

## Trace dopant/oxygen vacancy site determination in Al-doped $Y_2Ti_2O_7$ by 2D electron channeling EDX analysis

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Functional surface coatings with alternating  $Y_2Ti_2O_7$  and  $Al_2O_3$  multilayers exhibit high thermal reflectivity and oxidation resistivity, and are a promising application as environmental barrier coatings (EBCs) for next-generation advanced gas turbine blades [1]. Studies have confirmed that only slight Al doping to  $Y_2Ti_2O_7$  can significantly improve the structural stability of the multilayers, particularly against the oxygen permeability of  $Y_2Ti_2O_7$ , the detailed mechanism of which remains unclear. In the present study, we have determined the occupation sites and occupancies of Al in  $Y_2Ti_2O_7$  using beam-rocking energy dispersive X-ray spectroscopy (EDX) analysis, or statistical ALCHEMI (st-ALCHEMI), associated with scanning transmission electron microscopy (STEM) [2,3]. This method enables us to quantitatively derive the location and fraction of doped impurities in the crystallographic atomic sites; moreover, this method is applicable to any combinations of elements. We have also tried to extend this method to locate the oxygen vacancies (0.2% of the total oxygen amount) introduced to maintain the local charge balance associated with the hetero-valence doping.

Figure 1 shows X-ray ion channeling patterns (ICPs) around the [110] plane of Al-doped  $Y_2Ti_2O_7$ . Linear regression analysis of the Al-K ICP by Ti-K and Y-K ICPs according to the st-ALCHEMI scheme [3] revealed that Al occupies the Ti and Y sites in the ratio 7:3, which suggests the introduction of additional oxygen vacancies to compensate for the resultant charge imbalance, assuming nominal ionic charges as  $Ti^{4+}$ ,  $Y^{3+}$ , and  $Al^{3+}$ .

Figures 2(a) and (b) respectively show the O-K ICPs of Al-doped and pristine  $Y_2Ti_2O_7$  around the [111] plane obtained from areas of approximately 300 nm in thickness. By theoretical calculations, the oxygen-deficient sites could be specified by the change in the O-K ICP associated with Al-doping. Figure 2(c) shows the image obtained by dividing Fig. 2(a) by (b) to highlight the difference. By comparing (c) with theoretical calculations based on the dynamical inelastic electron scattering theory presented in Figs. 3(a) and (b), we concluded that the oxygen vacancies are mainly introduced in the 48f site, which is the first nearest neighbor of Ti, as seen in Fig. 3(c). This result can be understood as follows: considering the ionic radii of the elements of interest ( $Y^{3+}$ : 0.090 nm,  $Ti^{4+}$ : 0.0605 nm,  $Al^{3+}$ : 0.053 nm), Al preferentially occupies the Ti site to tolerate the local distortions associated with the different ionic radii, rather than keeping the total charge balance. Therefore, local charge neutrality is locally compensated for by introducing oxygen vacancies to the first nearest neighbor site of Al located on the Ti site.

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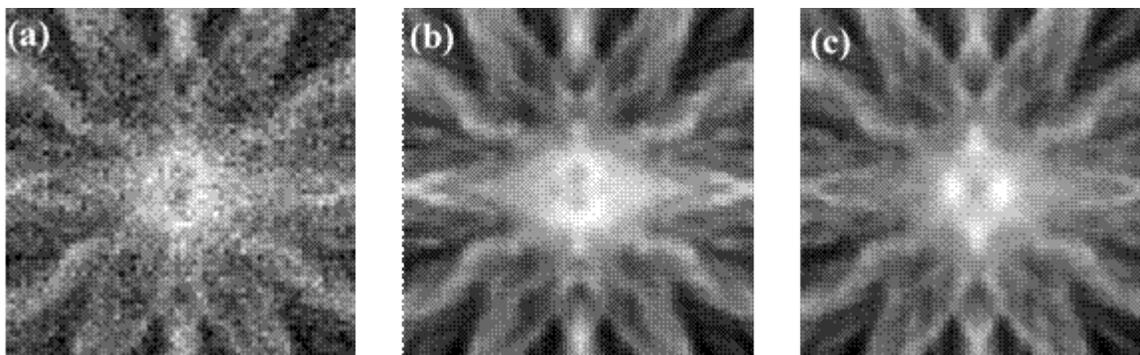


Fig. 1 (a)-(c) Experimental X-ray ICPs of Al-K, Ti-K, Y-K lines, respectively, of Al-doped  $Y_2Ti_2O_7$

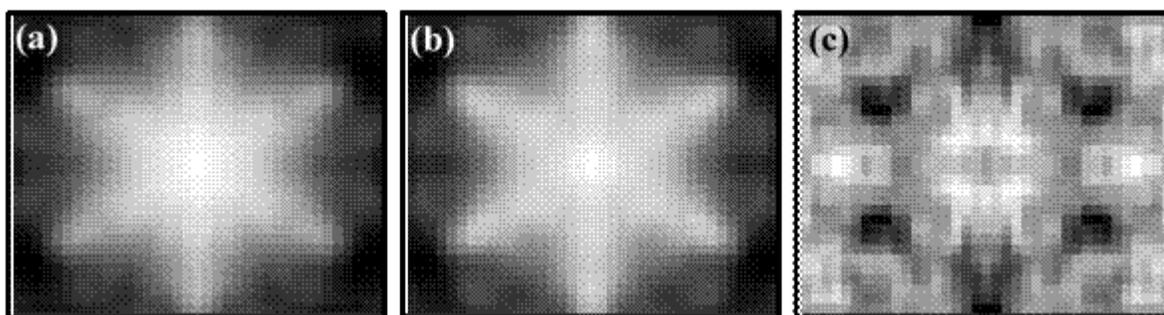


Fig. 2 (a), (b) Experimental O-K ICPs of Al-doped  $Y_2Ti_2O_7$  and non-doped  $Y_2Ti_2O_7$ , respectively, (c) The image obtained by dividing (a) by (b).

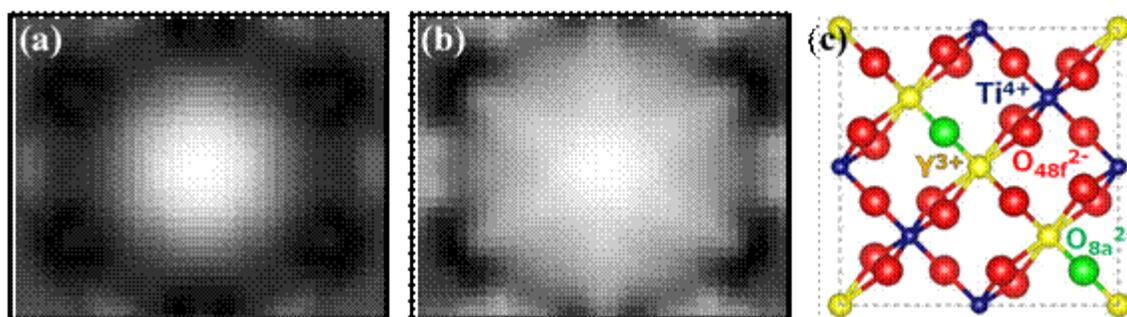


Fig. 3 (a), (b) Image obtained by dividing the theoretical O-K ICP of Al-doped  $Y_2Ti_2O_7$  by that of non-doped  $Y_2Ti_2O_7$ , respectively, (c) Crystal structure of  $Y_2Ti_2O_7$  showing the locations of cations and oxygen ions.