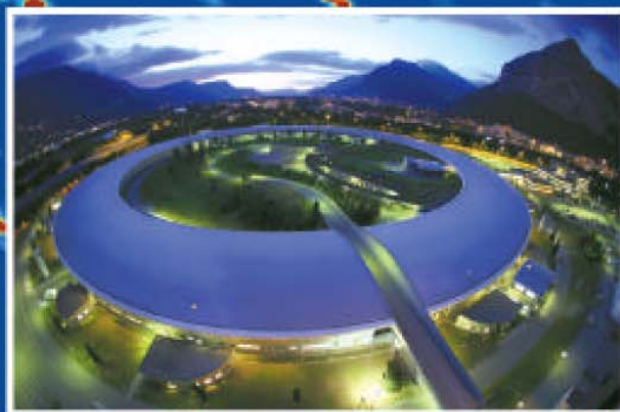


T H E E U R O P E A N L I G H T S O U R C E



# HIGHLIGHTS 2007



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**Principal publications and authors**

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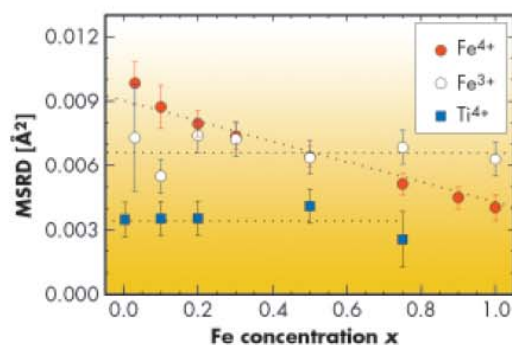
## Structural studies of $Sr(Fe_xTi_{1-x})O_{3-\delta}$ solid solutions by XAS and Raman spectroscopy

The perovskite solid solution series  $Sr(Fe_xTi_{1-x})O_{3-\delta}$ ,  $0 \leq x \leq 1$ , is an interesting system spanning the range from slightly iron-doped  $SrTiO_3$  as a model representative of acceptor-doped large band gap electroceramics, to iron-rich  $Sr(Fe_xTi_{1-x})O_{3-\delta}$  materials, which are good electronic and ionic conductors. Such materials can serve as key functional materials in fuel cells, electrochemical sensors and permeation membranes. In  $Sr(Fe_xTi_{1-x})O_{3-\delta}$ , the iron substitutes for  $Ti^{4+}$  partly in the oxidation state of  $Fe^{3+}$  and partly as  $Fe^{4+}$ , the actual  $Fe^{3+}/Fe^{4+}$  fraction depending on total iron concentration, oxygen partial pressure, and temperature. The charge compensation for  $Fe^{3+}$  occurs predominantly by the formation of mobile oxygen vacancies. For dilute  $Fe^{4+}$  centres (high spin  $d^4$  configuration) a Jahn-Teller distortion is predicted by quantum chemical calculations [1]. The formation of an iron impurity band occurs for iron concentrations higher than about 3-10% and represents a drastic change of the electronic structure [1]. The iron in

metallic conducting  $SrFeO_3$  is known to have an undistorted octahedral coordination. The transition between these limiting cases is addressed in this study.

For each Fe concentration an oxidised (almost all  $Fe^{4+}$ ) and reduced ( $Fe^{3+}$ ) sample was investigated. Fe and Ti K-edge XAS spectra were recorded at beamline **BM29**. EXAFS show different local inter-atomic distances, for oxidised samples,  $Fe^{4+}-O^{2-}$  distances are smaller than half-lattice constants obtained by XRD. Splitting of the first  $Fe^{4+}-O^{2-}$  coordination shell was not observed directly. However, for oxidised samples, we observe an increase of the mean square radial distribution (MSRD) with decreasing  $x$  (**Figure 105**). For low  $x$ , MSRD of  $Fe^{4+}$  is even larger than that of  $Fe^{3+}$  for which oxygen vacancies are present. These findings also remained in low temperature measurements proving a strong static disorder. All these observations can be explained plausibly by a local Jahn-Teller distortion around dilute  $Fe^{4+}$  centres.

Fig. 105: Concentration dependence of the MSRD for  $Fe^{4+}-O^{2-}$  and  $Ti^{4+}-O^{2-}$  bonds (oxidised samples) and  $Fe^{3+}-O^{2-}$  (reduced samples) in the first coordination shell, all at room temperature. Dotted lines are guides for the eye.



Raman spectra of oxidised samples show a new peak in the otherwise Raman-inactive cubic perovskite structure, **Figure 106**. This indicates a local symmetry breaking which is inseparably related to the presence of  $Fe^{4+}$ , and thus strongly suggests a Jahn-Teller distortion (Note that the reduced samples, in spite of oxygen vacancies present, exhibit no Raman peak). The Raman peak decreases with increasing iron concentration at

similar  $x$  where the iron impurity band starts to form, which is consistent with the absence of the Jahn-Teller distortion for  $\text{SrFeO}_3$ .

Although none of the individual observations alone gives the final proof of a Jahn-Teller distortion around  $\text{Fe}^{4+}$  ions, the combination of results obtained by XAS, especially the iron concentration dependence of the  $\text{Fe}^{4+}\text{-O}^{2-}$  MSRD, and Raman spectroscopy strongly supports its presence, most pronounced for  $x \sim 0.03$  and decreasing for higher iron concentrations. The decrease of the Jahn-Teller effect with increasing  $x$  can be understood qualitatively by the change in the electronic structure of the materials from insulator to metal. A quantitative modelling of the variation of the

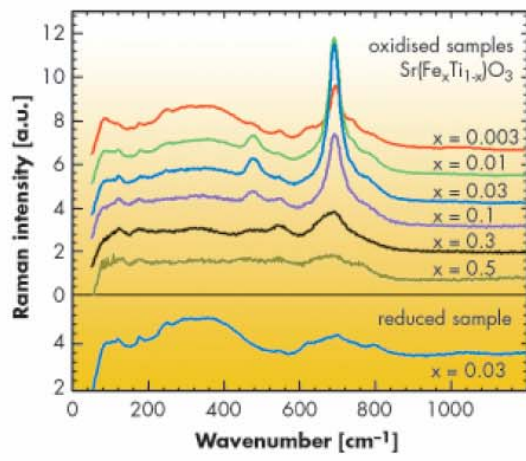


Fig. 106: Raman spectra for oxidised  $\text{Sr}(\text{Fe}_x\text{Ti}_{1-x})\text{O}_3$ . The spectra are scaled to comparable intensity in the 200-400  $\text{cm}^{-1}$  range and shifted upward for clarity. Bottom panel: reduced  $\text{Sr}(\text{Fe}_{0.03}\text{Ti}_{0.97})\text{O}_{2.985}$  sample.

$\text{Fe}^{4+}\text{-O}^{2-}$  MSRD and the intensities of the Raman lines remains a challenging theoretical problem.

**References**  
 [1] R.A. Evarestov, S. Piskunov, E.A. Kotomin, G. Borstel, *Phys. Rev. B* **67**, 064101 (2003).