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Synthesis and properties of lanthanum hexaaluminate ceramic $La_{1-x}Ca_xAl_{11-y-z}Mg_yTi_zO_{18}$

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Abstract

The aim of the present work is to obtain ceramic materials with a hexagonal structure and high density, hardness and mechanical strength at lower synthesis temperature. Ceramic samples with nominal composition $La_{1-x}Ca_xAl_{11-y-z}Mg_yTi_zO_{18}$ ($x=0$–1; $y=0$–3; $z=0$–3,5) are prepared. The samples are sintered at temperature 1500 °C by one-stage and two-stage ceramic technology. By X-ray diffraction and scanning electron microscopy, predominant phase $LaAl_{11}O_{18}$ and second phases $LaAlO_3$ and α-Al_2O_3 are identified. Ceramic materials are characterized with high physico-mechanical properties and may be find application for production of mill bodies and materials for immobilization of nuclear waste.

Keywords: Synthesis properties; Lanthanum hexaaluminate ceramics

1. Introduction

Two compounds are identified in the system La_2O_3–Al_2O_3: $LaAlO_3$ a cubic perovskite and $LaAl_{11}O_{18}$ a hexagonal compound known to have the β-Al_2O_3 structure [1]. The formation rate of $LaAl_{11}O_{18}$ from $LaAlO_3$ and Al_2O_3 is extremely slow at temperature below 1500 °C and temperatures above 1800 °C are required for full synthesis [2,3]. The "β-alumina-type compound" was first recognized by Roth and Hasko [3]. Further investigations [4] proved, that this compound is composed of β-alumina-type and magnetoplumbite-type unit cells, the ratio of which depended on the composition. Two groups of compounds with more complex composition have been studied extensively: $LnMgAl_{11}O_{19}$ with Ln = La, Ce, Pr, Sm, Eu and Gd [5,6,8] and $LaMAl_{11}O_{19}$ with M = Mn, Co, Fe, Ni [9,10]. The wide range of cation distributions found in magnetoplumbite structures [5–7] is one of the most interesting features, which makes this structures particularly suitable as mill bodies and materials for immobilization of nuclear waste [8].

In our previous works about the synthesis of Al_2TiO_5 at 1500 °C with La_2O_3, MgO and CaF_2 additives were proved, as second phase, the formation of solid solution with nominal composition $Ca_{1-x}La_xAl_{12-y-z}Mg_yTi_zO_{19}$ with magnetoplumbite structure type $AB_{12}O_{19}$ [11].

The idea in this study is that with introduction of some additive components, is possible to obtain lanthanum hexaaluminate ceramic with non-stoichiometric composition at lower temperatures. The aim is to obtain lanthanum hexaaluminate ceramic materials with nominal composition $Ca_{1-x}La_xAl_{11-y-z}Mg_yTi_zO_{18}$ with high density, hardness and mechanical strength at lower temperature of synthesis.

2. Experimental

Samples in the following compositions with common formula $La_{1-x}Ca_xAl_{11-y-z}Mg_yTi_zO_{18}$, where $x=0$–1; $y=0$–3; $z=0$–3, have been prepared using the standard solid state reaction techniques from La_2O_3 (99,9% Merck), TiO_2 (99,9% Merck), Al_2O_3 (99,9% Merck), $MgCO_3$ (99,9% Merck) and $CaCO_3$ (99,9% Merck). Powders are weighed in appropriate proportions and mixed by conventional ball-milling method using ethyl alcohol and corundum balls in a plastic vessel for 24 h. After drying at 80 °C for 5 h in air, the homogeneous mixed powders are uniaxially pressed at 100 MPa in a

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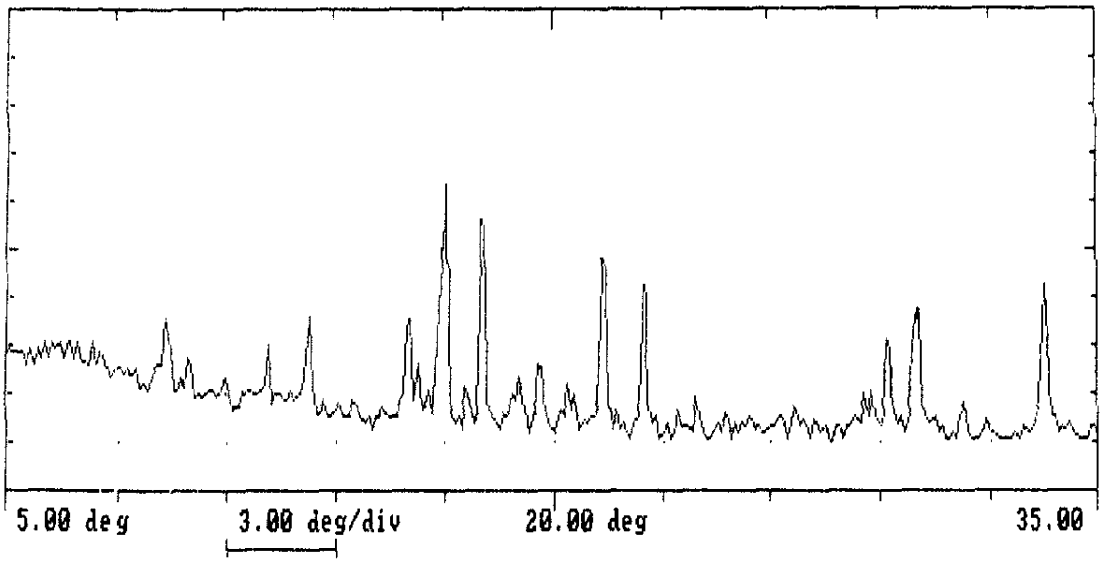

Fig. 1. XRD pattern of ceramic with nominal composition $La_{0.75}Ca_{0.25}Al_{8.5}Mg_{1.0}Ti_{1,5}O_{18}$ obtained by two-stage technology and fired at 1500 °C, 5 h.

hydraulic press to form pellets with diameter 30 mm and thick 10 mm. The compact pellets are sintered at 1500 °C for 5 h in air. Two-stage technology is applied also. Material is calcined in the first stage at 1500 °C for 10 h, after that wet milled in ball mill with corundum balls. In the second stage, the materials are dried, the pressed at 100 MPa to form pellets, which are fired at 1500 °C for 5 h. Phase identification are carried out by X-ray powder diffraction analysis using ''DRON UM'' diffractometer, CuK_α radiation. The microstructure of the ceramic sample, obtained by two-stage technology, is observed using a ''JCXL–733'' scanning electron microscope, produced of JEOC (Japan). The contents of chemical elements presenting in the identified phases are determined using an energy ''ESC LINN 10/85'' spectrometer. The apparent density and the water absorption of the sintered ceramic samples are examined by standard techniques. The micro-hardness of the samples are determined using ''MICRODUROMAT 400'' apparatus. The samples are examined for breaking load strength using loading press ''ZD''- Germany.

3. Results and discusion

In the ceramic samples with nominal composition $LaAl_{11}O_{18}$ ($x=0$; $y=0$; $z=0$) are found the formation of two phases $LaAl_{11}O_{18}$ and $LaAlO_3$. Consequently without the introduction of additives it is not possible to achieve full synthesis at temperature 1500 °C, which is in agreement with the results published by other authors [1–3]. On the other hand, at the full replacing of lanthanum with calcium ($x=1$; $y=0$; $z=0$) are found out simultaneously the phases—one with structure similar to $LaAl_{11}O_{18}$ and α-Al_2O_3. It is established, that with the introduction of magnesium and titanium in the

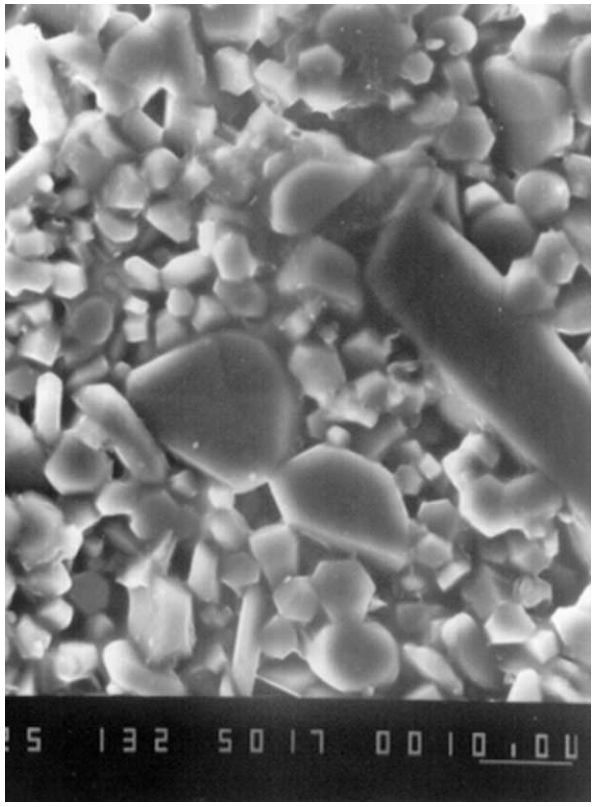

Fig. 2. Scanning electron micrographs of a $La_{0.75}Ca_{0.25}Al_{8.5}Mg_{1.0}$-$Ti_{1.5}O_{18}$ composition sintered at 1500 °C.

compositions, the content of the phase $LaAl_{11}O_{18}$ is increased. In ceramic samples, in which the contents of magnesium and titanium is constant ($y=1$; $z=1.5$) and content of calcium ($x=0.25$–0.75) is varied, a predominant phase of $LaAl_{11}O_{18}$ is established with traces of $LaAlO_3$. XRD analysis of ceramic material with nominal composition $La_{0,75}Ca_{0,25}Al_{8,5}Mg_{1,0}Ti_{1,5}O_{18}$,

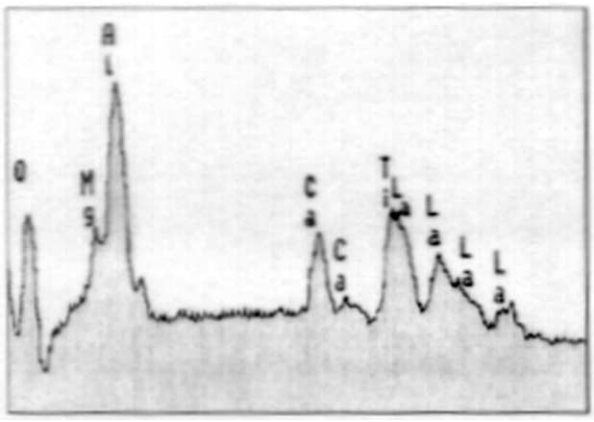

Fig. 3. X-ray microanalysis spectrum from the hexagonal phase.

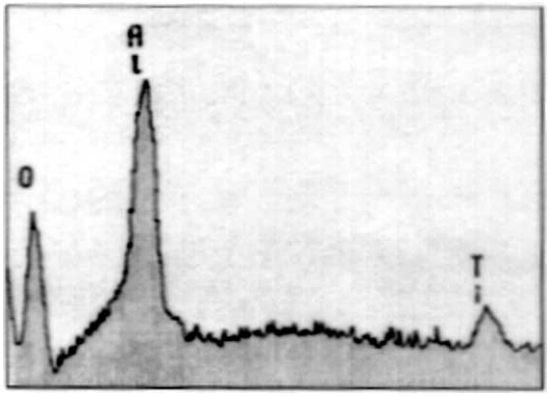

Fig. 4. X-ray microanalysis spectrum from the corundum phase.

Table 1
Properties of dense ceramics with nominal composition $La_{0.75}Ca_{0.25}Al_{8.5}Mg_{1.0}Ti_{1.5}O_{18}$

Properties	Ceramic sample with nominal composition $La_{0.75}Ca_{0.25}Al_{8.5}Mg_{1.0}Ti_{1.5}O_{18}$
Physic-mechanical	
Apparent density, g/cm^3	3.9
Water absorption, %	0
Bending strength, MPa	250
Breaking load strength, MPa	845
Micro-hardness, kg/mm^2	1100
Electric	
Dielectric constant, ε	13.7
Dielectric loss, $tg\delta$	$2–3\times10^{-3}$
Capacity, pF	$\approx$9
Breaking stress (100 V), GΩ	500–1500
Breakdown strength, kV/mm^2	$>$20

obtained by two-stage technology, shows that at 1500 °C is synthesized a single phase $LaAl_{11}O_{18}$ (Fig. 1). SEM of the same material shows that the predominant phase has hexagonal crystals with small amount of prismatic crystals of additive (Fig. 2) The X-ray microanalyses, recorded from the hexagonal crystals, show that they contained Al, Ca, La, Ti and Mg (Fig. 3). In the prismatic crystals is present an alumina phase, with a small amount Ti in solid solution (Fig. 4). The apparent density of the fired at 1500 °C samples with nominal composition $La_{0.75}Ca_{0.25}Al_{8.5}Mg_{1.0}Ti_{1.5}O_{18}$ are varied from 2.9 to 3.7 g/cm^3. With higher density are characterized compositions, in which is established predominant phase of lanthanum hexaaluminate, accommodating the elements Ca, Mg and Ti. The breaking load strength of the same samples varies in limits 670–840 MPa and shows the same tendency as the density. The properties of the ceramic sample obtained by two-stage technology are given in Table 1. It is posses very good mechanical strength and hardness and low dielectric loss.

4. Conclusion

By two-stage ceramic technology is obtained dense ceramic material with nominal composition $La_{0,75}Ca_{0,25}Al_{8.5}Mg_{1.0}Ti_{1.5}O_{18}$ at 1500 °C in which the predominant phase is with hexagonal structure.

By SEM is proved that obtained material consists of hexagonal crystals, and X-ray microanalysis spectra confirmed that this non-stoichiometric phase contains the elements La, Ca, Al, Mg and Ti.

The obtained ceramics possess high mechanical strength and hardness, low dielectric loss and may be find application for production of mill bodies and materials for immobilization of nuclear waste.

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