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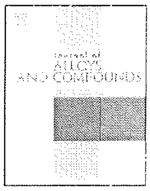

Synthesis and thermal behavior of $La_{9.33}Si_2Ge_4O_{26}$ apatite for SOFCs

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ABSTRACT

Powders of La_2O_3, GeO_2 and SiO_2 were dry milled in a planetary ball mill with different rotation speeds (150–350 rpm) and increasing milling times up to 35 h in order to obtain the $La_{9.33}Si_2Ge_4O_{26}$ apatite phase at room temperature. The results showed that the higher the rotation speed the lower the time required for the formation of the apatite phase. No reaction between the starting powders was observed at 150 rpm. Thermal analysis of the unreacted powders milled at 150 rpm showed formation of the apatite phase around 800 °C, with enthalpies ranging from 43.5 and 48.6 kJ mol^{-1}. An activation energy E_a of 65 kJ mol^{-1} was obtained applying the Kissinger equation. The mean Avrami exponent n calculated was 1.5, indicating that the apatite phase transformation occurs by a diffusion controlled process.

1. Introduction

Solid oxide fuel cells (SOFCs), based on an oxide ion-conducting electrolyte, offer a versatile, efficient, clean and environmental friendly technology to electrochemically generate electricity. Moreover, SOFCs provide some advantages over traditional energy conversion systems, namely fuel adaptability, reliability, modularity and durability [1]. Current commercially available SOFCs operate at temperatures higher than 800 °C, demanding materials and components able to withstand such severe conditions. Accordingly, intensive research work has been carried out in the last years with the aim of decreasing the service temperature and therefore increasing the durability and lowering the cost of materials and components [2]. One way to achieve this goal is to develop new electrolyte materials with higher ionic conductivity at temperatures in the range 500–700 °C, for intermediate temperature solid oxide fuel cells (IT-SOFCs). Amongst the potential materials suitable for such application are apatite-type rare earth based oxides, such as R-doped lanthanum oxides of general formula $La_{9.33}(RO_4)_6O_2$ with R = Ge, Si, which exhibit high ionic conductivity and low activation energy at moderate temperatures, when compared to the yttria-stabilized zirconia (YSZ) electrolyte commonly used [3,4]. These materials are currently produced by solid-state reaction methods [5]. Several problems in processing such apatite materials include the high temperature required, poor control of morphology, grain growth [6,7] and germanium volatilization (which is significant above 1250 °C) [8,9].

Mechanical alloying (MA) [10] is a potential alternative processing method to obtain the apatite like lanthanum oxide [3,11]. During the MA process, heavy deformation is introduced into the particles, increasing the defect density, which accelerates the diffusion process by decreasing the diffusion distances. Therefore, sintering is achieved at lower temperatures than the ones required by conventional routes.

In previous works, Si- and Ge-doped lanthanum oxide materials with apatite-type phase were produced by MA and subsequent annealing [12,13]. A dependence of apatite-type phase formation on the MA parameters was shown, the higher the MA rotation speed and/or processing time, the lower the annealing temperature required for its formation. In the present work, the influence of the milling atmosphere as well as of the particle size distribution of the raw materials on the structural evolution of powders during MA has been studied. The thermal behavior of the mechanically alloyed mixtures was studied by means of differential scanning calorimetry (DSC).

2. Experimental

Powders of crystalline La_2O_3 (99.9% purity), SiO_2 (quartz with 99.4% purity) and GeO_2 (99.9% purity), were used as starting materials. Mixtures with $7La_2O_3$:$3SiO_2$:$6GeO_2$ molar ratios were used in order to obtain the $La_{9.33}Si_2Ge_4O_{26}$ phase. The blends were dry milled in a Fritsch planetary ball mill using a 250 ml hardened steel vial and 15 balls with 20 mm diameter of the same material. About 24.5 g of the powder blend was loaded into the vial as to get a ball-to-powder weight ratio of 20:1. Some of the experiments were carried out under protective atmosphere (Ar at 2 bar), the remaining being performed under atmospheric air. The powders

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