

Synthesis of lanthanum metal organic framework using 1,4 benzenedicarboxylic acid

P. M. Thabede*, N. D. Shooto, S. J. Modise

Applied Chemistry and Nano Science Laboratory, Department of Biotechnology and Chemistry, Vaal University of Technology P.O. Box X021, Vanderbijlpark 1900, South Africa

Lanthanum nitrate and 1,4 benzenedicarboxylic acid were used to synthesize lanthanum metal organic framework (LaMOF) by conventional heating (reflux) method in dimethylformamide (DMF). The product lanthanum benzenedicarboxylic (LaBDC-MOF) structural morphology and optical properties were determined with SEM (scanning electron microscope), XRD (X-ray diffraction), TGA (thermogravimetric analysis), FTIR (Fourier-transform infrared) spectroscopy and photoluminescence spectroscopy. The characterization findings and results of LaBDC-MOF indicated that LaBDC-MOF was crystalline and significantly thermal stable. FTIR displayed that there was deprotonation in the carboxylic acidic COOH. SEM images showed that LaBDC-MOF was composed of different sizes of rods and small needles that are polyhedral-like in shape. Luminescence properties suggested that LaBDC-MOF can be used as a fluorescent probe.

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1. Introduction

Water pollution has become a global problem, henceforth it is getting significant attention. Pollutants exert an unfavourable effect on the human health and the environment; Therefore, many researchers have intensified their attention in developing ways to remove pollutants from wastewater. Various technologies such as biodegradation [1], adsorption [2], ion exchange [3] photoreduction [4], and many others have been used to remove pollutants in aqueous solutions. Apart from the methods used, materials such as sol-gel adsorbents [5], double-layered hydroxides [6], membranes [7], polymer resins [8], *Nigella sativa* seeds [9], etc have been used in the application of wastewater treatment. Some of the disadvantages of these materials is that their thermal and chemical stability is limited in water applications [10]. Moreover, their ion-exchange capacity and kinetics are low [10]. Therefore, developing new materials with high ion-exchange capacity and thermal chemical stability is still a challenging task.

Metal organic framework (MOFs) have emerged as powerful porous materials. MOFs gained their admiration due to their high surface area. The high surface area has made the MOFs to be used in applications such as gas storage [11], ion exchange [10], gas separation [12], photocatalysis [13] gas sensing [14], removal of dyes [15], encapsulated antibacterial drug [16], and supercapacitors [17]. MOFs are assembled by the coordination bond between an organic ligand and metal ions or metal clusters [18]. The 1,4 benzenedicarboxylic acid has been used as ligand for transition metals, namely; Zinc [19], Copper [20], Zirconium [21], Cobalt [22] and Chromium [23].

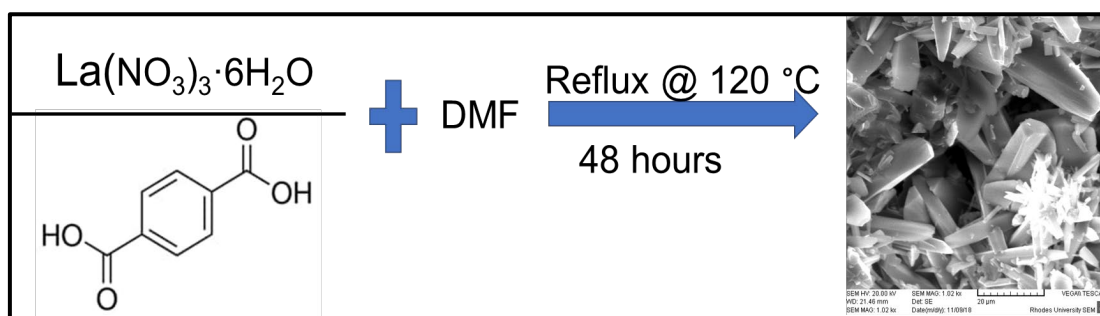
Synthesis of MOFs has been reported significantly. Rare-earth lanthanum (La) has been gaining momentum over the past years because lanthanum based MOFs have opportunities with respect to their topology and they can be used in industrial applications especially in catalysis [24].

* Corresponding authors: mapulepseabelo@gmail.com
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Lanthanum is believed to provide the adsorption sites for phosphate capture and also remove phosphate from water containing various ions [25]. Lanthanide metal ions have high affinity for donor atoms and oxygen-containing ligands, particularly multicarboxylate ligands, which are usually used in the designs for lanthanides [26]. Lanthanides can be used in sensors due to high oxophilicity and high coordination number, which ultimately makes the MOFs to be water-stable [27]. There are two types of coordination between lanthanum and terephthalic [25]. In this work, we report the stable lanthanum benzenedicarboxylic metal organic framework (LaBDC-MOF) which is characterized by X-ray diffraction, FTIR spectroscopy, TGA, SEM and PL.

2. Synthesis of LaBDC-MOF

Lanthanum nitrate hexahydrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, N,N-dimethylformamide (DMF) and 1,4 benzenedicarboxylic acid (BDC), were used during the synthesis of lanthanum benzenedicarboxylic metal organic framework (LaBDC-MOF) using a reflux set-up. The materials were prepared with a modification of the previous method reported by Shooto et al. (2017) [28]. Lanthanum nitrate hexahydrate (1.03 g) and benzene dicarboxylic acid (1.04 g) were mixed with dimethylformamide (80 mL). The reaction was left to stir for 48 h at 120 °C. The supernatant was decanted followed by washing the precipitate with methanol. The precipitate was dried in the oven at 40 °C. The preparation scheme is shown below.



Scheme 1. Preparation scheme for LaBDC-MOF.

3. Characterization of LaBDC-MOF

X-Ray diffraction (XRD) measurement was performed by Shimadzu Xrd 700, using a Cu source. Infrared was recorded on Thermo Fischer Scientific Nicolet iS50 FTIR Spectrometer. Scanning electron microscopy images were obtained using a Nova Nano SEM 200. Thermogravimetric (TGA) analysis was conducted using Perkin Elmer thermal analyzer STA 6000. The emission of the product was determined using Jasco Spectrofluorimeter FP-8600.

4. Results and discussion

4.1. XRD determination of LaBDC-MOF

To confirm the phase and structure of LaBDC-MOF, XRD analysis was conducted from 2θ of 15° to 80° using Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) as the source of X-rays. The XRD pattern of LaBDC-MOF in Fig.1 shows five peaks at 2θ values of 19.1°, 26.8°, 33.6°, 35.2° and 41.4°, with the remaining peaks that are not so clear. A similar pattern was observed in the study of Zhou et al. 2014 [29]. This suggests that LaBDC-MOF was successfully produced in this work.

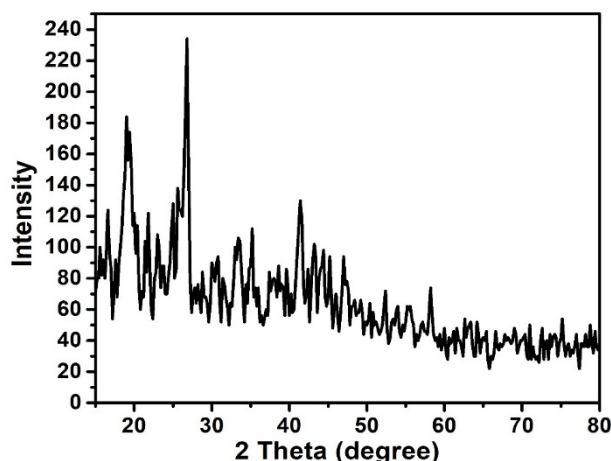


Fig. 1. X-ray diffraction pattern of the product of LaBDC-MOF.

4.2. FTIR spectroscopy determination of LaBDC-MOF

The FTIR spectrum of LaBDC-MOF material measured is shown in Fig. 2. The key functional groups of LaBDC-MOF structure could be observed with corresponding infrared absorption peaks as discussed shortly. The nonappearance of peaks at 1720 and 1680 cm^{-1} suggested that deprotonated had happened in the carboxylic acidic COOH^- [16]. The peak at 1664 cm^{-1} is due to the asymmetric carbonyl ($\text{C}=\text{O}$) vibrations [30-31]. The peaks at 1549 cm^{-1} and a small peak 1491 cm^{-1} are due to the asymmetric and symmetric stretching modes of carboxylic acid, respectively [32]. The bending $-\text{OH}$ vibrational peak indicating the presence of carboxylic acid group was observed at 1375 cm^{-1} [16], [33], [34]. The peak at 747 cm^{-1} is assigned to the to $\text{C}-\text{H}$ bending vibrations of the benzene [35]. The characteristic vibration at 502 cm^{-1} might be ascribed to $\text{La}-\text{O}$ stretching vibration, in which the oxygen atom was coordinated to La [36].

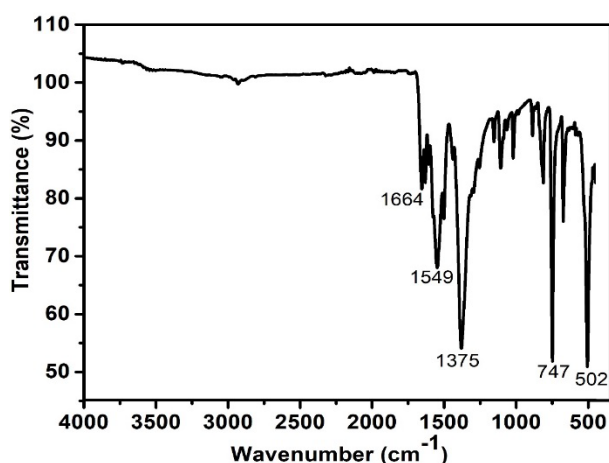


Fig. 2. FTIR synthesized products of LaBDC-MOF.

4.3. Physical Properties of LaBDC-MOF

The morphology of the synthesized LaBDC-MOF is shown in Fig. 3a-b. The images show rods and needles of different sizes with smooth surfaces. The larger images show that LaBDC-MOF is also polyhedral-like in shape and the material morphology is aggregated forming a flower-like structure. The SEM images of both (a) and (b) are similar in shape. The smooth surfaces and uniform-like structural shapes indicate a maximum degree of crystallinity and thermal stability with minimum surface area [37].

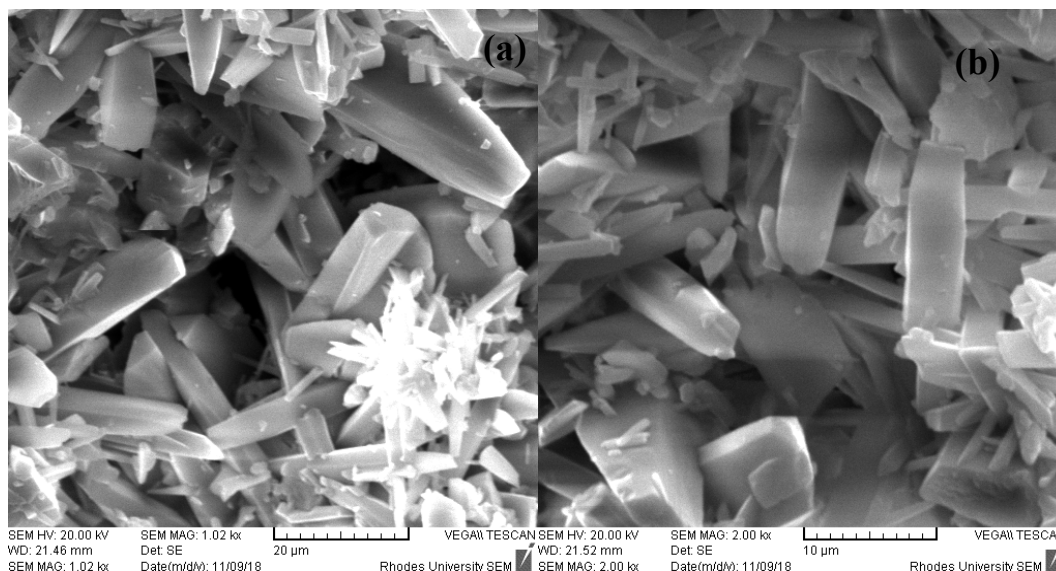


Fig. 3. SEM synthesized products (a) and (b) LaBDC-MOF.

4.4. Thermal determination of LaBDC-MOF

The TGA measurement was carried out to identify the thermal stability and it is shown in Fig 4. As demonstrated by the TGA curve, LaBDC-MOF has four decomposition steps. The first weight loss at 148.18 °C was due to adsorbed moisture on the surface of LaBDC-MOF [38]. While the second step at 251.03 °C was due to decomposition and desorption of N,N-dimethylformamide [39]. The third step at 515.44 °C indicates that LaBDC-MOF began to collapse [39].

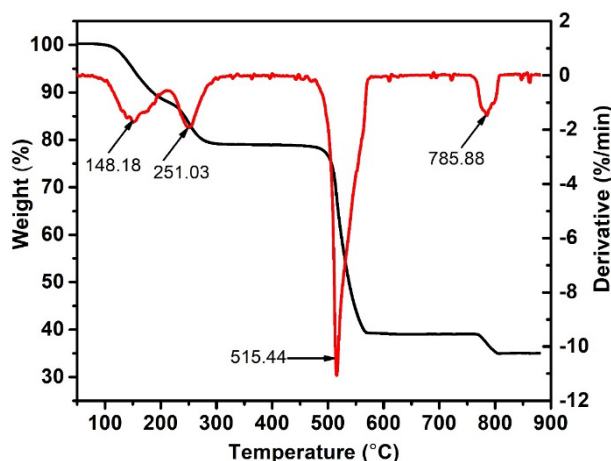


Fig. 4. TGA/DTA of the synthesized product of LaBDC-MOF.

4.6. Luminescence

Fluorescent properties of LaBDC-MOF and their potential applications as fluorescent-emitting materials become important in the research area over the years [40]. Moreover, luminescent lanthanide complexes can be used in medicinal diagnostics. Hence, the photoluminescence property was investigated at room temperature. The luminescent property of LaBDC-MOF investigated is shown in Fig.5. The emission peak of LaBDC-MOF is observed at 750 nm at the excitation of 375 nm. The high emission intensity obtained in the photoluminescence spectrum of LaBDC-MOF suggest that it is suitable as a fluorescent probe [14].

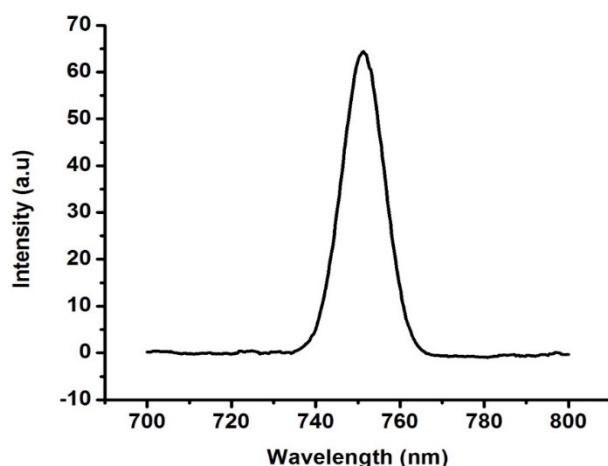


Fig. 5. Photoluminescence of the synthesized product of LaBDC-MOF.

5. Conclusion

LaBDC-MOF has been prepared from 1,4 benzenedicarboxylic acid using the reflux method. XRD showed that indeed La-MOF was successfully obtained. The SEM analysis showed that there were different sizes and morphology of the material. FTIR spectroscopy proposed that there was deprotonated in the carboxylic acidic COOH. TGA showed that LaBDC-MOF is thermally stability up to 785 °C.

Data Availability

The data was generated at the Vaal University of Technology (VUT). The data and their findings of this work may be made available from the corresponding author(s) on request.

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