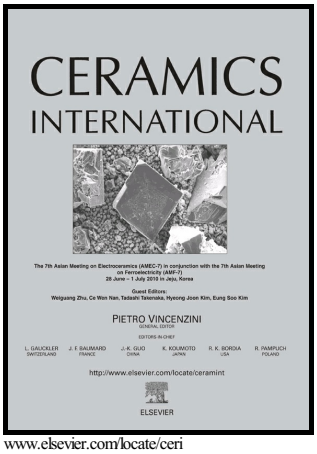

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PII: S0272-8842(17)32061-8
DOI: http://dx.doi.org/10.1016/j.ceramint.2017.09.130
Reference: CERI16301

To appear in: *Ceramics International*

Received date: 14 June 2017
Revised date: 1 September 2017
Accepted date: 16 September 2017

Cite this article as: T.H. Gayathri, A.A. Yaremchenko, J. Macías, P. Abhilash and S. Ananthakumar, MAGNESIUM-DOPED ZIRCON-TYPE RARE-EARTH ORTHOVANADATES: STRUCTURAL AND ELECTRICAL CHARACTERIZATION, *Ceramics International,* http://dx.doi.org/10.1016/j.ceramint.2017.09.130

MAGNESIUM-DOPED ZIRCON-TYPE RARE-EARTH ORTHOVANADATES: STRUCTURAL AND ELECTRICAL CHARACTERIZATION

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Abstract

Undoped $LnVO_4$ and magnesium-doped $Ln_{0.95}V_{0.95}Mg_{0.10}O_{4-\delta}$ (Ln = Pr, Sm, Gd, Dy and Er) orthovanadates were synthesized by solid state reaction method and characterized by XRD, SEM/EDS, electrical conductivity measurements in controlled atmospheres, and modified e.m.f. technique for determination of oxygen-ion transference numbers. XRD analysis showed the formation of phase-pure materials with tetragonal zircon-type structure and a decrease in lattice parameters with a decrease of ionic radius of rare-earth cations. Trace amounts of MgO and Mg-V-O phases revealed by SEM/EDS suggest that the solid solubility limit of magnesium cations in $LnVO_4$ lattice is somewhat lower than the nominal doping level, and that magnesium substitutes preferentially into the vanadium sublattice. $LnVO_4$ and $Ln_{0.95}V_{0.95}Mg_{0.10}O_{4-\delta}$ orthovanadates show semiconducting behavior under oxidizing conditions at 450-950°C and are predominantly oxygen-ionic conductors, except $PrVO_4$ that shows mixed conductivity. In the $LnVO_4$ series, electrical conductivity is the highest for $PrVO_4$ and $SmVO_4$ (~4×10^{-4} S/cm at 800°C) and decreases with increasing atomic number of rare-