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Microstructure, electrical and humidity sensing properties of light rare earths zirconates

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ABSTRACT

Light rare earths zirconates $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Eu, and Gd) from preparation to sensor application are analyzed. The materials were produced by liquid route and dried through three calcinations processes. XRD and SEM investigations were used to certify the composition and microstructure. The electrical investigation on different humidity conditions was performed at different frequency in order to highlight rare earths zirconates compositions suitable for sensor applications. Humidity sensors with light rare earths zirconates as active elements were investigated, obtaining high sensitivities, short response and recovery times, especially for zirconates materials with *Ln* elements based on right side of light rare earths group. The correlation between sensors characteristics and active material properties are also investigated. Due their high chemical and physical stability, humidity sensors based on light rare earths zirconates compositions are useful for monitoring corrosive environments.

1. Introduction

Minerals with the pyrochlore structure, are usually oxides with the general formula (Na, Ca)(Nb, Ta)O_6F-nH_2O. They are a well-known source of tantalum and niobium, and some old specimens also contain thorium or uranium [1]. The synthetic counterparts may accommodate a very broad spectrum of tri- and tetravalent cations in the $A_2B_2O_7$ structure [2]. The crystal structure of the pyrochlores may be easily described as a fluorite-type structure with a double unit cell and an ordered deficiency of 1/8 of the oxygen atoms (*Fd*–3*m* S.G., $Z = 8$). The A-site is generally occupied by large trivalent cations eightfold coordinated (a = 9–12 Å), while the B-one is filled by smaller tetravalent cations (*e.g.* Ti, Zr, Hf) and surrounded by six oxygen atoms in a distorted octahedron [3].

The structural features, synthesis procedures and practical applications of the pyrochlores are described and largely discussed in a comprehensive, although not recent review [4]. Thus, due to their resistance to corrosion and chemical alteration, pyrochlore zirconates ($Ln_2Zr_2O_7$) have been proposed as waste forms for nuclear waste disposal; [2] zirconates shows a good resistance against radiation damage when compared to equivalent hafniates/titanates [5]. Zirconates became also very attractive for high temperature applications, such as thermal coating [6]. Moreover, they exhibit other interesting physical properties such as photocatalyst, ionic conductivity, thermophysical and have been proposed as a candidate for high temperature solid-oxide fuel cells [7]. By the other hand, the versatility of rare earths makes them suitable for ultrafast switching devices [8,9], for sensor application in various compounds [10,11] etc.

As part of this general picture, we investigate here the electrical properties of $Ln_2Zr_2O_7$ zirconates of light rare earths elements (Ln = La, Nd, Sm, Eu, and Gd) under humidity influence in order to identify optimal composition and preparation for sensor applications [12–16], especially for the corrosive environments that demand high chemical and physical stability of active sensor materials [17], sensors features that can be borrowed from the zirconates compound. In subsequent sections are presented, from preparation to application, the microstructural, electrical and humidity sensing characteristics of light rare earths zirconates.

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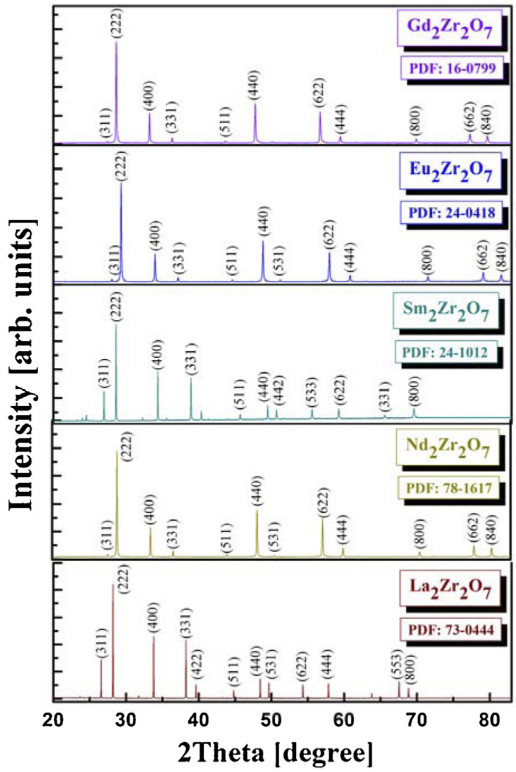

Fig. 1. XRD patterns of light rare earths zirconates $Ln_2Zr_2O_7$.

2. Materials preparation and microstructure characterization

There are a variety of methods for preparing zirconate material a through solid state reaction [18], complex-precipitation in aqueous media [19], sol-gel [20], easy-calcination sedimentation [7] etc. In our investigations, $Ln_2Zr_2O_7$ zirconates of light rare earths elements (*Ln* = La, Nd, Sm, Eu, and Gd) were produced by liquid route. Thus, first nitrate solutions of Ln_2O_3 (Alfa Aaesar, purity 99.95% or higher) and zirconyl-oxinitrate $ZrO(NO_3)_2 \cdot nH_2O$ (Fluka, 99.99% trace metal basis) have been prepared and their concentration determined by gravimetry. Then, the appropriate volumes of these solutions were mixed and slowly dried. The residue was calcinated in alumina crucibles under air at 900 °C (12 h), 1200 °C (12 h), and 1400 °C (72 h) with intermediate grindings, in order to end up with pure lanthanide zirconates with pyrochlore structure.

The samples composition was investigated by X-ray diffraction at room temperature using CuKα radiation (λ = 1.5405 Å) with 3 °/min scanning speed. The X-ray diffraction XRD patterns, as can be seen in Fig. 1, reveal that the samples are pyrochlore phase and belong to the zirconates ($Ln_2Zr_2O_7$) group; similar results being reported [21–31].

For humidity sensors applications perspective, some compounds characteristics are relevant, such as: porosity, shape and grain size, specific surface area etc [15,32]. In order to determine the shape and size of grains, the Scanning Electron Microscopy (SEM) investigations were performed. The investigations were carried out at room temperature by using a SEM Vega Tescan device. SEM micrographs of light rare earths zirconates $Ln_2Zr_2O_7$ highlight the influence of the *Ln* element (La, Nd, Sm, Eu or Gd) on to crystallite shape and size.

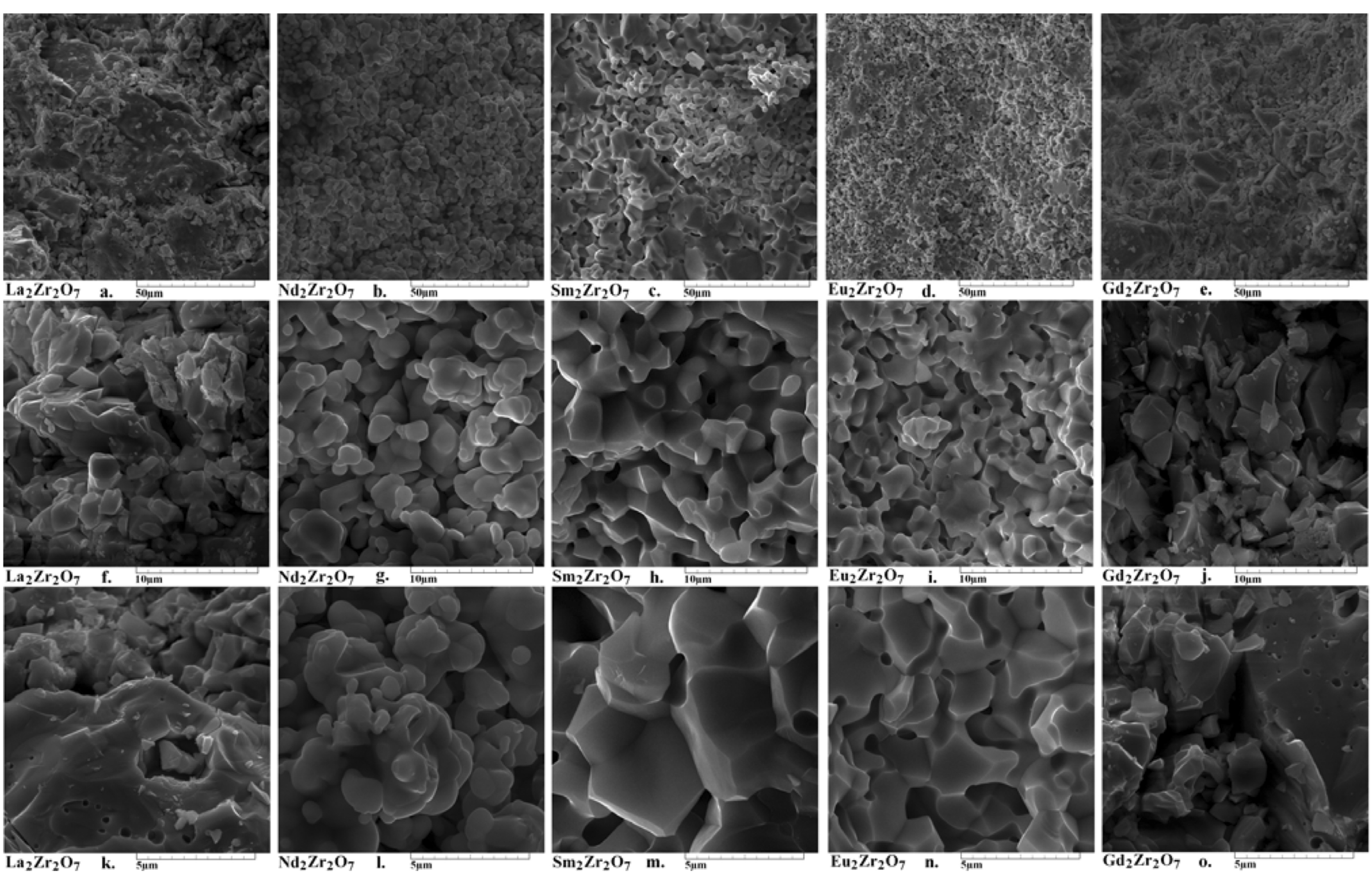

Fig. 2. SEM microstructures of light rare earths zirconates $Ln_2Zr_2O_7$ (*Ln* = La, Nd, Sm, Eu, and Gd).