Poster Presentations

[MS28-P04] Electrical properties of Ln6-xZrxMoO12+δ (Ln= La, Sm; x=0.2, 0.6, 1) multifunctional materials

S.N. Savvin[1], A.V. Shlyakhtina[2*], I.V. Kolbanev[2], D.A. Belov[2,3], A.V. Knotko[3], L.G. Shcherbakova[2], P. Nuñez[1]

[1]Department of Inorganic Chemistry, University of La Laguna, 38200, La Laguna, Tenerife, Spain
[2]Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119991 Russia
[3]Faculty of Chemistry, Moscow State University, Leninskie gory 1, Moscow, 119991 Russia
Email: annash@chph.ras.ru; annashl@inbox.ru

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 $x \leq 0.4$ these solid solutions show cubic structure and for $x \geq 0.6$ 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 ($x \leq 0.4$). 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 ~ $5 \cdot 10^{-4}$ S/cm at 800ºC in air. R-La5.8Zr0.2MoO12.1 has total conductivity ~ $8 \cdot 10^{-4}$ S/cm at 800ºC in air. Sm5.4Zr0.6MoO12.3 is shown to be electron-proton conductor. The 800ºC conductivity of Sm5.4Zr0.6MoO12.3 increases significantly from $2 \cdot 10^{-4}$ in dry air to $7 \cdot 10^{-4}$ in wet air, and from $1 \cdot 10^{-3}$ in dry Ar to $3 \cdot 10^{-3}$ in wet Ar. This material has high electron conductivity under dry and wet reducing conditions (0.15 S/cm at 800ºC). The grain boundary contribution of Sm5.4Zr0.6MoO12.3 becomes significant under wet conditions: $1.5 \cdot 10^{-5}$ S/cm and $7 \cdot 10^{-5}$ at 680ºC in wet air and wet Ar, respectively. La5.8Zr0.2MoO12.1 is shown to be electron-proton conductor. The 800ºC conductivity of La5.8Zr0.2MoO12.1 increases from $3 \cdot 10^{-4}$ in dry air to $5 \cdot 10^{-4}$ in wet air, and from $3 \cdot 10^{-4}$ in dry Ar to $4 \cdot 10^{-4}$ 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.

[1] S. Vishnu, S. Jose, M.L. Reddy. J. Am. Ceram. Soc. 94 (2011) 997.
[2] M. Amsif, A. Magraso, D. Marrero-Lopez, J.C. Ruiz-Morales, J. Canales-Vasquez, P. Nunez. ChemMat. 24 (2012) 3868.

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