Vishnu et al. [1] studied the structural and optical properties of a new series of nontoxic yellow dyes with the general formula Sm6-xW1-yZrxMoyO12+δ (x = 0–0.6, y = 0–1). Sm5.4Zr0.6MoO12+δ demonstrated the best chromatic properties among the Sm6-xW1-yZrxMoyO12+δ (x = 0–0.6, y = 0–1) solid solutions [1]. Recently molybdenum substituted lanthanum tungstate La28-y(W1-xMox)4+yO54+δ (x = 0–1; y = 0.923) was investigated as dense membrane materials for hydrogen separation [2]. For x ≤ 0.4 these solid solutions show cubic structure and for x ≥ 0.6 they show rhombohedral superstructure. A strong increase of electronic conductivity (n-type) under reducing conditions and high levels of proton and oxide-ion conductivity were observed in these materials at moderate concentrations of Mo (x ≤ 0.4). Combination of optical aspects of the Sm5.4Zr0.6MoO12+δ with new electrical properties would provide multifunctional material for advanced applications. In this paper, we report the electrical characteristic of Sm6-xZrxMoO12+δ (x = 0.6, 1) and La5.8Zr0.2MoO12.1 as potential materials with electron-proton (mixed) conductivity for hydrogen separation.

Zr-doped lanthanide molybdates Ln6-xZrxMoO12+δ (Ln= La, Sm; x=0.2, 0.6, 1) have been synthesized for the first time (1600 °C, 3 h, mechanical activation of starting oxide mixtures). The Sm compounds have a fluorite-like structure, whereas La5.8Zr0.2MoO12.1 has a rhombohedrally centered hexagonal structure. Fluorite-like Sm5.4Zr0.6MoO12.3 and Sm5ZrMoO12.5 have a similar total conductivity ~ 5×10⁻⁴ S/cm at 800°C in air. R-La5.8Zr0.2MoO12.1 has total conductivity ~ 8×10⁻⁵ S/cm at 800°C in air. Sm5.4Zr0.6MoO12.3 is shown to be electron-proton conductor. The 800°C conductivity of Sm5.4Zr0.6MoO12.3 increases significantly from 2×10⁻⁴ in dry air to 7×10⁻⁴ in wet air, and from 1×10⁻³ in dry Ar to 3×10⁻³ in wet Ar. This material has high electron conductivity under dry and wet reducing conditions (0.15 S/cm at 800°C). The grain boundary contribution of Sm5.4Zr0.6MoO12.3 becomes significant under wet conditions: 1.5×10⁻⁵ S/cm and 7×10⁻⁵ at 680°C in wet air and wet Ar, respectively. La5.8Zr0.2MoO12.1 is shown to be electron-proton conductor. The 800°C conductivity of La5.8Zr0.2MoO12.1 increases from 3×10⁻⁴ in dry air to 5×10⁻⁴ in wet air, and from 3×10⁻³ in dry Ar to 4×10⁻³ in wet Ar. The small symmetry loss for rhombohedral centered La5.8Zr0.2MoO12.1 has detrimental effect on the proton conductivity of Zr doped rare-earth molybdates.


Keywords: rare-earth, molybdate, fluorite, oxide ion conductivity, proton conductivity, electron conductivity, impedance spectroscopy

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