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Effect of heat treatment on the generation of structural defects in $LaTaO_4$ ceramics and their correlation with photoluminescent properties

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ABSTRACT

The synthesis, structure characterization, as well as luminescence properties of $LaTaO_4$ ceramics were investigated in this study. The materials were prepared through the Pechini method. The characterization techniques, including the X-ray diffraction (XRD) as well as the scanning electron microscopy (SEM) were used to analyze the structure and microstructure, respectively. Details of emissions as a result of the type V_O^{*} (or V_O^{**}) defects were determined using photoluminescence (PL) measurements.

1. Introduction

Doped and undoped rare-earth niobates and tantalates (RE-Nb/Ta) have a unique array of characteristics that include chemical and electrochemical stability, photo-electronic activity [1–5], ion conductivity [6–9] and luminescence [10–19].

The lutetium tantalate $LuTaO_4$, as well as gadolinium $GdTaO_4$ and all the tantalates of the series of lanthanides crystallize in the monoclinic form, besides their ability to possess two types of structure. The first belongs to the space group I2/a, known as the M-type structure or fergusonite. The second belongs to the space group P2/a, called the M'-type structure. In both cases the site of Ln^{3+} cation is a distorted square anti-prism (coordination number CN = 8), of point symmetry C2. In the M'-type structure, the site is occupied by a tantalum distorted octahedron (with coordination number CN = 6), in which four bonds (Ta–O) are smaller and two larger ones. In the M-type structure, the tantalum site is found to be a distorted tetrahedron (CN = 4). It can be observed that there is a crystallization tendency of $LnTaO_4$ in the M'-type structure at low temperature [12–20].

Tantalates can be prepared by different techniques. The synthesis of these materials by the mixture of oxides (solid state method) is relatively direct, though it is limited as a result of the fact that it produces low purity materials, large particles with wide size distribution and does not also allow the control of stoichiometry. In contrast, the synthesis using wet chemical routes allows the control of the particles size, including nanometric ones.

Among the wet chemical routes, the synthesis from alcohoxide metals produces very small particles in the order of 5–100 nm with a narrow range of particles size distribution and well-defined stoichiometry. However, this method has some disadvantages, which include expensive raw materials and long processing time. The polymeric precursor method, known as the Pechini method, produces a polyester matrix through which ceramic powders or thin films can be produced by thermal pyrolysis. This method is used to synthesize particles in the nanometric or micrometric range with good control of impurities, relatively fast processing times and low cost.

The purpose of the present work is to investigate the thermal treatment conditions in order to obtain crystalline $LaTaO_4$ by the Pechini method and to analyze the dependence of the structure as well as the luminescence properties with the temperature of phase formation.

2. Material and methods

The synthesis of $LaTaO_4$ was carried out by the Polymeric Precursor Method [21], similar to that described by Gasparotto et al. [22]. Lanthanum oxide and tantalum (V) ethoxide were used as starting materials. Ethylene glycol and citric acid were used as polymerization/complexation agents in the synthesis of citrate solutions for each cation. After homogenization, the solution containing La and Ta citrates were kept under continuous heating at 80–90 °C. These solutions became more viscous without any visible phase separation. Afterwards, the polyester resin was thermally treated at 200, 380 and 450 °C for 2 h to pave way for the polymer pyrolysis. The resulting porous material was easily deagglomerated in a mortar and annealing was carried out at 700, 900 and 1100 °C/3 h. The X-ray diffraction data (XRD) were collected using a RIGAKU® RINT2000 rotating anode diffractometer with Cu Ka radiation monochromatized by a curved graphite crystal, with the 2θ interval lying between

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20 and 100°, with a scanning rate of 0.02°/0.3 s. The photoluminescence (PL) measurements were carried out using spectroscopic excitation and emission from the solid powder samples. We used a Fluorolog Spex F212L spectrofluorimeter in the front face mode, with a 450 W xenon lamp as the light source and a water cooling photomultiplier Hamamatsu R298.

3. Results and discussion

The X-ray diffraction pattern of $LaTaO_4$ powders at 700, 900, and 1100 °C is shown in Fig. 1. At 700 °C, pure $LaTaO_4$ was still found to be non-crystalline. In addition, the compounds obtained from 900 °C onwards were observed to be in crystalline form, which are close to the data from Joint Committee on Powder Diffraction Standards (JCPDS) card no. 74-769. No peak of any other phases was detected, indicating that the sample has a high purity and the long range order. At 1100 °C, $LaTaO_4$ exhibits peaks associated to different polymorphic types: a major contribution of M'-$LaTaO_4$ and peaks associated to M-$LaTaO_4$ [12–20].

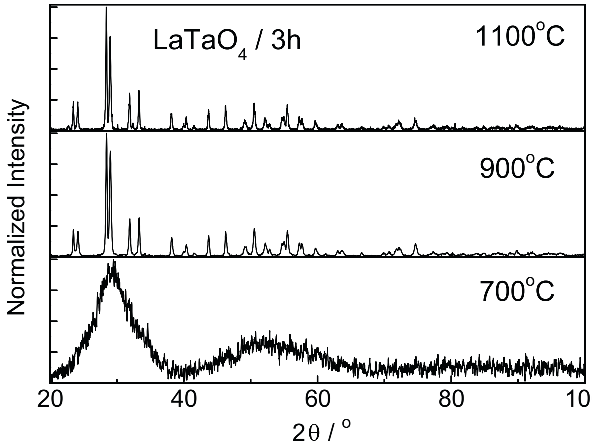


Fig. 1. XRD pattern of $LaTaO_4$ heat-treated at 700 °C, 900 °C and 1100 °C for 3 h.

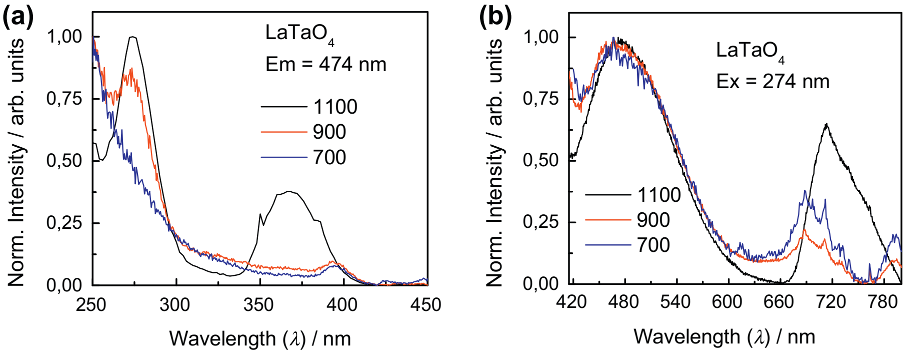
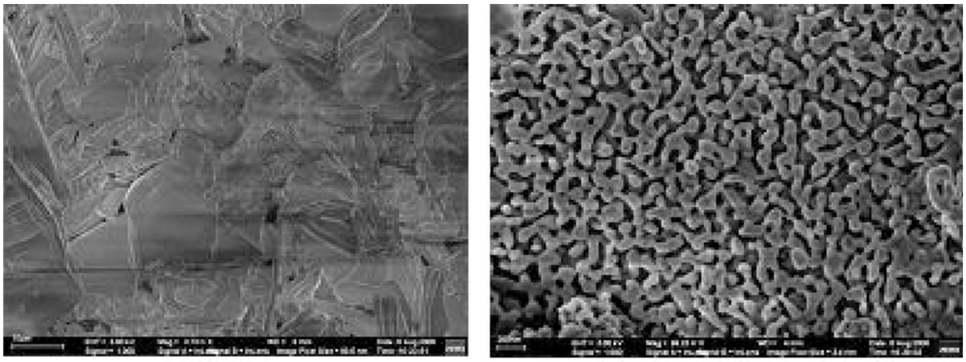
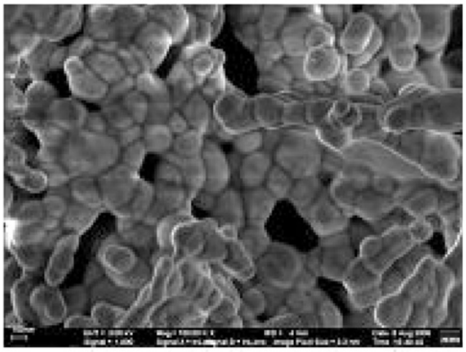


Fig. 2. (a) Excitation and (b) emission spectra of pure $LaTaO_4$ heat-treated at 700 °C, 900 °C and 1100 °C for 3 h.



700 °C/3h **900 °C/3h**



1100 °C/3h

Fig. 3. SEM images of $LaTaO_4$ heat-treated at 700 °C, 900 °C and 1100 °C for 3 h.

The photoluminescent emission of $LaTaO_4$ is shown in Fig. 2(a) and (b). The spectral profile can be divided into two categories: (i) matrix emission, and (ii) defects emission. The matrix emission is associated with charge transfer transition of the tantalate groups ($[TaO_4]$ sublattice), in which an asymmetric broad band is centered at 480 nm. The increase of firing temperature (700 → 1100 °C) of $LaTaO_4$ precursor induces a small red shift in the matrix emission band, and an intensification of the emission bands. The defect emission bands are centered in 690 nm. However, when treated at the temperature of 1100 °C, a shift to 715 nm can be observed probably due to $LaTaO_4$ polymorphism, as indicated by the DRX data. The defect emission can be related to singly charged oxygen vacancies (V_O^*), as observed in $ZnAl_2O_4$ [23] for example. During the firing treatment, the organic matter presented in the $LaTaO_4$ precursor are burned, resulting in a local reducing environment, that might produce singly (or doubly) charged oxygen vacancies. The excitation spectra give similar results: two excitation bands, i.e., at 280 nm (matrix) and 360 nm (defects). The matrix excitation was not observed in $LaTaO_4$ treated at 700 °C, though.

Fig. 3 shows the scanning electron microscopy (SEM) images of $LaTaO_4$ powders obtained by the Pechini method at 700, 900 and 1100 °C for 3 h. As can be observed, the product consisted of nano crystallites with particle size ranging from 86 to 200 nm. The SEM micrograph of the $LaTaO_4$ obtained at 700 °C presented non-crystalline morphology while at 900 °C the sample was found to present a grain size of around 86 nm. The particle size tended to increase to approximately 200 nm when the temperature reached 1100 °C.

4. Conclusion

The Pechini method enabled us to obtain $LaTaO_4$ crystalline phase, free from spurious phases from 900 °C and beyond. Through the photoluminescence measurements, emission was observed from the $LaTaO_4$ matrix, characterized by an asymmetric broad-band centered at 480 nm, suffering a slight shift towards the red one given the increase in temperature (700 °C → 900 °C). $LaTaO_4$ obtained at 700 °C presented amorphous morphology while the particle size was found to have increased for the sample calcined at 1100 °C, being around 200 nm.

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