

Atomic Structure and Chemistry of LaMnO₃ Heterointerfaces

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Interest in the oxide heterostructure has been stimulated to a large extent by their interfaces which contain lots of novel phenomena [1-3]. In our research, by atomically resolved imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM), we investigate the elemental interdiffusion and valence states across the interface of LaMnO₃ (LMO) thin film grown on SrTiO₃ (STO) and KTaO₃ (KTO) to understand the effects of the substrate on the interfacial configurations.

First, we examine the microstructure of the interfaces of LMO/KTO and LMO/STO by high annular angle dark field (HAADF) STEM and EELS as shown in figure 1. The interface of LMO/STO has an elemental interdiffusion of about 4 to 5 unit cells. For the determination of the valence states of the elements at the interface, we extract the Ti *L*_{2,3}- and Mn *L*_{2,3}-edge spectra across the interface. With the unchanged Ti valence state and the decreased Mn valence states, we consider that the interdiffusion of Ti⁴⁺ at the interface can lower the valence of the Mn for electric neutrality. In LMO/KTO, we also observe the microstructure of the interface and the map of EELS near edge structures of K *L*_{2,3}-, Mn *L*_{2,3}- and La *M*_{4,5}-edges. Compared to the LMO/STO, the elements at the LMO/KTO interfaces are much less interdiffused. After investigating the spectra of Mn *L*_{2,3}- and O *K*-edge, we believe that the formation of the oxygen vacancies at the LMO/KTO interface is the factor of the reduction in the Mn valence.

In summary, there are two different structural origins causing the decrease of the Mn valence at the interface in LMO/STO and LMO/KTO. Figure 2 shows the lower energy of Mn *L*_{2,3}-edge at the interface in both oxide heterostructures. One is the significant Ti⁴⁺ interdiffusion at the LMO/STO interface. The other is the existence of oxygen vacancies at the LMO/KTO interface. In the future, we would like to further investigate the relationship between atomic configuration and interfacial magnetism at the LMO/STO and LMO/KTO heterojunctions [4].

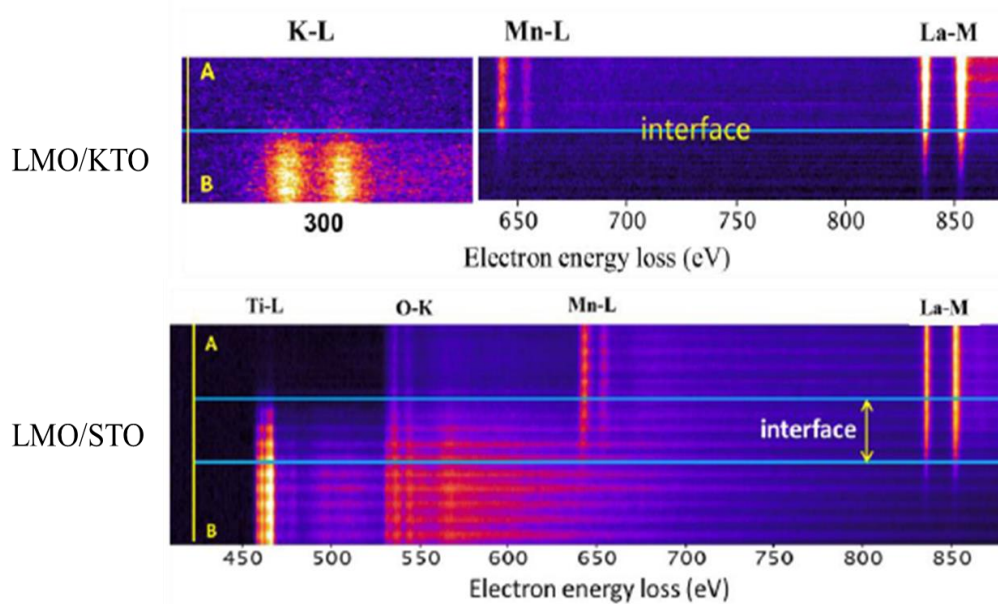


Figure 1. STEM-EELS of the interface in LMO/KTO and LMO/STO.

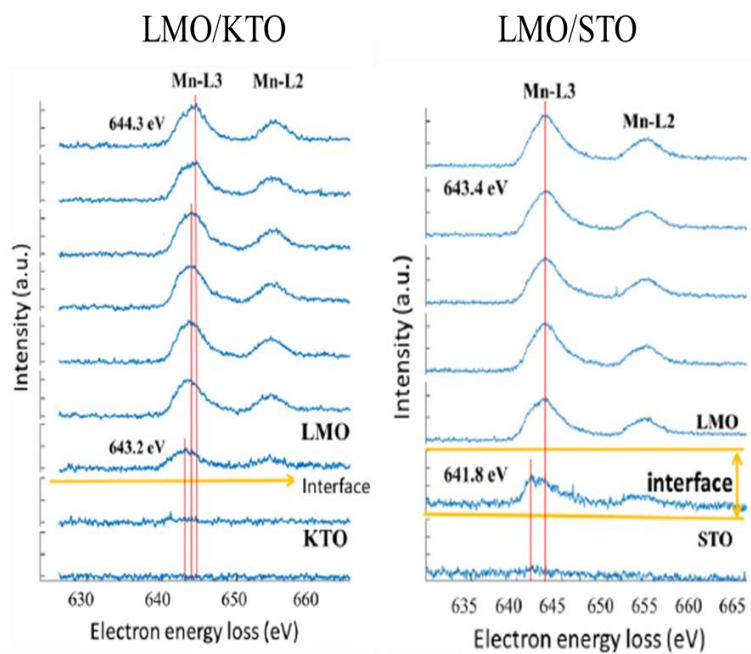


Figure 2. The map of EELS near edge structures of Mn L2,3-edges in LMO/KTO and LMO/STO.

References:

- [1] M Salamon and M Jaime, *Reviews of modern physics* **73** (2001), p. 583. doi:10.1103/revmodphys.73.583
- [2] K Xu et al., *Nanoscale* **13** (2021), p. 60. doi: 10.1039/d0nr07697j
- [3] XR Wang et al., *Science* **349** (2015), p. 716. doi:10.1126/science.aaa5198
- [4] This work was financially supported by National Natural Science Foundation of China (11834009, 52171014, 52011530124), Science, Technology and Innovation Commission of Shenzhen Municipality (HZQB-KCZYB-2020031, JCYJ20210324134402007), the Sino-German Mobility Programme by the Sino-German Center for Research Promotion (M-0265), Science and Technology Department of Sichuan Province (2021YFSY0016), CityU Strategic Interdisciplinary Research Grant (2020SIRG037), the City University of Hong Kong (Projects no. 9610484, 9680291) and the City University of Hong Kong Shenzhen Research Institute. The work described in this paper was substantially supported by a grant from the EU-HK Research and Innovation Cooperation Co-funding Mechanism sponsored by the Research Grants Council of Hong Kong Special Administrative Region, China (Project No. E-CityU101/20), Germany/Hong Kong Joint Research Scheme (DAAD-RGC) (Project No. G-CityU102/20) and the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. CityU 11302121). This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant No. 856538, project “3D MAGiC”). This work made use of the resources of the TRACE TEM center at the City University of Hong Kong and the National Center for Electron Microscopy in Beijing.