

Rare-earth zirconate pyrochlores $A_2Zr_2O_7$ ($A^{3+} = Nd, Sm, Pr, \text{ and } Er$) used as potential candidates for thermoelectric performance and for high temperature applications

Pirocloros de zirconato de tierras raras $A_2Zr_2O_7$ ($A^{3+} = Nd, Sm, Pr \text{ y } Er$) utilizados como posibles candidatos para el rendimiento termoeléctrico y para aplicaciones de alta temperatura

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Abstract

The increasing interest in ecological aspects related to the reduction of harmful emissions to the atmosphere and, at the same time, the need to achieve higher efficiencies of energy production are the driving forces that justify the current development of advanced ceramic materials for high temperature applications, namely those associated to energy and transportation industries. Ceramic matrix composites (CMCs), thermal barrier coatings (TBCs), environmental barrier coatings (EBCs) and solid oxide fuel cells (SOFCs) are increasingly used to work under the new demanding conditions. In this review, the recent progress and trends in the research and development of CMCs, TBCs, EBCs and SOFCs based on ceramic materials for high temperature applications are highlighted.

Solid-state reaction, Pyrochlore compounds, Crystal structure

Resumen

El creciente interés en aspectos ecológicos relacionados con la reducción de emisiones nocivas a la atmósfera y, al mismo tiempo, la necesidad de lograr mayores eficiencias en la producción de energía son las fuerzas motrices que justifican el desarrollo actual de materiales cerámicos avanzados para aplicaciones de alta temperatura, es decir, los asociados a las industrias de la energía y el transporte. Los compuestos de matriz cerámica (CMC), los recubrimientos de barrera térmica (TBC), los recubrimientos de barrera ambiental (EBC) y las pilas de combustible de óxido sólido (SOFC) se utilizan cada vez más para trabajar en las nuevas condiciones exigentes. El progreso y las tendencias recientes en la investigación y el desarrollo de CMC, TBC, EBC y se destacan las SOFC basadas en materiales cerámicos para aplicaciones de alta temperatura.

Reacción de estado sólido, Compuestos de pirocloro, Estructura cristalina

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Introduction

Nowadays, the development and use of ceramic materials for high temperature applications has two main driving forces in the worldwide context, which can be summarized in two concepts: ecology and energy. The first driving force is related to the conservation of the natural environment, minimizing the damage of the ozone layer through the reduction of emissions to the atmosphere. The second driving force is associated with economical benefits derived from the saving of energy, which at the same time, is also connected with the preservation of the current fossil fuel stocks.

The researchers have focused their efforts in achieving higher efficiencies of energy production in parallel with a marked decrease in harmful emissions, mainly in CO₂ and NO_x. This can be done, for instance, by increasing the operating temperature of engines and turbines combined with a reduction of the weight of their components. A higher operating temperature with little or no cooling air system will lead to superior thrust, less fuel consumption and reduced noxious emissions. Up to now, the materials employed in those applications were superalloys. However, the requirements to work under those new demanding conditions are over the limit of their capabilities, ceramic materials being excellent candidates to fulfill them.

They present good mechanical (strength, fracture toughness, creep, thermal shock resistance), tribological (erosion and wear resistance), chemical (oxidation and corrosion resistance), and physical properties (density, thermal conductivity, thermal expansion coefficient), which may be kept during long time at the service temperature. In this way, ceramic matrix composites (CMCs), thermal barrier coatings (TBCs) and environmental barrier coatings (EBCs) are increasingly used in high temperature applications in the energy and transportations industries.

Within this type of energy devices, solid oxide fuel cell (SOFCs), which are based on ceramic materials, are of great interest because their high operating temperatures (800 – 1000 °C) allow them to be powdered by hydrogen or light hydrocarbons, giving rise to almost clean energy production.

Numerous investigations are carried out the electrolyte the properties of their ceramic components, such as the ionic conductivity of the electrolyte or the chemical stability of the electrodes, in order to increase the efficiency of the device [M. Belmonte, 2006]. Recent studies performed by ionic bombardment on zirconate pyrochlores of general formula Ln₂Zr₂O₇ where Ln = lanthanide have shown a good resistance against radiation damage when compared with equivalent titanates [J. Lian, *et al.*, 2007].

The aim of this work is to structural and morphological properties study of rare-earth zirconate pyrochlores compounds A₂Zr₂O₇ (A³⁺ = Nd, Sm, Pr, and Er) synthesized by solid state reaction method. Towards the goal of a more directed and effective search for high-performance metal–oxide thermoelectric materials, we introduce this compounds that can be used potential candidates for thermoelectric performance and for high temperature applications.

Materials and Methods

Polycrystalline samples of the A₂Zr₂O₇ (A³⁺ = Nd, Pr, Sm, and Er) compounds were synthesized by solid-state reaction at ambient pressure in air. The starting materials were ZrO₂ (Riedel-de Haën pure), Nd₂O₃ (Aldrich, 99.9 %), Sm₂O₃ (Aldrich, 99.9 %), Pr₂O₃ (Cerac, 99.9 %), and Er₂O₃ (Aldrich, 99.9 %). Structure and purity of the starting materials were determined by XRD. The stoichiometric mixture of the starting materials was done in air during 30 minutes, grinded with an agate mortar, resulting in homogenous slurry.

The resultant A₂Zr₂O₇ mixture was compressed into pellets (13 mm diameter, 1.0-1.5 ± 0.05 mm thickness) by applying a pressure of 3 tons/cm² during 5 minutes under vacuum. The resulting compacted specimens were then sintered in air at 1400 °C during 3 days and then cooled down to room temperature following the natural cooling of furnace to 7 h. The thermal behaviors of A₂Zr₂O₇ compounds were studied from 25 to 1200 °C through differential thermal analysis (DTA), thermogravimetric analysis (TG) and differential thermal analysis using measuring equipment SDT Q600, TA instruments.

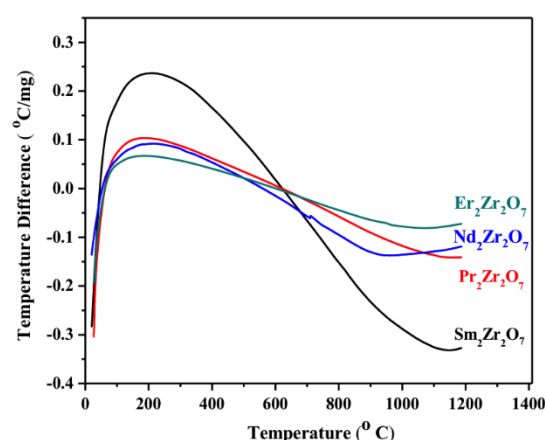
The powdered samples were characterized by X-ray powder diffraction (XRD) using an APD 2000 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a graphite monochromator. Diffraction patterns were collected at room temperature in air, over the 2θ range 10° - 90° with a step size of 0.025° and a time per step of 15 seconds. Changes in morphology and grain size were induced in the samples by performing different heat treatments during all the process of the samples preparation and examined by scanning electron microscopy (SEM) on a Hitachi S-3400N-II System. The 15.00 K.X micrographs were taken with a voltage of 15 kV, a current intensity of 1000 pA and WD = 4.5 mm. Energy Dispersive X-Ray (EDX) was performed on the same SEM system, which is equipped with an EDAX 9900 device.

Results and Discussions

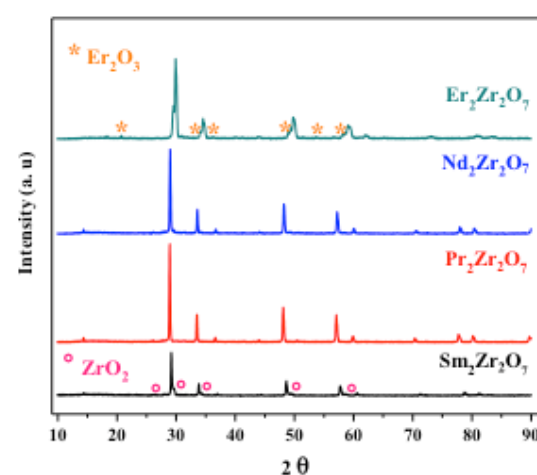
The DTA curves for $A_2Zr_2O_7$ compounds, with $A^{3+} = \text{Er, Nd, Sm, and Pr}$ are presented in Graphic 1. All the samples present a first endothermic effect at around 100°C , it is associated with a minimal loss of weight. The exothermic effect observed between 200°C and 700°C , together with the loss of weight in the same temperature range, could be attributed to the oxidation of the compounds. For temperatures higher than 700°C , endothermic effects are observed that are important to understand the stability in the solid solution formation mechanism as its thermal stability, except for the $\text{Sm}_2\text{Zr}_2\text{O}_7$ compound that reaches its formation stage more quickly than others compounds (Ciomaga-Hatnean *et al.*, 2015), (Rodríguez-Carvajal *et al.*, 1993), (Matsuhira *et al.*, 2009), (Ciomaga Hatnean *et al.*, 2014), (Koochpayeh *et al.*, 2014), (Ferro, 2011), (Raghuvanshi *et al.*, 2013), (Surble *et al.*, 2010), (Zhang *et al.*, 2008), (Shannon, 1976).

Graphic 2 presents the X-ray diffraction patterns of the sintered $\text{Er}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$, $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ compounds. Pyrochlores $A_2Zr_2O_7$, with $A^{3+} = \text{Nd, Sm, and Pr}$ have a cubic polycrystalline structure with $\text{Fd}\bar{3}\text{m}$ (No. 227) spatial group and hexagonal rhombus with R-3 (No. 148) spatial group for $\text{Er}_2\text{Zr}_2\text{O}_7$. In addition, we can see that there is a peaks shift small of the $\text{Er}_2\text{Zr}_2\text{O}_7$ compound with respect to the peaks of the $\text{Nd}_2\text{Zr}_2\text{O}_7$, $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ compounds.

This is because the ionic radius of $\text{Er}^{3+} = 0.890 \text{ \AA}$ is smaller than the radii ionic $\text{Nd}^{3+} = 0.983 \text{ \AA}$, $\text{Pr}^{3+} = 0.99 \text{ \AA}$ and $\text{Sm}^{3+} = 0.958 \text{ \AA}$ (Shannon, 1976) and also has a structural change. For the $\text{Er}_2\text{Zr}_2\text{O}_7$ sample, it detected two phases that are identified as $\text{Er}_2\text{Zr}_2\text{O}_7$ and Er_2O_3 compounds. The solid line corresponds to a hexagonal rhombus phase with $\text{Fd}\bar{3}\text{m}$ (No. 227) space group and it is identified as $\text{Er}_2\text{Zr}_2\text{O}_7$ compound with PDF (01-071-1024). The phase marked with an asterisk (*) corresponds to the Er_2O_3 compound, PDF (03-065-3175). The presence of this very small amount of Er_2O_3 compound indicated that occur an overload of the reagent in the compound.



Graphic 1 Differential thermal analysis curves of pyrochlores $\text{Nd}_2\text{Zr}_2\text{O}_7$, $\text{Sm}_2\text{Zr}_2\text{O}_7$, $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Er}_2\text{Zr}_2\text{O}_7$ compounds



Graphic 2 XRD Patterns evolution of pyrochlores $A_2Zr_2O_7$ compounds, with $A^{3+} = \text{Nd, Sm, Pr, and Er}$

We performed an EDX analysis on all samples to verify the chemical composition. The results are present in Table I. The error range of the analysis is between 1 and 6wt% (Beaman, 1972); therefore it can be said that the experimental and theoretical atomic percentages of the elements resemble each other.

Figure 1 shows the SEM image of the $Nd_2Zr_2O_7$, $Sm_2Zr_2O_7$, and $Pr_2Zr_2O_7$ samples. The image shows the effect of heat treatments and processing route on the grain morphology of the compounds. Considerable variations in sizes, very few phases and shapes of polycrystals can be observed from the micrograph.

Elements					
Compounds	Nd	Pr	Sm	Zr	O
$Nd_2Zr_2O_7$	52.55			24.35	23.11
$Pr_2Zr_2O_7$		50.26		29.35	20.39
$Sm_2Zr_2O_7$			53.05	24.30	22.66
$Nd_2Zr_2O_7$	52.55			24.35	23.11

Table 1 EDX analysis of the $A_2Zr_2O_7$ (A= Nd, Pr, and Sm) Compounds

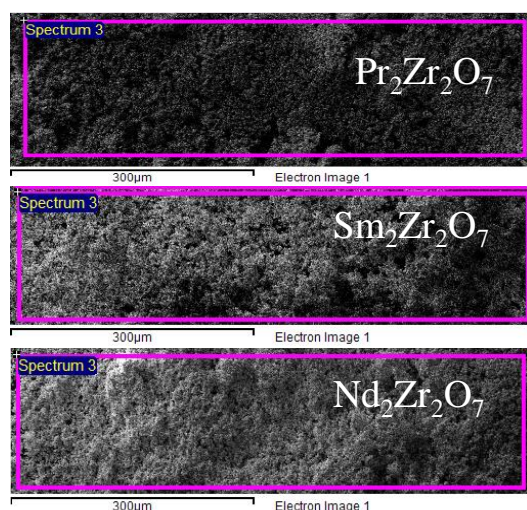


Figure 3 EDX of the $Nd_2Zr_2O_7$, $Sm_2Zr_2O_7$, and $Pr_2Zr_2O_7$ compounds

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Conclusion

In this work, we obtained polycrystalline compounds of $Nd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $Pr_2Zr_2O_7$, and $Er_2Zr_2O_7$ by solid-state reaction method in air at atmospheric pressure. The crystal structure of the compounds and final product $A_2B_2O_7$ is a mixed, were determined by X-ray powder diffraction and Scanning electron microscopy. SEM micrographs shows the effect of heat treatments and processing route on the grain morphology of the compounds.

Perspectives

As future considerations, we can expand the determination of the thermoelectric, electrical properties and the calculation of the Seebeck coefficient. This has attracted a renewed interest as a fundamental technology for environmentally friendly energy conversion. In particular, thermoelectric power generation has been now considered as a possible renewable energy resource.

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