Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2013, **23**, 17–18
Mendeleev Communications

Synthesis of finely dispersed $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$ oxides

Vladimir G. Sevast'yanov,*[a] Elizaveta P. Simonenko,[a,b] Nikolai P. Simonenko,[a] Konstantin A. Sakharov[b] and Nikolai T. Kuznetsov[a]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 954 4126; e-mail: v_sevastyanov@mail.ru*
[b] *M. V. Lomonosov Moscow State University of Fine Chemical Technology, 119571 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2013.01.005

A unified citrate-based method was developed and used to synthesize finely dispersed powders of practically important complex refractory lanthanum and gadolinium zirconates and hafnates with the structure of pyrochlore. The agglomeration of particles in the powders and pellets of the test compounds was characterised.

The development of materials capable of prolonged service at high temperatures (above 1800–2000 °C) in oxygen-containing environments is an important problem of considerable current interest. Owing to their structure, chemical inactivity, thermal stability and absence of phase transitions up to melting points (mainly >2000 °C), the zirconates and hafnates of lanthanides with the general formula $A_2B_2O_7$ and the cubic structure of pyrochlore are promising materials for the preparation of heat-resistant oxide ceramics, protective antioxidation coatings[1–4] and refractory oxide matrices for high-temperature composite materials. The use of finely dispersed lanthanide zirconates and hafnates for these purposes has obvious advantages. In particular, it becomes possible to obtain uniform layers of controlled thicknesses and to reduce the sintering temperature of the composite oxide matrix in the components of power plant units operating under extreme conditions, *i.e.* at elevated temperatures and in high-enthalpy gas flows.

Currently, high demand exists for the development of advanced high performance methods for the preparation of the zirconates and hafnates of lanthanum and gadolinium with the structure of pyrochlore (though data are available that for $A_2Hf_2O_7$ compounds the pyrochlore structure is preserved up to $Tb_2Hf_2O_7$) not only having a predefined elementary composition but also possessing a high surface area, which is important for the creation of thermally and chemically resistant supports for catalysts and materials for chemosensors. In this study, we used a modified citrate method[5–9] also called the Pechini method[6] to obtain the desired compounds. We identified $La_2Zr_2O_7$, $La_2Hf_2O_7$, $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$ and studied their morphology, degree of dispersion, thermal stability and sintering.

The finely dispersed powders of lanthanum and gadolinium zirconates and hafnates were obtained from the inorganic salts of hafnium, zirconium and gadolinium and lanthanum oxide, which were dissolved in water with the addition of concentrated nitric acid followed by the addition of aqueous ammonia, citric acid and ethylene glycol. Evaporation to a viscous state and a redox reaction at 250–350 °C gave powdered oxides of predefined composition with an admixture of residual carbon, which was burnt out by subsequent heating at 650–700 °C for 1–2.5 h. As a result, the powder retained a developed surface and low bulk density (*e.g.*, 0.02 g cm^{-3} for $La_2Zr_2O_7$). The product yield after the burn-out was 98–99%.

Laser mass spectrometry (an EMAL-2 instrument) allowed us to determine the ratio between the metals in the synthesized oxides, which was consistent with the specified value [the deviation of the Ln : Zr(Hf) did not exceed 2% in all cases]. The total concentration of transition metal admixtures was lower than 0.5 at% in all of the synthesized compounds.

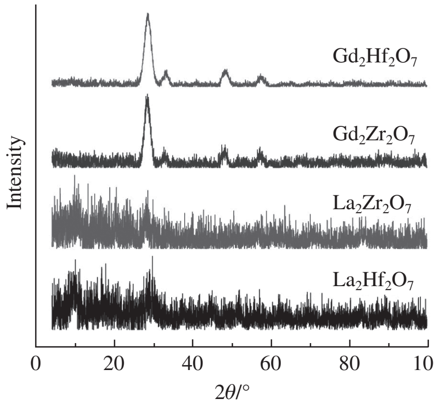

Figure 1 X-ray diffraction patterns of the products after purification from residual carbon.

X-ray diffraction analysis (DRON 2, Huber chamber, Imaging Plate detector, germanium monochromator, CuKα1 radiation) showed that the cubic phases of gadolinium zirconate and hafnate are formed under the synthesis conditions, whereas lanthanum zirconate and hafnate specimens are X-ray amorphous (Figure 1). The mean crystallite size calculated for $Gd_2Zr_2O_7$ and $Gd_2Hf_2O_7$ using the Scherrer formula was ~5 nm.

The specific surface area of powders determined by the BET method (nitrogen sorption at 77 K, ASAP 2020 gas adsorption analyzer) ranged from 20–21 (for $La_2Zr_2O_7$ and $La_2Hf_2O_7$) to 30–37 m^2 g^{-1} (for $Gd_2Hf_2O_7$ and $Gd_2Zr_2O_7$).

The TGA/DSC/DTA method (an SDT Q-600 combined TGA/DSC/DTA analyzer) was used to study the thermal behaviour of the products at 20–1200 °C in a stream of air. At these temperatures, the thermograms did not show any thermal effects attributable to phase transitions in the oxide. The mass loss was 4–6%, which may be due to the desorption of surface gases and oxidation of non-burnt carbon (a minor exothermic effect with a maximum at 900–920 °C accompanied by an abrupt mass loss by ~2%) resulting from the opening of closed pores and structurization upon heating.

A study of the morphology of oxide surfaces by scanning electron microscopy (NVision 40 three-beam workstation, Carl

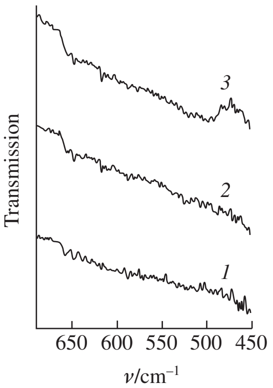

Figure 2 IR spectra of milled $La_2Zr_2O_7$ pellets sintered for 1 h at (*1*) 800, (*2*) 900 and (*3*) 1000 °C.

Zeiss) suggests that the powders are films of complicated form, tens to hundreds nanometers thick, with hidden porosity.

The sintering of pellets (20 mm in diameter, ~2 mm in height; formation pressure, 64 atm cm^{-2}) from the powders was studied in air at 800, 900 and 1000 °C for 1, 2 and 4 h (after exposure and cooling, the pellets were milled). The formation of a cubic phase with the pyrochlore structure was observed in all the specimens even at minimum temperature and exposure time, though IR spectroscopic data (Figure 2) allow us to state that the structure is more ordered in pellets kept at 1000 °C: characteristic absorption bands are observed in the range of 400–650 cm^{-1}.[10]

The X-ray diffraction analysis of gadolinium hafnate $Gd_2Hf_2O_7$ suggests that the mean crystallite size increases during sintering from ~5 nm (800 °C, 1 h) to 19 nm (1000 °C, 4 h). Under similar thermal treatment conditions, the mean crystallite size of gadolinium zirconate $Gd_2Zr_2O_7$ increases from 7 to 103 nm. The crystallite size of lanthanum hafnate and zirconate grows from 38 to 53 nm and from 17 to 38 nm, respectively. It has been found that an increase in temperature affects the crystallite growth to a greater extent than an increase in exposure time.

The enlargement of grains upon the sintering of metal oxide pellets was accompanied by changes in the specific surface area. The specific surface area of gadolinium hafnate sintered for 1 h monotonically decreased from 19 (800 °C) to 9 m^2 g^{-1} (1000 °C). Lanthanum hafnate demonstrates an increase in the specific surface area from 6 (800 °C) to 13 m^2 g^{-1} (900 °C) followed by a decrease to 12 m^2 g^{-1} (1000 °C). This phenomenon can be explained by pore opening as a pellet was heated to 900 °C, which is in good agreement with thermal analysis results.

Scanning electron microscopy of the surface of powders obtained by the milling of pellets after sintering at 1000 °C for 4 h suggests that oxide particles grow considerably upon thermal treatment. In this case, the mean particle size of gadolinium and lanthanum hafnates and lanthanum zirconate powders was 45–55 nm. The mean particle size of gadolinium zirconate was ~130 nm [Figure 3(*a*)].

The growth of powder particles (without preparation of pellets) at higher temperatures was studied for lanthanum and gadolinium zirconates. The powders were heated twice to 1200 °C during thermal analysis but were not kept at this temperature (in a stream of air, 100 nm min^{-1}, heating rate of 20 K min^{-1}), followed by an SEM morphology study. It was found that the oxide films acquired a network morphology upon sintering [Figure 3(*b*)]. The mean particle size of gadolinium zirconate was 30 nm, and that of lanthanum zirconate was 40 nm.

Thus, we have developed a fast high-performance method for the preparation of the finely dispersed nanocrystalline metal oxides $Gd_2Hf_2O_7$, $Gd_2Zr_2O_7$, $La_2Hf_2O_7$ and $La_2Zr_2O_7$ with the pyrochlore structure, in which the fraction of transition metal admixtures did not exceed 0.5 at%. Their phase compositions, morphology and dispersion were determined. Their thermal behaviour at 20–1200 °C was studied. The dependences of the crystallite size and specific surface area on temperature and thermal treatment duration were obtained.

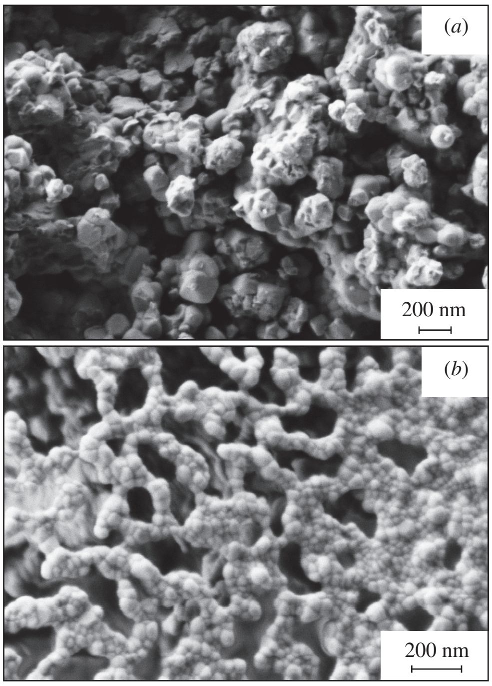

Figure 3 (*a*) Microstructure of a $Gd_2Zr_2O_7$ specimen after pellet sintering at 1000 °C for 4 h and (*b*) powder after twice repeated heating to 1200 °C in air.

This study was supported in part by the Russian Foundation for Basic Research (grant no. 12-03-33005-mol_a_ved). We are grateful to the ‘ASPEKT’ association for its assistance in the determination of the surface areas of specimens.

References

1 J. Wang, Sh. Bai, H. Zhang and Ch. Zhang, *J. Alloys Compd.*, 2009, **476**, 89.

2 Zh. Xua, L. He, R. Mu, X. Zhong, Y. Zhang, J. Zhang and X. Cao, *J. Alloys Compd.*, 2009, **473**, 509.

3 G. Moskal, L. Swadźba, M. Hetmańczyk, B. Witala, B. Mendala, J. Mendala and P. Sosnow, *J. Eur. Ceram. Soc.*, 2012, **32**, 2035.

4 C. S. Ramachandran, V. Balasubramanian, P. V. Ananthapadmanabhan and V. Viswabaskaran, *Ceram. Int.*, 2012, **38**, 4081.

5 V. G. Sevastyanov, E. P. Simonenko, N. A. Ignatov, R. G. Pavelko and N. T. Kuznetsov, *Kompozity i Nanostruktury* (*Composites and Nanostructures*), 2009, (1), 50 (in Russian).

6 M. P. Pechini, *US Patent 3,330,697*, 1967 (*Chem. Abstr.*, 6409880).

7 N. T. Kuznetsov, V. G. Sevast’yanov and E. P. Simonenko, *Ross. Khim. Zh.*, 2010, **53**, 116 (*Russ. J. Gen. Chem.*, 2010, **80**, 658).

8 V. G. Sevast’yanov, E. P. Simonenko, D. V. Sevast’yanov, N. P. Simonenko, V. L. Stolyarova, S. I. Lopatin and N. T. Kuznetsov, *Zh. Neorg. Khim.*, 2013, **58**, 3 (*Russ. J. Inorg. Chem.*, 2013, **58**, 1).

9 V. G. Sevastyanov, E. P. Simonenko, N. P. Simonenko, Yu. S. Ezhov, V. L. Stolyarova, S. I. Lopatin and N. T. Kuznetsov, in *High Temperature Ceramic Materials and Composites [Proc. 7th International Conference on High Temperature Ceramic Matrix Composites (HT-CMC 7)]*, eds. W. Krenkel and J. Lamon, Bayreuth, Germany, 2010, p. 761.

10 W. E. Klee and G. Weitz, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2367.

Received: 17th September 2012; Com. 12/3978