.

Rare earth LIII edge EXAFS experiments are limited to the elements beyond Eu due to overlap from Ce and Ba L edges. The K edge data for all the rare earth doped  $\text{BaCeO}_3$  samples are consistent with a model in which the dopant is on the Ce site. This is consistent with the predictions of the computer simulations. In simple terms the difference in ionic radii ( $\text{Ba}^{2+} = 1.35 \text{ \AA}$ ,  $\text{Ce}^{4+} = 1.01 \text{ \AA}$ ) is such that the trivalent rare earths (radii ranging from  $\text{La}^{3+} = 1.15 \text{ \AA}$  to  $\text{Lu}^{3+} = 0.93 \text{ \AA}$ ) make it extremely unlikely that these ions would occupy the Ba site, as indicated by our data.

## References

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