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Synthesis and conductivity of $Yb_2Ti_2O_7$ nanoceramics

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Abstract

The ordering processes in $Yb_2Ti_2O_7$ ceramics are studied by thermal analysis, IR spectroscopy, X-ray diffraction, SEM and electrical conductivity measurements. $Yb_2Ti_2O_7$ was obtained by a co-precipitation method followed by freeze drying and thermal annealing at 350–1670 °C. The existence of the fluorite–pyrochlore low-temperature transition near 800 °C and the pyrochlore–fluorite high-temperature transition near 1700 °C was established. The conductivity of $Yb_2Ti_2O_7$ sintered at 1670 °C seems to be ionic in the range of 300–950 °C, with a bulk activation energy of 0.81 eV. $Yb_2Ti_2O_7$ ceramics had a grain size of about 30 nm over a wide range of sintering temperatures (1400–1670 °C).

Keywords: Ytterbium titanate; Co-precipitation; Freeze drying; Pyrochlore; Fluorite; Order–disorder transformation; Nanocrystalline ceramics

1. Introduction

Disordered pyrochlore oxides $A_2B_2O_7$ find potential applications in solid oxide fuel cells [1], chemical sensors and electrochemical oxygen membranes [2]. The ionic conductivity in this type of materials usually is related with order–disorder (pyrochlore–fluorite) transformations [3,4].

At present the order–disorder transitions in $Gd_2Zr_2O_7$ ($T_{P\rightarrow F}$=1530 °C [5]), $Sm_2Zr_2O_7$ ($T_{P\rightarrow F}$=2000 °C [5]), $Nd_2Zr_2O_7$ ($T_{P\rightarrow F}$=2000 °C [5]), $Gd_2Hf_2O_7$ ($T_{P\rightarrow F}$=2400 °C [6]) are known. However, similar high-temperature pyrochlore–fluorite transformations were unknown for $Ln_2Ti_2O_7$. The experimental observation of similar transformations for a large number of pyrochlore $A_2B_2O_7$ is difficult as they occur at high temperatures. It is known, that the temperature of such order–disorder transitions may be lowered by doping with cations of different sizes or valence in the pyrochlore structure ($(Sc_zYb_{1-z})_2Ti_2O_7$ [4], $Gd(Zr_xTi_{1-x})_2O_7$ [3]) due to anti-site disorder Ln–Ti which leads to higher ionic conductivity.

Some reports about anti-site disorder in $Ln_2Ti_2O_7$ [7] and nearness of ionic radius ratios R_A^{3+}/R_B^{4+} for $Gd_2Zr_2O_7$ and $Yb_2Ti_2O_7$, as well as the high melting temperature of $Yb_2Ti_2O_7$ ~1860 °C allow us to hope to observe order–disorder transformation at 1500–1800 °C. Then the synthesis of a compound $Yb_2Ti_2O_7$ with disordering in the oxygen array is possible.

For $Gd_2Zr_2O_7$ it is known about existence of low temperature fluorite modification at 550–800 °C [8] and high temperature pyrochlore–fluorite transformation near 1530 °C. It was established ionic conductivity type of high temperature modification $Gd_2Zr_2O_7$. We observed also the

Table 1
Characteristics of the samples

Sample	Thermal processing scheme	Characteristic
No 1 $Yb_2Ti_2O_7$ (A)	740 °C-2 h+1400 °C-10 h	Light-yellow, transparent, density (92.5%)
No 2 $Yb_2Ti_2O_7$ (B)	740 °C-2 h+1670 °C-10 h	Pinkish, transparent, density (93%)

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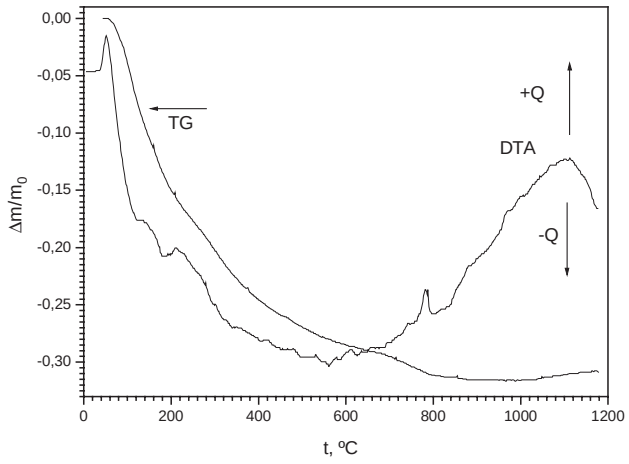

Fig. 1. DTA and TG data for freeze dried co-precipitation product Yb : Ti = 1 : 1.

existence of a low temperature fluorite phase for $Lu_2Ti_2O_7$ at 600–800 °C [9].

The main object of this article are searches of high temperature pyrochlore–fluorite phase transformation in the temperature interval 1400–1670 °C and low temperature fluorite modification for $Yb_2Ti_2O_7$ at 600–800 °C and effect of these transformations on the conductivity.

2. Experimental

Yb^{3+} and Ti^{4+} hydroxides were co-precipitated in the stoichiometric ratio $Yb^{3+}:Ti^{4+}=1:1$ from chloride solutions by adding ammonium hydroxide at pH = 11. Then they were separated from the solution by centrifuge and washed several times with distilled hot water to remove the chloride ions. The residues were frozen and freeze dried ($P=5\cdot10^{-2}$ mBar, $T=-30\rightarrow+30$ °C, $t=48$ h). Further heat treatment of as-obtained precursors was performed by isothermal annealing in air at 350, 650, 680, 740, 800, and 850 °C. Ceramic samples were prepared in two stages: annealing of the co-precipitation products at 740 °C, pressing them at 10 MPa into pellets and a second annealing at higher temperatures: 1400 and 1670 °C. Characteristics of all synthesized samples are presented in Table 1. The chemical composition of ceramics was checked by mass-spectrometry (EMAL 2). XRD analysis of the powder and ceramic samples was carried out using a DRON-3M automatic diffractometer with a copper tube (Cuk_α) operating at 35 kV and 28 mA. The diffraction data were collected in 2θ range from 15 to 45° counting for 3 s at each 0,1° 2θ step. Electric conductivity of ceramic samples between 300 and 1000 °C was tested by impedance spectroscopy with four wires/two electrodes setup, using a balance bridge Hewlett-Packard 4284A with a frequency range from 20 Hz to 1 MHz. For electrical measurements, ceramic specimens were Pt-coated on both sides with Engelhard 6926 Platinum ink and then fired at 1000 °C. Thermal analysis (TGA, DTA) was performed in air with a SETARAM TG-DTA-92 at a heating rate of 20°/min.

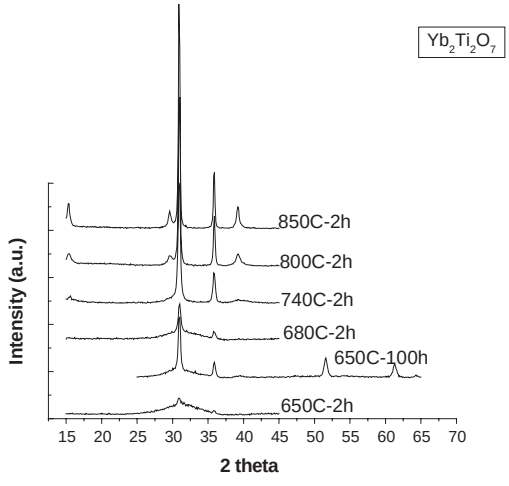

Fig. 2. X-ray diffraction patterns for freeze dried co-precipitation product annealed in the temperature range of 650–850 °C.

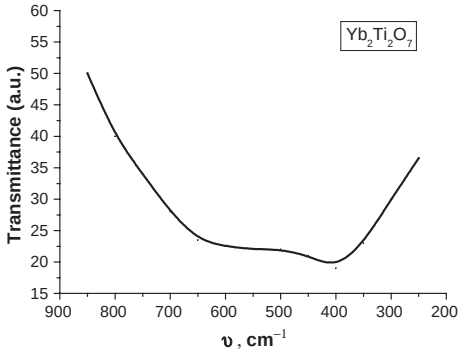

Fig. 3. IR absorption spectra of $Yb_2Ti_2O_7$ (650 °C-100 h).

3. Results and discussion

The thermal analysis data of freeze dried co-precipitation products with cation ratio Yb : Ti = 1 : 1 show a sharp exothermic maximum at 780 °C (Fig. 1). Mass loss took place up to 800 °C (Fig. 1). This process is related to water

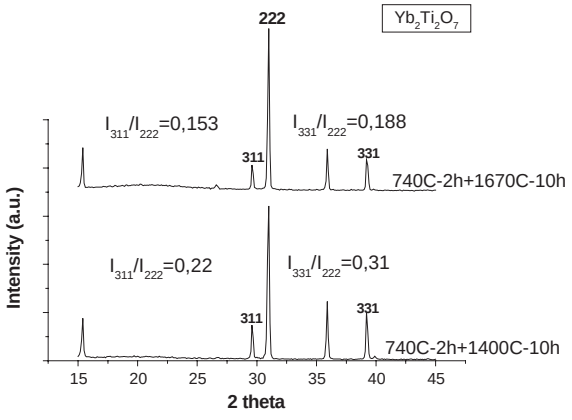

Fig. 4. XRD patterns for $Yb_2Ti_2O_7$, processed at 1400 and 1670 °C.