

## Ion Irradiation Damage in (La,Sr)TiO<sub>3</sub> Perovskites

M.G. Blackford<sup>\*</sup>, K.L. Smith<sup>\*</sup>, M. Colella<sup>\*</sup>, C.J Howard<sup>\*</sup>, Z. Zhang<sup>\*</sup> and N.J. Zaluzec<sup>\*\*</sup>

<sup>\*</sup> Materials and Engineering Science, Australian Nuclear Science & Technology Organisation, PMB 1, Menai, NSW 2234, AUSTRALIA

<sup>\*\*</sup> Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue., Argonne, IL, USA

The immobilisation of high level radioactive waste (HLW) in a solid waste form with subsequent geological isolation from the biosphere is one of the preferred strategies for the management of HLW. The radiation resistance of a waste form may affect the long-term aqueous durability of the waste form. Therefore, it is crucial to understand the radiation damage process and its consequences (amorphisation, cation disordering, volume expansion, cracking, accelerated leaching, etc.).

Alpha decay is the dominant radiation damage mechanism in actinide-bearing HLW waste forms. The amount of damage accumulates over time, resulting in regions of amorphous material and eventually to complete amorphisation at a critical dose,  $D_c$ . This process can be simulated using energetic heavy ion irradiation. Perovskite is an important host for actinides in some ceramic waste forms. In this study, we report radiation damage effects in the  $La_{0.67}[\ ]_{0.33}TiO_3 - SrTiO_3$  perovskite solid solution series (where  $\]$  represents a vacancy). This study was initiated to assess the effect of structure and/or vacancies on radiation resistance.

The critical doses of 1 MeV  $Kr^{2+}$  ions for amorphisation,  $D_c$ , of perovskite as a function of temperature (T) were determined by irradiating specimens using the IVEM-Tandem Facility at Argonne National Laboratory, USA. Progression of damage was followed *in situ* by alternately irradiating and examining specimens using TEM and selected area diffraction.  $D_c$  was taken to be the average of the dose at which all Bragg reflections had disappeared and the dose immediately prior to that dose. Figure 1 shows a typical series of selected area electron diffraction patterns (SADP) as a function of dose. Figure 2 shows  $D_c$  versus T curves for three compositions  $La_{0.67}TiO_3$ ,  $La_{0.3}Sr_{0.55}TiO_3$  and  $SrTiO_3$ . The critical temperatures,  $T_c$ , above which samples cannot be amorphised and/or recrystallisation is complete, of  $La_{0.67}TiO_3$ ,  $La_{0.3}Sr_{0.55}TiO_3$  and  $SrTiO_3$ , are 825, 300 and 385 K respectively, i.e.  $T_c$  does not vary systematically with bulk vacancy content.

X-ray diffraction patterns of various (La,Sr)TiO<sub>3</sub> perovskites were recorded using the Australian National Beam Line Facility's powder diffractometer on beamline 20B, at the Photon Factory, KEK, Japan. The Rietveld program, Rietica, was used to determine lattice parameters and to refine structural models. Figure 4 shows fitted XRD data for  $La_{0.6}Sr_{0.1}TiO_3$ . The quality of these data is typical. Figure 3 is a tentative phase diagram of the  $La_{0.67}[\ ]_{0.33}TiO_3 - SrTiO_3$  perovskite solid solution series on the basis of our data and that of Shimane and Yamada [1].

In conjunction, our radiation damage and x-ray data suggest that there may be some connection between structure and  $T_c$  value. The  $T_c$  value of *Cmmm*-structured  $La_{0.67}TiO_3$  (825 K) is much greater than the  $T_c$  values of *Pm-3m*-structured  $La_{0.3}Sr_{0.55}TiO_3$  and  $SrTiO_3$  (300 and 385 K). Future work will focus on refining the phase diagram, and will include collecting and refining low temperature (100-300K) x-ray data. [2]

[1] Shimane and Yamada Phys. Rev. B 177 (1969) 858

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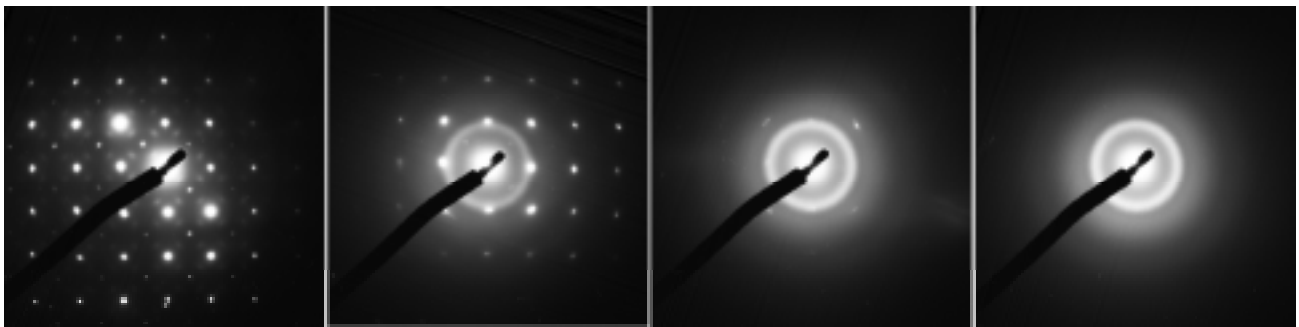


Fig. 1 SADPs recorded from  $\text{La}_{0.3}\text{Sr}_{0.55}\text{TiO}_3$  as a function of ion irradiation dose (in fractions of  $D_c$ ), a)  $0.0 D_c$ , b)  $0.4 D_c$ , c)  $0.8 D_c$  and d)  $1.0 D_c$ .

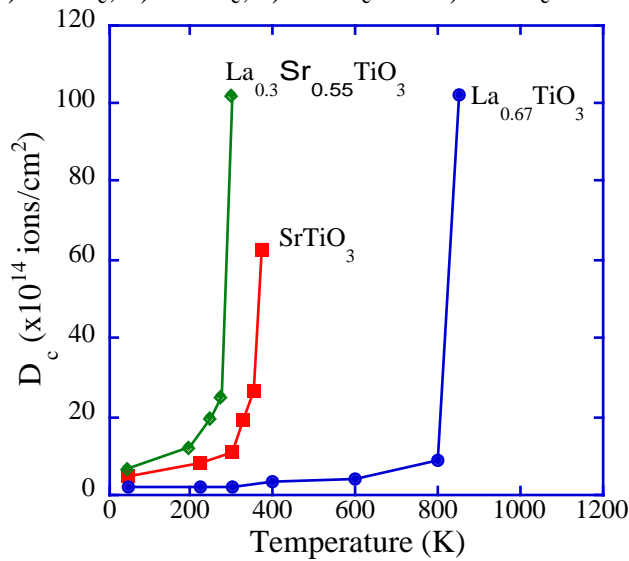


Fig. 2 Temperature dependence of  $D_c$  for three compositions from the  $(\text{La,Sr})\text{TiO}_3$  solid solution series illustrating the dramatic change in behaviour with composition.

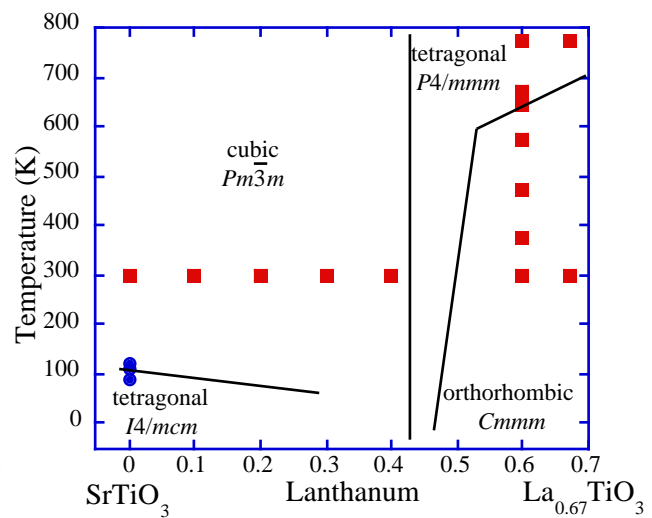


Fig. 3 Tentative phase diagram showing the variation of structure with composition and temperature. Red square = our data, blue circles = Shimane and Yamada [1] data.

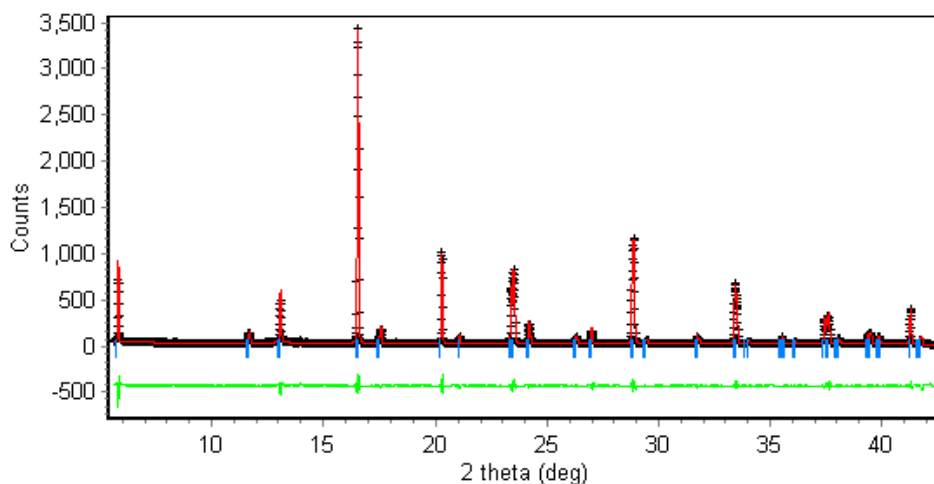


Fig. 4 Synchrotron x-ray powder diffraction pattern from  $\text{La}_{0.6}\text{Sr}_{0.1}\text{TiO}_3$  recorded at room temperature. The structure has been determined to be orthorhombic ( $Cmmm$ ).