

Hydrothermal synthesis and characterization of polycrystalline gadolinium aluminum perovskite (GdAlO₃, GAP)

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Gadolinium aluminum perovskite (GdAlO₃, GAP) is a promising high temperature ceramic material, known for its wide applications in phosphors. Polycrystalline gadolinium aluminum perovskites were synthesized using a precursor of co-precipitate gel of GdAlO₃ by employing hydrothermal supercritical fluid technique under pressure and temperature ranging from 150 to 200 MPa and 600 to 700 °C, respectively. The resulted products of GAP were studied using the characterization techniques, such as powder X-ray diffraction analysis (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDX). The X-ray diffraction pattern matched well with the reported orthorhombic GAP pattern (JCPDS-46-0395).

Keywords: *perovskite; hydrothermal process; co-precipitated gel; supercritical temperature*

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1. Introduction

The rare earth aluminates are of considerable interest because of their optical and magnetic properties and technological applications [1–3]. Rare earth aluminates serve as neutron absorbers, flux suppressors and high temperature container materials. These materials are also of considerable interest due to their magnetic and optical properties [4, 5]. Gadolinium aluminum perovskites are a kind of ceramics based on the Ln₂O₃–Al₂O₃ system (Ln-lanthanide element) and they are promising materials for optical, electronic and structural applications [6–8]. Perovskite aluminates doped with a lanthanide element offer advantages of longer lifetimes and higher polarized cross sections in comparison to most other oxide matrices. They are useful as hosts for solid-state lasers, luminescence systems and window materials for a variety of

lamps. Transition metal perovskites are usually considered to be the most promising multiferroic materials. There exist hundreds of magnetic and ferroelectric perovskites. A good collection is presented in the tables compiled by Goodenough et al. [8]. Gadolinium aluminates are currently under development as candidate materials for the neutron absorption and control rod applications. Gadolinium compounds are widely used in the preparation of phosphors for color TV tubes. About 1 % of gadolinium in iron, chromium and related alloys improves the workability and resistance to high temperature and oxidation. Since gadolinium is ferromagnetic, it can be used as a magnetic component in different sensing devices. Related ceramic perovskite materials are currently being incorporated into automobile catalytic converters; they are also promising substrates for the epitaxy of thin oxide films having potential use as buffer layers for the epitaxial growth of various perovskite-type films, such as high temperature superconductors,

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ferroelectrics, piezoelectric and colossal magnetoresistance oxides. Some perovskites also exhibit very large values of electric permittivity [2, 11–15].

Crystals of GdAlO_3 perovskites have been prepared by several workers using different high temperature techniques, such as conventional and sol-gel techniques [14], melt method [15], flux method [16], microwave synthesis [17], organic synthesis with metal complexes [18] etc. However, these high temperature processes of preparation consume a lot of energy and lead to certain thermally induced strain in the resultant products, thus, affect their quality. The authors have explored the hydrothermal route for the preparation of GdAlO_3 . The first ever successful synthesis of orthorhombic GdAlO_3 crystals employing hydrothermal technique under the influence of supercritical water/carbon dioxide is reported here for the first time.

2. Experimental

2.1. Materials

Gadolinium oxide (LOBA Chemie Co. Ltd, purity 99.9 %, extra pure), aluminum oxide (LOBA Chemie Co. Ltd., purity 99 %, neutral), nitric acid (LOBA Chemie Co. Ltd., purity 69 %, pure), ammonium solution (LOBA Chemie Co. Ltd.) and double distilled water have been used in the experiments. All the reagents were of analytical grade and used without further purification. Deionized water was used for post treatment processes.

2.2. Preparation of gel

Gadolinium aluminate (GdAlO_3 , GAP) polycrystalline ceramics were synthesized by a hydrothermal supercritical technique which was carried out using externally heated (Tuttle-Roy test tube type) pressure vessels. The used precursors were in a form of co-precipitated gels of gadolinium and aluminum. The co-precipitated gels were prepared by the method described by Hamilton *et al.* [19] for the preparation of silicate minerals. The targeted amount of GdAlO_3 gels was prepared using stoichiometric amounts of analytic-grade $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or Gd_2O_3 as Gd^{3+}

raw materials and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or Al^{3+} metal powder as Al^{3+} sources neutralizing the nitrate solution of gadolinium and aluminum oxide. The schematic flow chart of different steps involved in the preparation of co-precipitated gel was described by Basavalingu *et al.* [20]. The precipitate thus obtained was then scintillated above 600 °C until constant weights as well as the predetermined amount were achieved. If there was a weight deviation of more than 0.5 %, such gels were discarded.

2.3. Hydrothermal synthesis of gadolinium aluminum perovskite

The starting charge comprising the co-precipitated gel and water solvent were enclosed in platinum/gold capsules (4 mm diameter, 40 mm length, having a wall thickness of 0.1 mm) and sealed by arc welding. The capsules were checked for any leakage after sealing and then placed in autoclaves. The experiments were carried out at different temperatures and pressures at different durations. The authors extended the process duration in order to check whether the crystal size improves with time. The crystalline GdAlO_3 was obtained at a temperature of 700 °C and pressure 180 MPa after 92 hour duration. The temperature and pressure were monitored constantly until they achieved the set values. The run was quenched with air blast followed by dipping the autoclave into a cold-water bath. The capsules were opened and the products were recovered carefully, washed, dried and subjected to XRD, FT-IR, SEM and EDAX studies for further characterization.

3. Results and discussion

3.1. Characterization techniques

X-ray diffraction measurements of the obtained product were performed at room temperature on an X-ray diffractometer, RIGAKU, Miniflex II Series with a $\text{CuK}\alpha$ radiation. The infrared spectra in the range of 4000 to 400 cm^{-1} were recorded using FT-IR spectrophotometer, Jasco 460 PLUS, Japan. Energy dispersive X-ray analyses (EDAX) were used for quantitative analysis and scanning electron microscope (SEM) model JEOL JSM-6380LA was

used for studying the morphology and microstructure of the ceramic samples.

3.2. X-ray diffraction

The X-ray diffraction studies of the precursor, i.e. the co-precipitated gel (after scintillation in air above 600 °C) used as the starting material confirmed that it was amorphous. The experimental run products were subjected to XRD studies, which confirmed that the obtained product is crystalline and belongs to orthorhombic GdAlO_3 phase (Fig. 1). The XRD patterns match well with that reported for GdAlO_3 phase of PDF = 46-0395. The refinement of cell parameters was done using CHECKCELL and the obtained cell parameters are given in Table 1. The peaks in the region 23.8, 33.1, 42.0, 48.9, 53.8 and 55.0 correspond to (002), (200), (202), (004), (114) and (312) planes, respectively. From the XRD pattern of the GdAlO_3 , it is clear that the synthesised compound possesses highly crystallized phase without any impurity.

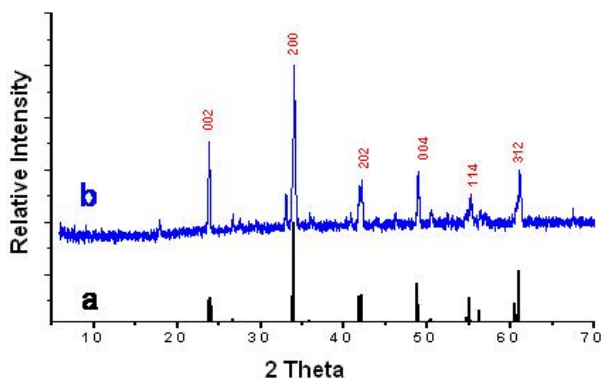


Fig. 1. XRD pattern of (a) JCPDS = 46-0395, (b) synthesized GdAlO_3 .

3.3. Infrared spectra

The results of the X-ray diffraction analysis are consistent with the crystallization process observed by the IR measurements. IR analysis of synthesized samples is important for the control of both the reaction process and properties of obtained materials. Fig. 2 shows the FT-IR spectrum of GdAlO_3 . The sample of GdAlO_3 exhibits the characteristic spectral pattern consisting of

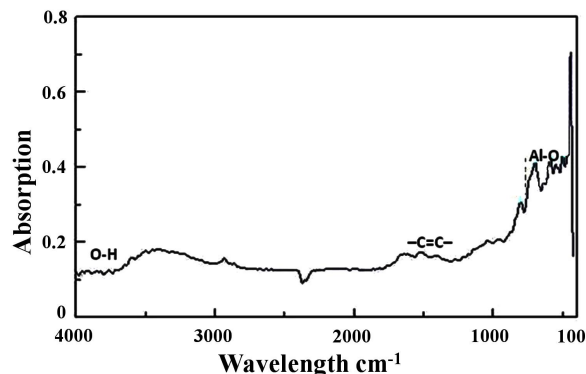


Fig. 2. FT-IR spectra of GdAlO_3 .

well-defined groups of sharp peaks in the range of 300 to 900 cm^{-1} , which is in agreement with the reported data [21]. The band observed in the low-frequency region of the spectrum, corresponds to the lattice vibration mode and may be attributed to gadolinium oxygen (Gd–O) vibration at 520 cm^{-1} . The IR spectra of GdAlO_3 show peaks at frequencies of 660 and 465 cm^{-1} which are typical of the Al–O stretching frequencies characteristic vibrations in the perovskite structure compounds [22–24]. The strong and broad absorption band in the region from 3000 cm^{-1} to 3800 cm^{-1} corresponds to the OH mode which is due to the distilled water used in the post treatment process; on the other hand –C=C– bond in the synthesized compound is represented by the peak at 1.570 cm^{-1} which is due to the absorption of atmospheric carbon.

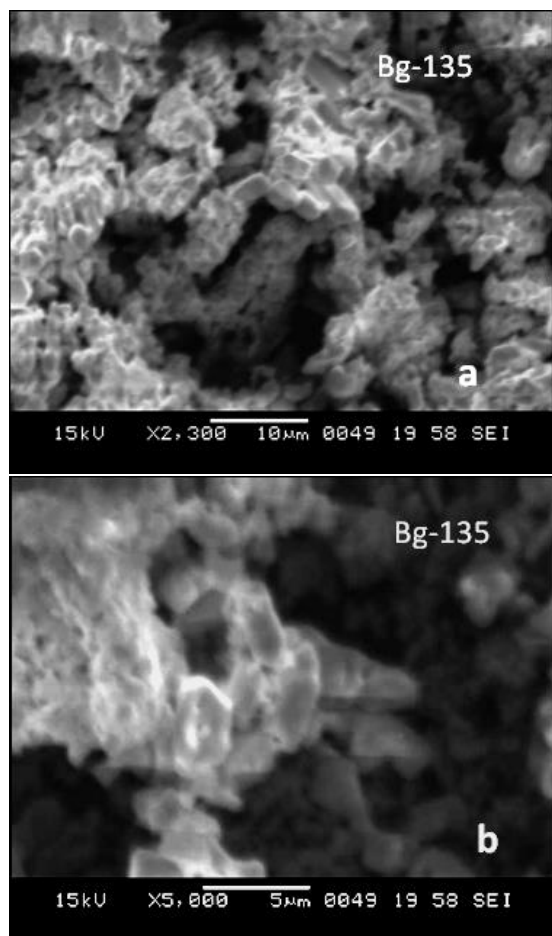
3.4. SEM and EDAX analysis

The morphology and the particle size of obtained crystals were analyzed using SEM. The SEM images of a single phase GdAlO_3 sample, obtained using the prepared co-precipitated gel of GdAlO_3 as a precursor, are given in Fig. 3. The SEM images of the synthesized polycrystalline GdAlO_3 show that all the crystals have a cubical shape and the size of 1.5 to 2.5 μm , and are highly crystalline and agglomerated.

The morphological study supported by the compositional analysis confirms again that the obtained crystals are orthorhombic and posses

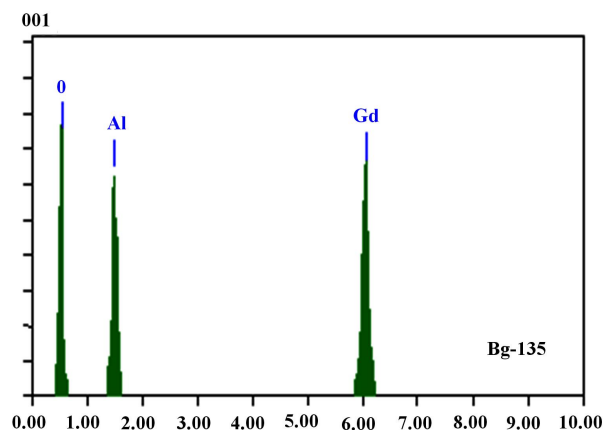
Table 1. Refined cell parameters of synthesized GdAlO_3 compared with reported data.

Compound	a axis (Å)	b axis (Å)	c axis (Å)	Cell volume (Å ³)
GdAlO_3 (PDF = 46-0395)	5.251	5.301	7.445	207.27
Synthesized GdAlO_3	5.244	5.301	7.444	207.00

Fig. 3. SEM images of GdAlO_3 .Table 2. Percentage composition of GdAlO_3 .

Run product	O at. %	Al at. %	Gd at. %	Total at. %
GdAlO_3	21.17	11.56	67.27	100

nominal phase stoichiometry. The EDAX (energy dispersive analysis of X-rays) spectrum of a selected area of the GdAlO_3 crystal is shown in Fig. 4. The atomic percentages of Gd, Al and O were determined and are given in Table 2. The

Fig. 4. EDAX of GdAlO_3 crystal.

characteristic X-ray radiation of the elements stimulated by electron impact was detected up to a depth of several thousands micrometers.

4. Conclusions

The synthesis of GdAlO_3 crystals under hydrothermal condition is sensitive to the nature of the used starting materials and the synthesis temperature. A single phase GdAlO_3 has been difficult to synthesize so far due to the requirement of controlled stoichiometric composition. In this paper, we have clearly demonstrated the synthesis of GdAlO_3 crystals employing hydrothermal technique, under the influence of supercritical fluid, which is encouraging for further investigations on the synthesis of similar oxides with several transition metals and the rare earth elements as dopants for specialized applications, such as lasers and phosphors.

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