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BaTiO₃ OXIDE SEMICONDUCTORS WITH ALIOVALENT SUBSTITUTIONS IN BARIUM SUBLATTICE.

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The aim of the presented work was to clearly explain, why the formation of semiconducting properties depends on the nature of rare-earth ions. The properties of $(\text{Ba}_{1-x}\text{Ln}_x)\text{TiO}_3$, where $\text{Ln} = \text{Sc, Y, Ln, Nd, Sm, Dy, Lu}$ were investigated by thermogravimetric, X-ray diffraction analysis (XRD), electron microscopy and resistivity measurements. It has been shown that aliovalent substitutions lead to the formation of perovskite structure over a wide concentration range, in which tetragonal phase, a mixture of cubic and tetragonal phase and a cubic phase exist. Semiconducting properties are formed only in tetragonal crystal system; the widest range of existence of tetragonal phase is observed in the case of aliovalent substitution of barium by yttrium. XRD shows that the reduced $(\text{Ba}_{1-x}\text{Ln}_x)\text{TiO}_3$ perovskite lattice parameters $\bar{a} = (a^2c)^{1/3}$ as a function of rare-earth ion concentration pass through a maximum. At low rare-earth ion concentrations, the increase in this parameter may be attributed to the appearance of Ti^{3+} ions, whose radius is larger than that of Ti^{4+} ions. It should be noted that the increase in lattice parameter cannot be attributed either to the aliovalent substitution of barium by rare-earth ions or to the aliovalent substitution of titanium by rare-earth ions. The reduced parameter maximum corresponds to the concentration at which a distance minimum is observed. At high concentrations, this parameter decreases due to both a decrease in Ti^{3+} ion concentration and the aliovalent substitution of barium by elements with smaller ionic radius. It is known that in the case of complicated perovskite compounds the crystal electroneutrality requirement and definite requirement to ion size must be met. The calculations of steric parameters for complex perovskites showed that the perovskite structure must be formed independent of the Ln^{3+} radius value in the aliovalent substitution concentration ranges studied. The arising of semiconductor properties in $(\text{Ba}_{1-x}\text{Ln}_x^{2+})\text{TiO}_3$ perovskites can be associated with the formation of solid solutions $(1-x)\text{Ba}^{2+}\text{Ti}^{4+}\text{O}_3 - x\text{Ln}^{3+}\text{Ti}^{3+}\text{O}_3$. The calculation of steric parameters for Ti^{3+}O_3 showed that the perovskite structure must form when Ln is Y and La-Ho and must not form when Ln is Tm, Yb and Lu. The ionic radius of erbium is close to the maximum radius, for which the existence of the $\text{Ln}^{3+}\text{Ti}^{3+}\text{O}_3$ perovskite structure is still possible. It has been found that when the $(\text{Ba}_{1-x}\text{Ln}_x)(\text{Ti}_{1-x}^{4+}\text{Ti}_x^{3+})\text{O}_3$ solid solution is oxidized, barium metatitanate and phase of BaTiO_7 type are formed at grain boundaries, leading to the formation of a dielectric interlayer at grain boundaries.