Heterometallic group 4–lanthanide oxo-alkoxide precursors for synthesis of binary oxide nanomaterials.

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Streszczenie

In this study, an efficient procedure for the synthesis of uncommon group 4–lanthanide oxo-alkoxide derivatives was developed. Heterometallic clusters with the structures $[La_2Ti_4(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)_8(OEt)_6(Cl)_2(HOEt)_2]$ (**1**), $[La_2Zr_2(\mu_3\text{-}O)(\mu\text{-}OEt)_5(\mu\text{-}Cl)(OEt)_2(HOEt)_4(Cl)_4]_n$ (**2**), $[La_2Hf_2(\mu_3\text{-}O)(\mu\text{-}OEt)_5(\mu\text{-}Cl)(OEt)_2(HOEt)_4(Cl)_4]_n$ (**3**), $[Nd_2Ti_4(\mu_4\text{-}O)_2(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)_8(OEt)_6(HOEt)_2(Cl)_2]$ (**4**), $[Nd_4Zr_4(\mu_3\text{-}O)_2(\mu\text{-}OEt)_{10}(\mu\text{-}Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (**5**), and $[Nd_4Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OEt)_{10}(\mu\text{-}Cl)_4(OEt)_8(HOEt)_{10}(Cl)_2]$ (**6**) were synthesized via the reaction of a metallocene dichloride, $Cp_2M'Cl_2$ (where M′ = Ti, Zr, and Hf), and metallic lanthanum or neodymium in the presence of excess ethanol. This procedure gave crystalline precursors with molecular stoichiometries suitable for obtaining group 4–lanthanide oxide materials. Compounds **1**–**6** were examined by analytical and spectroscopic techniques and single-crystal X-ray diffraction. The magnetic properties of **5** and **6** were investigated by using direct and alternating current (dc and ac) susceptibility measurements. The results indicated weak antiferromagnetic interactions between Nd^{III} ions and a field-supported slow magnetic relaxation. Lanthanum–titanium compound **1** decomposed at 950 °C to give the perovskite compound $La_{0.66}TiO_3$ and small amounts of rutile TiO_2. Under the same conditions, **4** decomposed to give a mixture of $Nd_4Ti_9O_{24}$ and $Nd_{0.66}TiO_3$. When **4** was calcined at 1300 °C, decomposition of $Nd_4Ti_9O_{24}$ to $Nd_{0.66}TiO_3$ and TiO_2 was observed. Calcination of **2**, **3**, **5**, and **6** at 950–1500 °C led to the selective formation of heterometallic $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Nd_2Zr_2O_7$, and $Nd_2Hf_2O_7$ phases, respectively.

Słowa kluczowe

Physical and chemical processes, Oxides, Mathematical methods, Materials, Ions