

## Thermal Stability and Electrical Conductivity of $\text{Ca}_5\text{Mg}_{4-x}\text{M}_x(\text{VO}_4)_6$ ( $0 \leq x \leq 4$ ) where $\text{M} = \text{Zn}, \text{Ni}$ Measured by Impedance Spectroscopy

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**Abstract :** Calcium oxovanadates with garnet related structure are multifunctional oxides in various fields like photoluminescence, microwave dielectrics, and magneto-dielectrics. For example, vanadate garnets are self-luminescent compounds. They attract attention as RE-free broadband excitation and emission phosphors and are candidate materials for UV-based white light-emitting diodes (WLEDs).  $\text{Ca}_5\text{M}_4(\text{VO}_4)_6$  ( $\text{M} = \text{Mg}, \text{Zn}, \text{Co}, \text{Ni}, \text{Mn}$ ) compounds are also considered promising for application in microwave devices as substrate materials. However, the relation between their structure, composition and physical/chemical properties remains unclear. Given the above-listed observations, goals of this study are to synthesise  $\text{Ca}_5\text{M}_4(\text{VO}_4)_6$  ( $\text{M} = \text{Mg}, \text{Zn}, \text{Ni}$ ) and to study their thermal and electrical properties. Solid solutions  $\text{Ca}_5\text{Mg}_{4-x}\text{M}_x(\text{VO}_4)_6$  ( $0 \leq x \leq 4$ ) where  $\text{M}$  is  $\text{Zn}$  and  $\text{Ni}$  have been synthesized by sol-gel method. The single-phase character of the final products was checked by powder X-ray diffraction on a Rigaku D/MAX-2200 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation in the  $2\theta$  range from  $15^\circ$  to  $70^\circ$ . The dependence of thermal properties on chemical composition of solid solutions was studied using simultaneous thermal analyses (DSC and TG). Thermal analyses were conducted in a Netzsch simultaneous analyser STA 449C Jupiter, in  $\text{Ar}$  atmosphere, in temperature range from 25 to  $1100^\circ\text{C}$  heat rate was  $10 \text{ K}\cdot\text{min}^{-1}$ . Coefficients of thermal expansion (CTE) were obtained by dilatometry measurements in air up to  $800^\circ\text{C}$  using a Netzsch 402PC dilatometer; heat rate was  $1 \text{ K}\cdot\text{min}^{-1}$ . Impedance spectra were obtained via the two-probe technique with an impedance meter Parstat 2273 in air up to  $700^\circ\text{C}$  with the variation of  $\text{pH}_2\text{O}$  from 0.04 to 3.35 kPa. Cation deficiency in  $\text{Ca}$  and  $\text{Mg}$  sublattice under the substitution of  $\text{MgO}$  with  $\text{ZnO}$  up to 1/6 was observed using Rietveld refinement of the crystal structure. Melting point was found to decrease with  $x$  changing from 0 to 4 in  $\text{Ca}_5\text{Mg}_{4-x}\text{M}_x(\text{VO}_4)_6$  where  $\text{M}$  is  $\text{Zn}$  and  $\text{Ni}$ . It was observed that electrical conductivity does not depend on air humidity. The reported study was funded by the RFBR Grant No. 17-03-01280. Sample attestation was carried out in the Shared Access Centers at the IHTE UB RAS.

**Keywords :** garnet structure, electrical conductivity, thermal expansion, thermal properties

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