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SYNTHESIS OF APATITE-TYPE $Ce_{4.67}(SiO_4)_3O$ VIA GLYCINE-NITRATE COMBUSTION

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Abstract

The pure $Ce_{4.67}(SiO_4)_3O$ with the apatite-type of structure was obtained for the first time from cerium nitrate, glycine and tetraethyl orthosilicate (TEOS) through the self-combustion of the gel. The solution of the reactants with the molar ratio of TEOS to water 1: 42 and glycine to NO_3^- 1: 3 was transformed into gel. During combustion of the gel the ash containing nanostructured CeO_2 and noncrystalline SiO_2 was formed. The phase identification and the measurement of the crystallite size was done by XRD diffraction. $Ce_{4.67}(SiO_4)_3O$ was synthesized from the ash subsequently fired in argon at 1200 °C.

Introduction

Rare earth silicates with the apatite-type structure can be used as electrolytes for solid oxide fuel cells (SOFCs) because of their high ion conductivities. Beside the solid-state reaction between oxides [1], and the sol-gel synthesis using metal alkoxides [2], combustion procedure is applied to prepare some silicates [3] recently. Combustion synthesis involves a highly exothermic redox reaction between metal nitrates and an organic fuel to produce a fine solid powder of metal oxide. Properties of the as-synthesized powders are dependent on the fuel-to-oxidizer ratio, which also determines the reaction temperature [4]. The second component SiO_2 is mostly obtained from alkoxide, TEOS during its hydrolysis [5]. The hydrolysis of TEOS is a sol-gel process and proceeds via series of condensation reactions forming Si-O-Si linkages as well as the ethanol as a side product. Owing to that, the products of combustion synthesis are strongly affected by the ratio TEOS: H_2O : ethanol.

In this study the self-combustion of the gel obtained from solution of cerium nitrate, glycine and TEOS, was performed that produced nanostructured CeO_2 and noncrystalline SiO_2 , which have formed $Ce_{4.67}(SiO_4)_3O$ during firing. This is according to our knowledge, the first experiment described in the literature for production of nanosized Ce-apatite by glycine-nitrate method using TEOS as starting chemical.

Experimental

The starting materials were $Ce(NO_3)_3 \cdot 6H_2O$, TEOS ($Si(OC_2H_5)_4$), glycine (2-aminoacetic acid, NH_2CH_2COOH) and ethanol (C_2H_5OH). $Ce(NO_3)_3 \cdot 6H_2O$ (10.769 g) was first dissolved in 20 ml of ethanol. Then, stoichiometric amount of TEOS (Ce:Si = 4.67:3), distilled water and, finally, glycine were added into solution. The

molar ratio of TEOS to added water was 1: 42, while the molar ratio of glycine to NO_3^- was 1: 3. At every stage of this procedure, reactants were stirred at room temperature with a magnetic stirrer for appropriate time, until clear solution was obtained. During heating at 60 °C the solution got transformed into transparent gel which was then dried. Afterwards, the dried gel was heated on the hot plate when the spontaneous ignition occurred and self-propagating combustion continued producing yellow-white and voluminous ash and large amounts of gases. Ash was calcined at 600 °C for 3 h to remove the organic contents, then uniaxially pressed into pellets and sintered in flowing argon at 1200 °C for 5 h.

X-ray diffraction (XRD) analyses performed by $\text{CuK}\alpha$ radiation was used for phase identification and crystallite size determination.

Results and Discussion

In the performed combustion process, glycine acts as an organic fuel while the cerium nitrate is an oxidizer. For stoichiometric redox reaction between a fuel and an oxidizer, the net oxidizing valency of metal nitrate should be equalized to the net reducing valency of the fuel [4]. With the aim to obtain nanostructured oxides by combustion process fuel-deficient ratio was chosen (glycine: $\text{NO}_3^- = 1: 3$). This ratio is only something above the lowest ratio (0.3) needed for autoignition to occur, but provides the low flame temperature and the minimum evolved gaseous products. As a consequence, the crystallites growth is suppressed as well as the loss of the ashes out of the reaction bottle that are released along with gaseous products. N_2 , CO_2 and H_2O are primarily evolved during combustion. The unstable Ce^{3+} -ions of cerium nitrate produce CeO_2 during combustion in air.

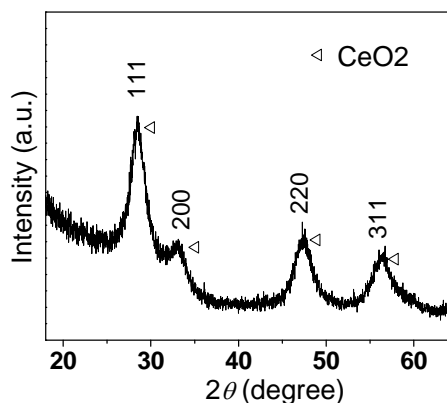


Fig. 1. XRD pattern of ash

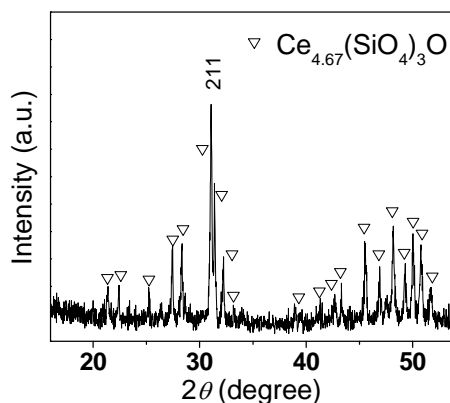


Fig. 2. XRD pattern of fired ash

On the XRD pattern (Fig. 1) of the powder produced by self-combustion only the broad peaks of CeO_2 (JCPDS 34-0394) are visible, indicating that SiO_2 is noncrystalline. The crystallite size of CeO_2 was calculated from the full width at half maximum (FWHM = $1.909^\circ 2\theta$) of the 111 peak using Scherrer equation. The

obtained value of 4 nm confirmed the nanostructure of CeO_2 . Only the $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ phase was identified (JCPDS 43-0441) on the diffraction pattern (Fig. 2) of the sample fired in argon 5 h at 1200 °C, that is considerably lower temperature in comparison with the 1550 °C at which this compound was obtained by solid-state reaction [6]. The temperature decrease resulted in the 43 nm crystallite size of $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ calculated from 211 peak (FWHM = 0.224 °2 θ). This crystal structure of $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ will likely enable to get dense sintered product, also at a lower temperature. The formation of solely $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ phase is mostly influenced by chemical homogeneity of the solution and the gel in which the constituents are mixed at the molecular level. In the solution, glycine molecules with two complexing groups, amino and carboxylic acid make the complex ions of cerium, which prevent precipitation and maintain homogeneity among the constituents.

Conclusion

The $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ with the apatite-type structure was synthesized at 1200 °C in argon from nanostructured CeO_2 and noncrystalline SiO_2 obtained through the glycine-nitrate combustion procedure. The homogenous solution of cerium nitrate dissolved in ethanol, glycine, TEOS and water was prepared at room temperature by stirring. The molar ratio of TEOS to water was 1: 42, while the molar ratio of glycine to NO_3^- was 1: 3. The heated solution was transformed into gel. The thermally induced autoignition of the gel and its self-propagated combustion gave the mixture of CeO_2 and SiO_2 powders. The crystallites size of CeO_2 , determined by XRD diffraction, was 4 nm, while $\text{Ce}_{4.67}(\text{SiO}_4)_3\text{O}$ contained crystallites of 43 nm.

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References

- [1] P. Panteix, I. Julien, D. Bernache-Assollant, P. Abelard, *Mat. Chem. Phys.* 2006, **95**, 313-320.
- [2] S. Tao, J. Irvine, *Mater. Res. Bull.* 2001, **36**, 1245-1258.
- [3] C. Tian, J. Liu, J. Cai, Y. Zeng, *J. Alloys Compd.* 2008, **458**, 378-382.
- [4] R. Purohit, B. Sharma, K. Pillai, A. Tyagi, *Mater. Res. Bull.* 2001, **36**, 2711-2721.
- [5] S. Celerier, C. Laberty, F. Ansart, P. Lenormand, P. Stevens, *Ceram. Int.* 2006, **32**, 271-276.
- [6] S. Zec, S. Bošković, *J. Mater. Sci.* 2004, **39**, 5283-5286.