Lanthanum niobate \((\text{LaNbO}_4)\) is a promising material system in application as a novel proton conductor due to its combination of properties allowing to withstand high levels of humidity and \(\text{CO}_2\) containing atmospheres [1]. The materials conductivity can be further enhanced by suitable choice of the type and amount of dopants and in particular a co-doping strategy is highly attractive as a route towards improving functional properties of the \(\text{LaNbO}_4\) [2].

We present a detailed study of co-doping influence on the microstructure and compositional homogeneity of \(\text{LaNbO}_4\) proton conductor using combination of high-resolution STEM-HAADF imaging and spectroscopy techniques.

Series of co-doped \(\text{LaNbO}_4\) alloys were synthesized, where Ca, Ba or Sr acted as substitutes on La-sites, and Ge, Ti or Al on Nb-sites. As an example, 1\%-Ca and 1\%-Ti co-doped \(\text{LaNbO}_4\) proton conductor with nominal formula \(\text{La}_{0.99}\text{Ca}_{0.01}\text{Nb}_{0.99}\text{Ti}_{0.01}\text{O}_{4-\delta}\) (LCNT) is discussed in more detail in the following. A low-magnification STEM-HAADF image acquired from an as-sintered sample is shown in Fig. 1. LCNT is predominantly composed of low temperature monoclinic, randomly oriented and well packed large grains showing hexagonal shapes and stress-induced stripy patterns. Strong elemental contrast STEM-HAADF images provided indication for curved shape secondary phase grains present in the host matrix, like grains denoted by letter ‘S’ in Fig. 1. Core-loss EELS spectra revealed the compositional nature and established the presence of a dopant-rich phase in LCNT (see Fig. 2). Furthermore, valence EELS spectroscopy confirmed the same chemical nature for all studied secondary phase grains (not shown). Fig. 3 shows a high-resolution STEM-HAADF image together with the corresponding electron diffraction pattern acquired from one of the ‘S’ grain oriented along a low index zone axis. The crystal structure of the secondary phase grain is highly ordered, layered and defect-free in the observed projection. The layering was characterized by a representative periodicity of \(\approx 12.92\) Å perpendicular to the layers. High spatial resolution core-loss EELS line profiles of the Ca-L\(_{23}\), Ti-L\(_{23}\), and La-M\(_{45}\) absorption edge intensities are shown in Fig. 4. The ‘S’ grains contain La-rich layers (also accommodating some amount of Ca) which are separated by Ti-Ca rich layers accommodating some amount of La. By correlating experimental data with crystal structure models, we identified that the secondary phase grains possess the lanthanum titanate \((\text{La}_2\text{Ti}_4\text{O}_7)\) crystal structure with substantial amounts of Ca incorporated into them, where Ca partly substitutes La.

References:


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Fig. 1: Overview STEM-HAADF image acquired from \( \text{La}_{0.99}\text{Ca}_{0.01}\text{Nb}_{0.99}\text{Ti}_{0.01}\text{O}_{4-\delta} \) sample showing the presence of secondary phase grains denoted by ‘S’.

Fig. 2: Core-loss EELS spectra recorded from the host matrix and the ‘S’ grain.

Fig. 3: High-resolution STEM-HAADF image acquired from the ‘S’ grain together with corresponding electron diffraction pattern in the inset.

Fig. 4: High spatial resolution core-loss EELS elemental line profiles plotted as a function of probe scanning position perpendicular to the layers in the ‘S’ grain.