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SYNTHESIS AND CHARACTERIZATION OF LITHIUM GARNET-BASED MATERIALS FOR APPLICATION IN LITHIUM-ION BASED ELECTROCHEMICAL POWER SOURCES

1. PI & Co PI

NAME OF THE PI: Dr. A. Samson Nesaraj

DESIGNATION: Professor & Director (SA)

PHOTO:

TITLE OF THE PROJECT: Synthesis and characterization of lithium garnet based materials for application in lithium-ion based electrochemical power sources

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PROJECT AGENCY: Tamil Nadu State Council for Science and Technology

2. SDG INVOLVED

Our research project is relevant to the SDG 7 (Affordable and clean energy). Energy is the most fundamental element of human resources. Now-a-days, our society relies on coal and petroleum for energy generation. However, climate change, pollution and limited reserves of fossil fuels all require us to find cleaner and more sustainable energy sources. Renewable energy sources such as solar and wind power are promising substitutes. However, unlike fossil fuels which both store and generate energy, the generation of solar energy and wind power depends largely on Mother Nature. As a result, there is a great mismatch between energy generation and

energy consumption so energy storage devices are needed. Batteries, being the most successful electrochemical storage devices, have been and will continue to serve the purpose in the foreseeable future. Figure.1 describes about the comparison of different battery technologies in terms of gravimetric and volumetric energy densities. It clearly reveals that lithium-ion batteries possess the highest energy density among common rechargeable batteries systems. Lithium-ion batteries are becoming increasingly competitive in terms of cost and performance as its technology progresses. Like, other electrochemical cells, lithium-ion batteries also consist of three major components: cathode, anode and electrolyte. The potential of the cell originates between the two electrodes, the first electronically connected via external circuit and the other ionically connected through internal circuit (i.e. electrolytes). During discharging process, electrons flow from anode to cathode, converting chemical energy into electrical energy. Meanwhile, Li ions also move from anode to cathode through electrolyte to balance the charge as shown in Fig. 1.

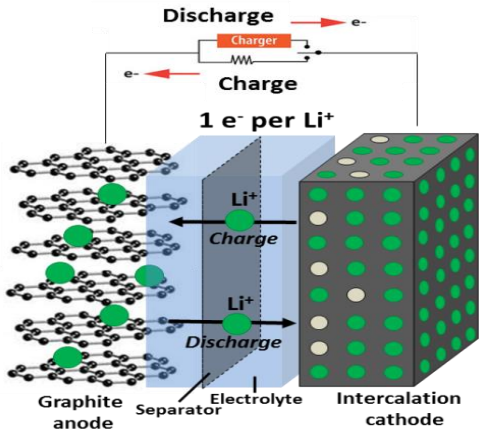


Fig. 1. Electrochemistry of Li-ion battery

Although, the garnet type is a well understood system with the general formula of $A_3B_2(XO_4)_3$, where A, B and X are eight, six and four oxygen-coordinated cation sites. Highly Li-staffed garnet contains more than three lithium per formula, e.g. $Li_7La_3Zr_2O_{12}$ and $Li_5La_3Ta_2O_{12}$. They possess much useful technological oriented physio-chemical properties which make them as potential candidate for both magnetic and optical devices. Also, it has another unique and most important characteristic of Li-excess garnet type materials is ionic conduction. Commonly studied garnets typically contain five to seven Li atoms per formula unit, and are referred to as Li-stuffed (Li-rich) garnets, that is, they have more Li than that can be accommodated at the tetrahedral sites, leaving excess Li which occupy the octahedral sites in the garnet structure. The first reported Li ion conducting Li-stuffed garnets are $Li_5La_3M_2O_{12}$ (M = Nb, Ta), which were developed by Thangadurai et al. in 2003. It was reported that zinc oxide can be applied as a sintering aid that facilitate the formation of the highly conducting cubic $Li_7La_3Zr_2O_{12}$ garnet phase in a single-step sintering procedure. The garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) has excellent

environmental stability; experiments and computational analyses showed that this solid electrolyte has a high lithium (Li) ionic conductivity (10^{-4}–10^{-3} S·cm^{-1}), an electrochemical window as wide as 6 V, stability against Li metal anode, and compatibility with most of the cathode materials. Ahmad et al. have studied the effect of Ga^{+3} substitutions on the Ta^{+5} sites in $Li_{5+2x}La_3Ta_{2-x}Ga_xO_{12}$ (LLT-Ga) lithium conducting garnets (with x = 0.1–0.5) in order to enhance the ionic conductivity of these materials.

Kim et al have especially focused on research progress on garnet-type solid electrolytes ($Li_7La_3Zr_2O_{12}$) because they have shown high ionic conductivity, good chemical stability with Li metal, and a wide electrochemical potential window. Ohta et al have demonstrated the fabrication of a solid-state Li/LLZ/Li($Ni_{1/3}Co_{1/3}Mn_{1/3}$)O_2 battery at a remarkably low temperature (400 °C) using our invented "low temperature sintering triggered by an ion-exchange reaction (LTI)". Synthesis of these compounds has been attempted many times since, and has consistently shown the Li-ion conductivity of ~10^{-3} to 10^{-6} S/cm at 25 ºC and good chemical stability at a wide range of operating temperatures. Further research has since been done to understand the crystal structure, electrical conductivity, and the mechanism of Li ion conduction. Attempts have also been made to incorporate these materials in an all-solid-state Lithium ion batteries. In this research work, we describe the wet chemical synthesis of Sr doped $Li_7La_3Zr_2O_{12}$ fine garnet particles and their physico-chemical characterization for use as cathode materials in lithium-ion batteries.

3. **AIM OF THE PROJECT:** To prepare Sr doped $Li_7La_3Zr_2O_{12}$ garnet based materials by chemical precipitation technique for application in Li-ion batteries.

4. **OBJECTIVES OF THE PROJECT AND ITS DIRECT RELATION TO A PARTICULAR SDG GOAL**

This project is relevant to the SDG level (Affordable and clean energy). The strontium doped $Li_7La_3Zr_2O_{12}$ garnet materials ($Li_7La_{3-x}Sr_xZr_2O_{12-\delta}$; x=0, 0.10, 0.20, 0.30 and 0.40) nanoparticles were prepared by wet chemical method. In the beginning, appropriate concentration of NaOH in 100 mL was prepared. To this solution the appropriate strength of lithium nitrate, zirconium oxy chloride, lanthanum nitrate and strontium nitrate solutions were added slowly with continuous stirring for about four hours in a magnetic stirrer set-up. The entire reagent mixing was completed at room temperature. During the addition of aqueous salt solution, the pH was maintained above 9 by the addition of sodium hydroxide pellets. The resultant precipitate mixture [LiOH, $La(OH)_3$, $Sr(OH)_2$ and $Zr(OH)_4$] was filtered and washed with pure water for about 5 – 10 times. The washed product was dried at 80^o C in air oven for whole night. Then, the dried product was calcined in a furnace at different temperatures, viz., 150, 300, 450 and 600^o C for 2 hours each. During the high temperature calcination, unwanted organic impurities were completely removed and ultra-pure strontium doped $Li_7La_3Zr_2O_{12}$

garnet materials were resulted. The flow chart to fabricate the materials by soft chemical method is presented in Fig.2. The synthesis steps are indicated in Fig. 3. The reagents used in this process are given in Table 1. The chemical reactions involved in the preparation of Cu doped BaO nanoparticles is given in Equation 1.

$$7\ LiNO_{3(aq)} + (1\text{-}x)\ 3\ La(NO_3)_{3(aq)} + x\ Sr(NO_3)_{2\ (aq)} + 2\ ZrOCl_{2(aq)} + 20\ NaOH_{(aq)} \rightarrow$$
$$7\ LiOH_{(s)} + (1\text{-}x)\ 3\ La(OH)_{3(s)} + x\ Sr(OH)_{2(s)} + 2\ Zr(OH)_{4(aq)} + 16\ NaNO_{3(aq)} + 4\ NaCl_{(aq)} \quad \text{-- (1)}$$

$$7\ LiOH_{(s)} + (1\text{-}x)\ 3\ La(OH)_{3(s)} + x\ Sr(OH)_{2(s)} + 2\ Zr(OH)_{4(aq)} \xrightarrow{\Delta}$$
$$Li_7La_{3-x}Sr_xZr_2O_{12-\delta\ (s)} + x\ H_2O_{(l)}\uparrow \quad \text{-- (2)}$$

The crystallographic properties of Sr doped $Li_7La_3Zr_2O_{12}$ nanoparticles were studied by X-ray diffraction (Bruker D 8 Advance Eco-Powder X-ray diffractometer). The FTIR spectra of Sr doped $Li_7La_3Zr_2O_{12}$ nanoparticles were examined using Fourier Transform Infra Red Spectrometer (Shimadzu IRTracer-100 FTIR Spectrophotometer) with KBr pellet method in the range from 4000-400 cm^{-1}. The particle size of the Sr doped $Li_7La_3Zr_2O_{12}$ was measured using Malvern Particle Size Analyzer using triple distilled water as medium. The morphology and the element ratio of Sr doped $Li_7La_3Zr_2O_{12}$ nanoparticles nanoparticles were studied by scanning electron microscope (XFlash® 6 | 30) equipped with an energy dispersive X-ray (EDAX) spectrophotometer.

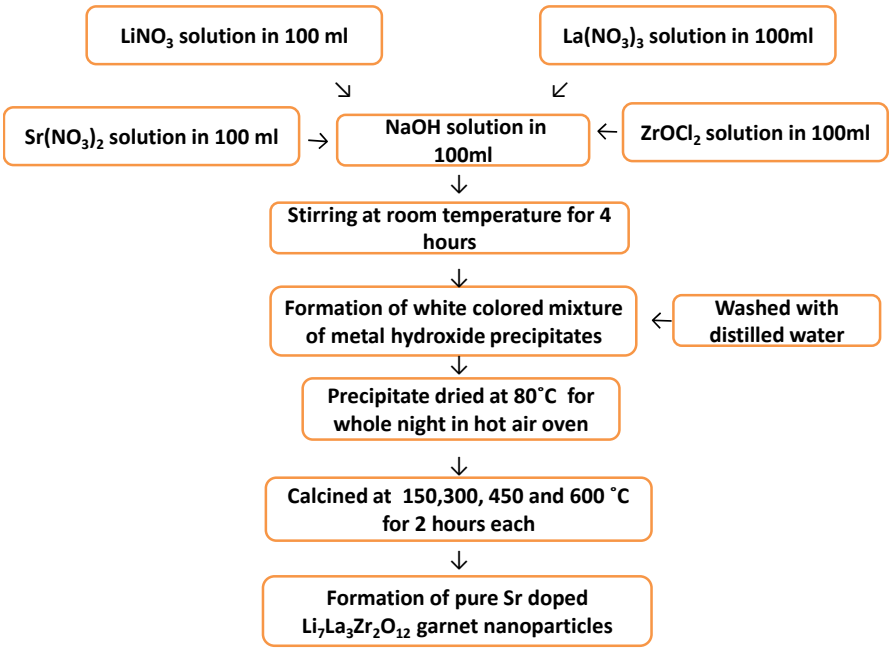
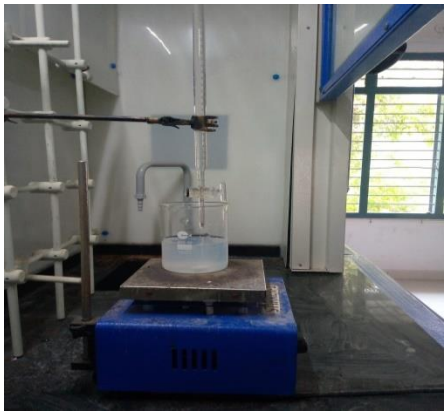


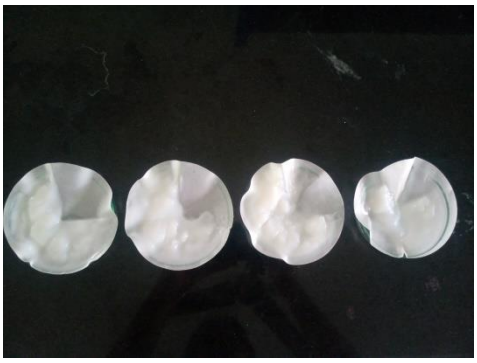
Fig. 2. Flow chart to prepare Sr doped $Li_7La_3Zr_2O_{12}$ garnet nanoparticles by wet chemical synthesis

Reagents before mixing



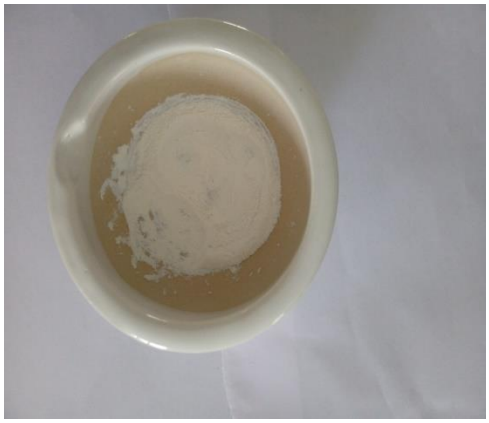
During precipitation

Filtration of precipitate



Filtered precipitates

Garnet nanoparticles after calcination



Garnet nanoparticles after grinding process

Fig. 3. Synthesis steps during the preparation of Sr doped $Li_7La_3Zr_2O_{12}$ garnet by chemical precipitation technique

5. DETAILS OF RESEARCHERS @ KARE ASSOCIATED WITH THIS PROJECT

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6. PROJECT PH.D STUDENTS/MASTERS STUDENTS/UG STUDENTS

NAME OF THE PG STUDENT: K. Mohamed Ibrahim

DESIGNATION: M.Sc. Chemistry student

PHOTO OF THE PG STUDENT:

7. PUBLICATIONS PRODUCED FROM THIS PROJECT

Mohamed Ibrahim, **Samson Nesaraj A**, Synthesis and characterization of lithium garnet based materials for application in lithium – ion based electrochemical power sources, Proceedings of the Student Project Scheme, TNSCST, 2022-2023, pp. 1134-1135 (ISBN: 978-81-957624-1-5)