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Structural and thermoelectric properties of the $Pr_2Zr_2O_7$ compound

Propiedades estructurales y termoeléctricas del compuesto $Pr_2Zr_2O_7$

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Abstract

In this research, it is presented a detailed study of the structural and thermoelectric properties of the pyrochlore zirconium $Pr_2Zr_2O_7$ compound prepared by solid-state reaction (SSR) in air at ambient pressure. The synthesized sample was characterized using powder X-ray diffraction. The thermal stability of the thermoelectric compound (TE) $Pr_2Zr_2O_7$ was tested by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Scanning electron microscopy shows that the crystal size varies between 0.69 and 2.81μm. Electrical conductivity (σ) of the sample calcined at 1400 °C presented values increase irregularly with the increasing temperature from 0.001 to 0.018 S cm^{-1} as expected in a semiconductor material. The thermal conductivity is lower than 0.44 - 775 W m^{-1} K^{-1} which is quite anomalous in comparison with the thermal conductivity of other oxides.

Solid-state reaction, Pyrochlore compounds, Crystal structure

Resumen

En esta investigación, se presenta un estudio detallado de las propiedades estructurales y termoeléctricas del compuesto pirocloro de circonio $Pr_2Zr_2O_7$ preparado por reacción en estado sólido (SSR) en aire a presión ambiente. La muestra sintetizada se caracterizó utilizando difracción de rayos-X en polvo. La estabilidad térmica del compuesto termoeléctrico (TE) $Pr_2Zr_2O_7$ se probaron mediante análisis termogravimetrico (TGA) y análisis térmico diferencial (DTA). Microscopía electrónica de barrido muestra que el tamaño del cristal varía entre 0.69 y 2.81μm. La conductividad eléctrica (σ) de la muestra calcinada a 1400 ° C presentó valores que aumentan irregularmente con el aumento de la temperatura de 0.001 a 0.018 Scm^{-1} como se esperaba en un material semiconductor. La conductividad térmica es inferior a 0.44 - 775 W m^{-1} K^{-1} , lo cual es bastante anómalo en comparación con la conductividad térmica de otros óxidos.

Reacción en estado sólido, Compuestos de pirocloro, Estructura cristalina

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Introduction

Thermoelectric devices are a technology that converts waste heat into electric power or vice versa through the thermoelectric phenomena in semiconductor solids [1]. Since this technology is a direct energy conversion in solids, it 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 source. The thermoelectric materials comprises from semimetals, semiconductors, ceramics to polymers. However, thermoelectric oxide materials have been extensively investigated as a promising thermoelectric power generator because they are stable at high temperatures in air. Oxides were considered to be poor thermoelectric materials, but after the discovery of a large thermoelectric power factor in Na_xCoO_2, some cobalt oxides are recognized as good p-type thermoelectric oxides [2,3]. In contrast, not yet discovered is an n-type counterpart to the cobalt oxides. Some of the transparent conductors such as ZnO and In_2O_3 show indeed good thermoelectric performance above 1000 K, [4,5] but the lattice thermal conductivity is much higher than the conventional thermoelectric materials. The doped titanates [6,7] and niobates [8-10] are fairly good n-type thermoelectric materials at room temperature, but they are easily oxidized at high temperature to lose conductivity in air. Recently, a large Seebeck coefficient and low thermal conductivity have been reported in polycrystalline samples of the double perovskite ruthenate Sr_2LRuO_6 (L; rare-earth) [11]. Although the magnetic properties and ground states of the titanate pyrochlores have been investigated in detail, similar studies of the zirconate pyrochlores have been hampered by the lack of large, good quality single crystals. With the exception of a few investigations on $Pr_2Zr_2O_7$ single crystals [12-14], most of the research on the zirconate pyrochlores has used powder samples [15-22].

The aim of this investigation was to synthe- size the polycrystaline $Pr_2Zr_2O_7$ compound via the solid-state reaction method and a detailed study of the precise time for obtaining the compound. In the present contribution, we report the relationship between structural, Seebeck Coefficient, electrical conductuvity and termal conductivity properties of the pirochlore $Pr_2Zr_2O_7$.

These properties make rare-earth zirconates suitable for a variety of applications such as solid electrolytes, catalysts, nuclear waste forms, and especially high-temperature TBCs (Thermal barrier coatings) materials [23].

Materials and Methods

Polycrystalline sample of the $Pr_2Zr_2O_7$ compound was synthesized by solid-state reaction at ambient pressure in air. The starting materials were ZrO_2 (Riedel-de Haën pure), and Pr_2O_3 (Cerac, 99.9 %). Structure and purity of the materials were determined by XDR. The stoichiometric mixture of the starting materials was done in air during 30 minutes, agrided with an agata mortar, resulting in homogenous slurry [24].

The resultant $Pr_2Zr_2O_7$ mixture was compressed into pellets (13 mm diameter, 1.0-1.5 ± 0.05 mm thickness) by applying a pressure of 3 tons/cm^2 during 5 minutes under vacuum. The resulting compacted specimens were then sintered in air at 1400 ℃ during 3 days and then cooled down to room temperature following the natural cooling of furnace to 7 h.

The thermal behavior of $Pr_2Zr_2O_7$ compound was studied from 25 to 1200 ℃ through differential thermal analysis (DTA), and thermogravimetric analysis (TGA) using measuring equipment SDT Q600, TA Instruments. Sample was characterized by X-ray powder diffraction (XRD) using an APD 2000 diffractometer with Cu Kα radiation (λ = 1.5406 $\dot{A}$) and a graphite monocromator.

Diffraction patterns were collected at room temperature in air, over the 2θ range 10^o – 90^o with a step size of 0.025^o and a time per step of 15 seconds. Changes in morphology and grain size were induced in the sample by performing different heat treatments during all the process of the sample preparation and examined by scanning electron microscopy (SEM) on a Hitachi S-3400N-II System.

The 10.00 K.X micrograph was taken with a voltage of 20 kV, a current intensity of 1000 pA and WD = 10 mm. Energy Dispersive X-Ray (EDX) was performed on the same SEM system, which is equipped with an EDAX 9900 device.

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For thermoelectric characterization, square-shaped compact of dimension 10 mm x 10 mm x 0.5 mm was prepared using a 3-ton hydraulic press, Seebeck coefficient and electric conductivity were measured simultaneously under a 10 sscm N_2 flux, from 100 to 800 ℃ in a high- precision SBA 458 Nemesis Netzsch system imposing a 0.05 A current; the heater voltage for Seebeck measurements was 1.0 V, the temperature increment was 5 Ks^{-1}, and the temperature difference threshold is 15 K. The thermal conductivity was measured in a LFA 467 HyperFlash Netzsch apparatus equipped with a xenon flash lamp and an InSb detector, in the temperature range from 100 to 600 ℃, with pulsed energy up to 10 J/pulse and pulse width of 20–1200 μs.

Results and Discussions

Thermogravimetric Analysis (TGA). The TGA curves are important to determine the temperatures to which the formation of organic matter and subproducts take place during the solid-state reaction method. The results obtained from this technique did help to control the process parameters to produce the $Pr_2Zr_2O_7$ compound. The TGA results obtained from the $Pr_2Zr_2O_7$ were analyzed separately and are shown in Figure 1. The TGA (a) curve is divided in three most relevant regions: 25-350 ℃, 350–700 ℃, and 700-1200 ℃. In the next ascend TGA curve start with a hydrated material at room temperature up to 350 ℃. After 350 ℃ an increase in curve means, the formation of $Pr_2Zr_2O_7$ compound (seen in some reaction conditions by XRD). Around 700 ℃ it is detected a weak lost of energy peak that may be due to the melting of reagents, binary and ternary compounds corroborated by XRD.

The DTA (b) curve for $Pr_2Zr_2O_7$ compound is presented in Figure 1. The sample present a first exothermic effect around 300 ℃, which is unusual; it means that the strcuture that is obtained between 300 and 1200 ℃ is metaestable and the DTA exotherm signs a decrease in enthalpy of the sample and therefore a change to a more stable structure. For temperatures higher than 1200 ℃, exothermic effects are observed that are important to understand the stability in the solid solution formation mechanism as its thermal stability.

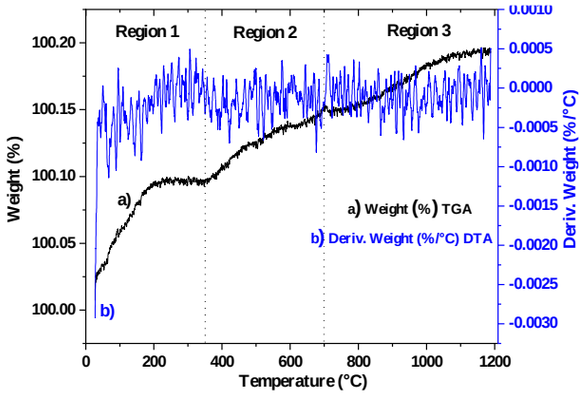

Figure 1 TGA and DTA of the $Pr_2Zr_2O_7$ sample

Figure 2 presents the X-ray diffraction pattern of the sintered $Pr_2Zr_2O_7$ compound. The combination of the XRD and TGA analysis proved to be useful when observing the number of phases that changed during the applied heat treatments to $Pr_2Zr_2O_7$ sample. The solid line corresponds to a cubic polycrystalline phase with $Fd\bar{3}m$ (No. 227) space group and it is identified as $Pr_2Zr_2O_7$ compound with PDF (04-008-6354).

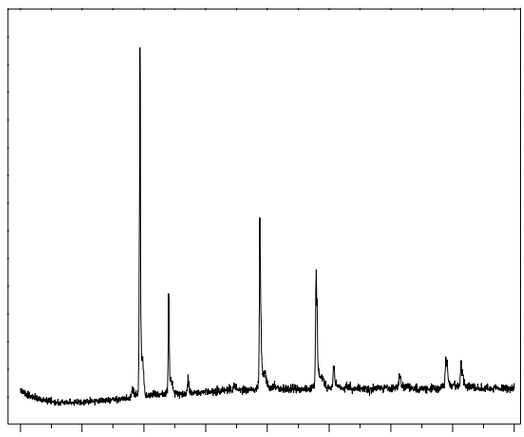

Figure 2 XRD Pattern evolution of pyrochlore $Pr_2Zr_2O_7$ compound

The EDX elemental analysis of the $Pr_2Zr_2O_7$ compound is shown in Figure 3. The atomic percentage for the Pr, Zr and O was 54.14%, 28.11% and 19.75%, respectively.

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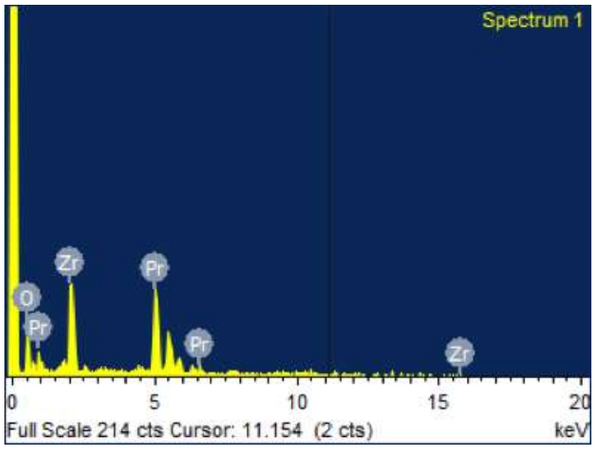

Figure 3 Spectrum of EDX analysis for the $Pr_2Zr_2O_7$ compound after applying the heat treatment at 1400 ^{o} C during 3 days

Figure 4 shows the elemental SEM mapping performed to the produced $Pr_2Zr_2O_7$ compound. This analysis confirmed the homogeneous distributions of the $Pr_2Zr_2O_7$ compound in the sample. The sample calcined at 1400 ℃ shows the formation of different particle sizes between 0.69 and 2.81 μm, and some of them present a well-defined grain boundary, while the rest are agglomerations.

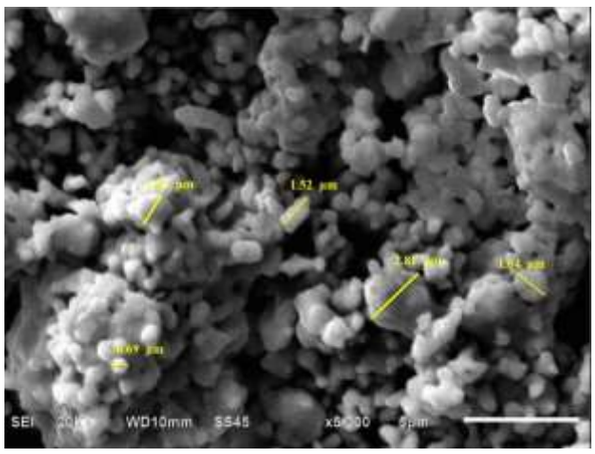

Figure 4 SEM for the $Pr_2Zr_2O_7$ compound

Electrical conductivity (σ) of the sample calcined at 1400 ℃ is presented in Figure 5. Sample calcined at 1400 °C show a electrical conductivity low. The σ values increase irregularly with the increasing temperature from 0.001 to 0.018 Scm^{-1} as expected in a semiconductor material [25].

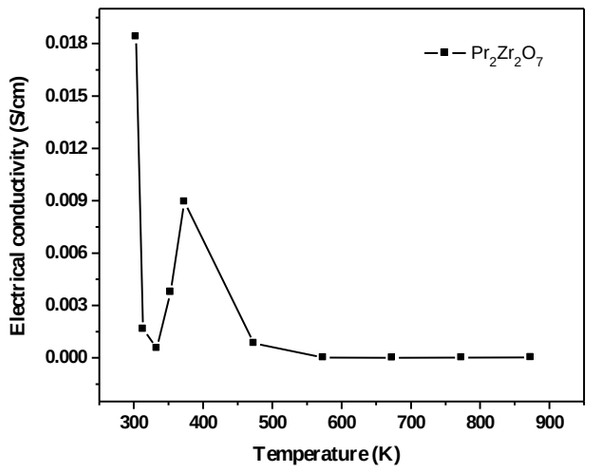

Figure 5 Temperature dependence of electrical conductivity for $Pr_2Zr_2O_7$ sample obtained at 1400 ℃

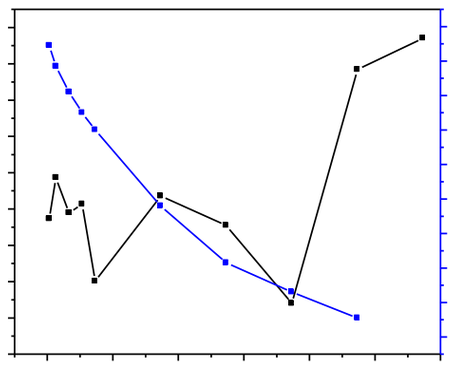

Figure 6 Seebeck coefficient and thermal conductivity in the temperature range 300–900 °K

Seebeck coefficient and thermal conductivity measured as a function of temperature are presented in Figure 6. The Fig. 6 (a) show S values, ranging from -0.00025 to 0.0005 μVK^{-1}, are positive and negative over the temperature range confirming the semiconductor p and n-character, where the holes and electrons are the main charge carriers. The p-character in $Pr_2Zr_2O_7$ has been attributed to the deviation from stoichiometric composition and ionized and / or interstitial oxygens generate positive holes [26-28].

The sign for the sample is negative, and the magnitude systematically decreases with increasing temperature. These results show that the Pr^{+3} ion acts as a donor to supply electrons to the system. The calculated thermal conductivity of Pr2 Zr2O7 ceramic as a function of temperature are plotted in Fig. 6 (b). The thermal conductivity of Pr2Zr2O7 ceramic gradually decrease with the increase of temperature up to 800^{o} C, which is attributed to the lattice thermal conduction.

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Conclusion

In this work, was obtained polycrystalline $Pr_2Zr_2O_7$ compound by solid-state reaction method in air at atmospheric pressure. SEM micrograph shows the effect of heat treatments and processing route on the grain morphology of the compound. The σ values increase irregularly with the increasing temperature from 0.001 to 0.018 Scm^{-1} as expected in a semiconductor material.

Perspectives

As future considerations, with the result of the measurements obtained in this study we have as future research to improve the electrical conductivity property of our new compounds using small quantities of Sr^{+2} doping and to decrease the thermal conductivity, which will help us obtain a zirconium pyrochloro with better thermoelectric properties for applications in solid electrolytes, catalysts, nuclear waste forms, and especially high-temperature TBC materials.

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