A rare phenomenon inversion in mullite-type $RAlGeO_5$ for R = Y, Sm – Lu

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Mullite-type RMn_2O_5 (R = Y, rare-earth element) ceramics are of ongoing research attentions because of their interesting crystal-chemical, physical, and thermal properties. The crystal structure of RMn_2O_5, can be described in the orthorhombic space group *Pbam* [1], where the edge-sharing MnO_6 octahedra form infinite chains running parallel to the crystallographic **c**-axis, which are interconnected by double-pyramidal $[Mn_2O_2O_{6/2}]$ building units formed by two edge-sharing MnO_5 tetragonal pyramids. Substitution of transition cations in octahedral and pyramidal sites by non-transition cations can offer a plenty number of phases of this O10-mullite-type family. Though the ionic radii [2] and Al/Ge-O bond distances are quite similar, a complete series of this mullite-type compounds with R-cations and Al^{3+}/Ge^{4+} are still missing. We report a detailed structural, spectroscopic and thermal analysis of the series of mullite-type $RAlGeO_5$ (R = Y, Sm-Lu) phases [3]. Polycrystalline samples are prepared by solid-state synthesis methods. Each sample is characterized by X-ray powder diffraction followed by Rietveld refinements, showing that they are isotypic and crystallize in the space group *Pbam*. The change of the metric parameters is explained in term of the lanthanide contraction effect. A rare inversion of Al/Ge between octahedral and pyramidal sites have been observed for these mullite-type so called O10 compounds, and the inversion parameter found to be between 0.22(1) and 0.30(1) for different R-cations. The <Al/Ge-O> bond distances and their bond valence sums (BVSs) support the respective inversions. Density functional theory (DFT) calculated phonon density of states (PDOS) and electronic band structures are compared for the vibrational and electronic band gap features, respectively. Analysis of UV/Vis absorption spectra using both derivation of absorption spectra fitting (DASF) and Tauc's methods demonstrates that each of the $RAlGeO_5$ O10 compounds is high bandgap semiconductor, possessing direct transition between 4.1(1) and 5.4(1) eV. Both Raman and Fourier transform infrared spectra show clear red shift (quasi-harmonic) of the vibrational wavenumbers with respect to the ionic radii of the R-cations. Selective Raman bands at higher wavenumber region further complement the inversion of Al/Ge between two coordination sites. The higher decomposition temperature of the $RAlGeO_5$ compounds, compared to those of RMn_2O_5 phases, is explained in terms of higher bond strength of Al/Ge-O than those of Mn-O. Irrespective to the inversion between Al- and Ge-sites, the decomposition temperature also depends on the type of R-cation in $RAlGeO_5$.

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