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# Structural and optical properties of un-doped and doped $Sr_3Al_2O_6$ obtained through the tartarate precursor method

Ioana Mindru[a], Dana Gingasu[a,*], Luminita Patron[a], Gabriela Marinescu[a], Daniela C. Culita[a], Jose Maria Calderon-Moreno[a], Silviu Preda[a], Mihail Secu[b,*]

[a] *Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, Splaiul Independentei 202, Bucharest 060021, Romania*
[b] *National Institute of Materials Physics (NIMP), Atomistilor Street 405A, P. O. Box Mg-7, Bucharest, Magurele 077125, Romania*

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ABSTRACT

Un-doped and doped strontium aluminates ($Sr_3Al_2O_6$, $Sr_3Al_2O_6$:$Tb^{3+}$, $Sr_3Al_2O_6$:$Tb^{3+}$,$Eu^{3+}$ and $Sr_3Al_2O_6$:$Tb^{3+}$,$Eu^{3+}$/$Eu^{2+}$) were synthesized through a soft chemical method – the tartarate precursor route. The tartarate precursors were characterized by infrared spectroscopy (IR) and thermal analysis. The strontium aluminates were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and infrared spectroscopy (IR). The XRD patterns confirmed the formation of single-phase cubic structure $Sr_3Al_2O_6$ with average crystallite size of 18 nm. SEM micrographs showed porous polycrystalline powder microstructures and EDX analysis confirmed the incorporation of the dopant in the $Sr_3Al_2O_6$ powders. The photoluminescence spectrum recorded on $Sr_3Al_2O_6$: $Tb^{3+}$,$Eu^{3+}$ (obtained from tartarate precursor calcined in air) showed the typical f-f luminescences of the RE-ions. Subsequent calcination of this sample in reducing atmosphere is accompanied by new photoluminescence and thermoluminescence features associated to the $Eu^{2+}$ ions.

## 1. Introduction

Luminescence materials are attracting increasing attention because of their applications in solid-state light sources, display devices, detector systems and luminous paints with long persistent phosphorescence [1–4], etc.

Luminescence materials can be classified into three types, namely the 'host' type, the 'host + activator' type and the 'host + sensitizer + activator' type [1]. Strontium-based aluminate ($Sr_3Al_2O_6$) is one of the most well known host materials; it is also the most covalent and alkaline phosphor among all aluminates [5]. The rare-earth ions ($Eu^{3+}$, $Eu^{2+}$, $Dy^{3+}$, $Tb^{3+}$, $Ce^{3+}$, $Sm^{3+}$) are considered to be excellent luminescence activators. The doped strontium aluminates, such as $Sr_3Al_2O_6$:$Eu^{2+}$ [2,5,6], $Sr_3Al_2O_6$:$Eu^{3+}$ [7], $Sr_3Al_2O_6$:$Eu^{3+}$, $Dy^{3+}$ and $Sr_3Al_2O_6$:$Eu^{2+}$,$Dy^{3+}$ [3,8–10], have been widely studied. There are also a number of reports on $Sr_3Al_2O_6$:$Tb^{3+}$ [11], $Sr_3Al_2O_6$:$Ce^{3+}$,$Tb^{3+}$ and $Sr_3Al_2O_6$:$Tb^{3+}$,$Eu^{3+}$ [12] and $Sr_3Al_2O_6$:$Eu^{3+}$,$Sm^{3+}$ phosphors [13].

These aluminates have been obtained through various methods, such as the solid-state reaction [2,14], the microwave combustion [15] and the soft chemistry methods – the hydrothermal route [7], the sol-gel assisted by microwave irradiation/sol-gel-combustion [6,8,9,11,12,16] and the citric acid precursor method [3,17].

All methods belonging to the soft chemistry are based on molecular precursors. For example, Y. Pan et al. highlight the formation of a hydrogarnet $Sr_3Al_2(OH)_2$(SAH) through a hydrothermal process under mild conditions, in a wide range of pH [7].

The molecular precursors offer the advantage of achieving an intimate mixing of the metal ions at molecular-level. The decomposition of these precursors is simultaneous with/or is immediately followed by the formation of the oxide. The single phase oxide is obtained at low temperatures and the oxide nanoparticles possess superior characteristics [17].

The main goal of this work is the preparation of the nanocrystalline $Sr_3Al_2O_6$, $Sr_3Al_2O_6$:$Tb^{3+}$, $Sr_3Al_2O_6$:$Tb^{3+}$,$Eu^{3+}$ and $Sr_3Al_2O_6$:$Tb^{3+}$, $Eu^{3+}$/$Eu^{2+}$ through the precursor method – the thermal decomposition of tartarate multimetallic complex compounds. The photoluminescence and thermoluminescence properties of the strontium aluminates are discussed.

## 2. Experimental

### 2.1. Reagents

All chemicals: $Al(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$, $Tb(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 5H_2O$ and the tartaric acid ($C_4O_6H_6$) were of reagent quality (Merck).

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* Corresponding authors.
*E-mail addresses:* d_gingasu@yahoo.com (D. Gingasu), msecu@infim.ro (M. Secu).

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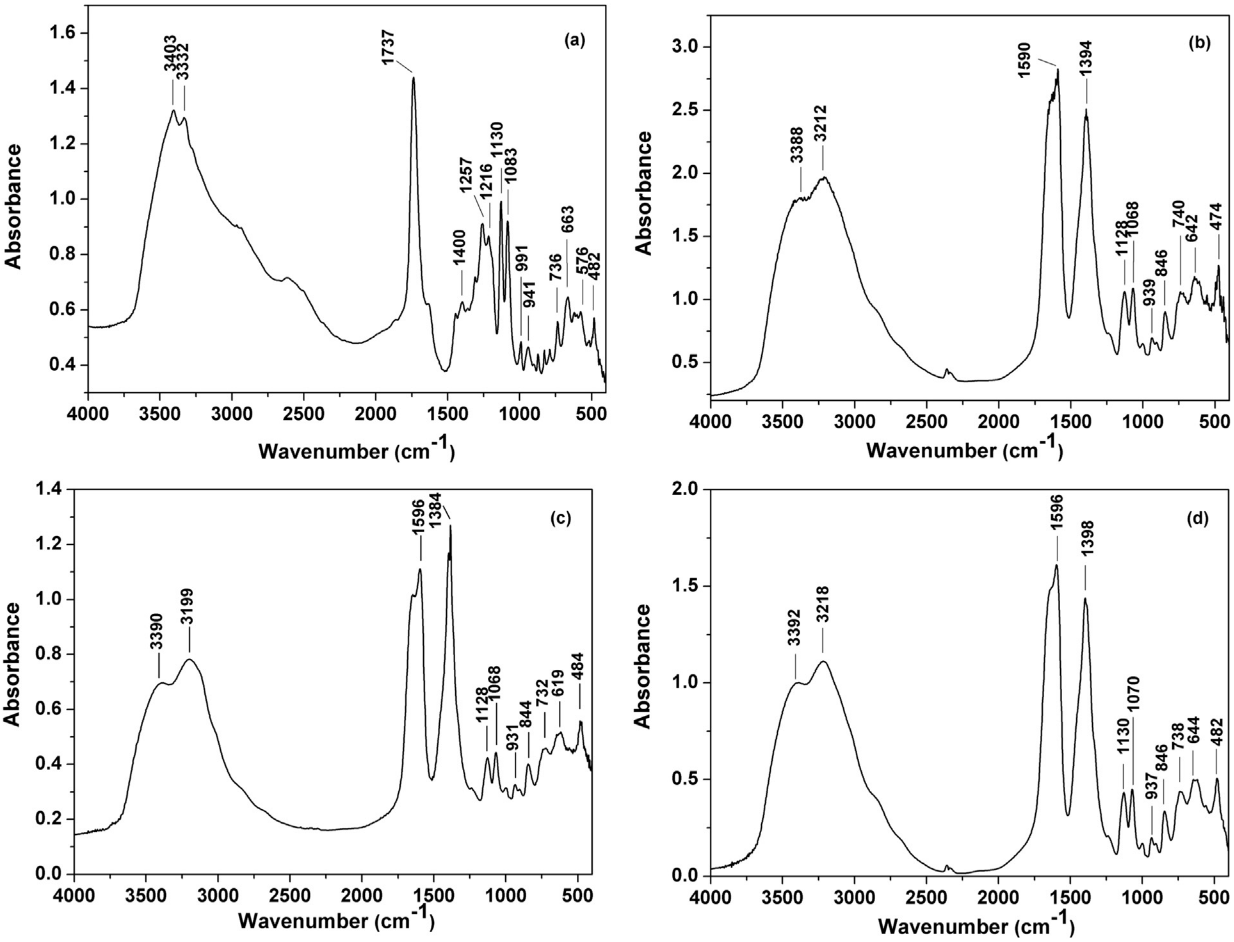

**Fig. 1.** IR spectra of: (a) tartaric acid, (b) tartarate precursor (**I**), (c) tartarate precursor (**II**) and (d) tartarate precursor (**III**).

### *2.2. Synthesis of the tartarate precursors*

Aluminium(III), strontium(II) and lanthanides nitrates (terbium/europium) were dissolved in minimum amount of distilled water and mixed with an aqueous solution of tartaric acid in the molar ratio: $3Sr^{2+}:2Al^{3+}:4C_4O_6H_4^{2-}$ (**I**); $3Sr^{2+}:1.99Al^{3+}:0.01Tb^{3+}:4C_4O_6H_4^{2-}$ (**II**) and $3Sr^{2+}:1.99Al^{3+}:0.01Tb^{3+}:0.005Eu^{3+}:4C_4O_6H_4^{2-}$ (**III**). Methanol was added to the final solution until white precipitates were formed. The pH was raised to 6 by adding a solution of $NH_4OH:CH_3OH$ (1:1). After 24 h at 4 °C, the white tartarate compounds (precursors (**I**), (**II**), (**III**)) were filtered and dried over $P_4O_{10}$.

These precursors were thermally treated in air, at 1000 °C/2 h in order to obtain: $Sr_3Al_2O_6$ (**S1**), $Sr_3Al_2O_6:Tb^{3+}$ (**S2**) and $Sr_3Al_2O_6:Tb^{3+},Eu^{3+}$ (**S3**). Sample **S3** was also subject to calcination at 1000 °C/2 h in a reducing atmosphere of (95% Ar/5% $H_2$) gas flowing in order to obtain $Sr_3Al_2O_6:Tb^{3+},Eu^{3+}/Eu^{2+}$ (sample **S4**).

### *2.3. Physical measurements*

The IR spectra of the tartarate precursors and strontium aluminates were recorded on KBr pellets with a JASCO FTIR 4100 spectrophotometer in the 4000–400 $cm^{-1}$ range.

The UV–Vis absorption spectra (200–850 nm) were recorded on a Jasco V-750 spectrophotometer equiped with an 150 integrating sphere ILV-924 for diffuse reflectance measurements, using Spectralon as reference. The optical band-gap energy ($E_g$) has been estimated [18] by the following formula:

$$(h\nu\alpha)^2 = h\nu - E_g$$

where α is the absorption coefficient ($cm^{-1}$), h is the Plank constant and ν is the frequency of incident photons.

The thermal behavior of the tartarate precursors was analyzed with a Netzsch STA 449 C Jupiter apparatus. The samples were placed in an open alumina crucible and heated from room temperature up to 1100 °C at 10 °C $min^{-1}$, under a dried air flow of 20 mL $min^{-1}$.

The X-ray diffraction patterns of the powder oxides were recorded using Rigaku's Ultima IV multipurpose diffraction system. The diffractometer was set in a parallel beam geometry, using Cu Kα radiation (λ = 1.5406 Å), CBO optics and operated at 40 kV and 30 mA, 0.02° step size and 5° $min^{-1}$ scan speed. The phase identification was performed using Rigaku's PDXL software, connected to ICDD PDF-2 database. The lattice constants were refined using Whole Powder Pattern Fitting (WPPF) and the crystallite size was calculated by the Williamson-Hall method.

The microstructure of the obtained powders was studied by scanning electron microscopy (SEM) in a FEI Quanta 3D FEG apparatus operating at 10–20 kV, using secondary electron micrographs. Elemental analysis measurements were carried out using an energy dispersive X-ray spectrometer with an excitation electron beam at accelerating voltage of 20 kV.

The photoluminescence (PL) measurements were performed on the powder samples at room temperature by using a Fluoromax 4P spectrophotometer. Thermoluminescence (TL) measurements were performed using a Harshaw 3500 TL reader, in the 50–340 °C temperature range with a heating rate of 1 °C/s. Prior to the TL measurements, the samples were X-ray irradiated at room temperature (RT) for 5 min using a copper anode at 40 kV and 40 mA or with an unfiltered mercury vapor lamp (50 W) for 45 min.