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RESEARCH ARTICLE

DEVELOPMENT AND CHARACTERIZATION OF TITANIUM PHOSPHATES (TiP₂O₇) AND LITHIUM TITANIUM PHOSPHATE (LiTiP₂O₇) AND THEIR THERMAL AND ELECTRIC PROPERTIES.

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Abstract

In this present study, the Titanium phosphates (TiP₂O₇) and Lithium titanium phosphate (LiTiP₂O₇) materials were synthesized by using soft hydrothermal method at moderate pressure and temperature conditions. The resultant materials were characterized by using P-XRD, SEM, EDAX, FTIR, TGA, DSC and Electrochemical impedance spectra (EIS). From P-XRD, confirms the well crystalline rhombohedral phase and was found to be in the range below 100 nm. FTIR spectra indicated that there is an increase in the degree of splitting and stretching of the vibration bands, whereas the splitting of vibration bands and polymerization of [PO₄] decreased as the Ti ions. The TGA/DSC studies revealed that, these materials display endothermic reactions due to the liberation of ligands and diffusion. Thermal stability of the materials improved and the dielectric constant decreases. AC conductivity measurements for both the samples were carried and results are plotted. From AC conductivity studies, it is observed that the ionic conductivity of dc conductance of sample was measured show the frequency dependence dc capacitance of LiTiP₂O₇ material. The frequency response dc capacitance also depends on doping with titanium.

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Introduction:-

Titanium phosphates (TiP₂O₇) and Lithium titanium phosphates (LiTiP₂O₇) is used as an active electrode material for the energy storage devices. Because its advantages such as economical, environmental sustainability, excellent performance in electrochemical applications [1–3]. Both TiP₂O₇ and LiTiP₂O₇ is a suitable cathode-active material in batteries for their application in electric vehicles and hybrid electric vehicles.

Most of the synthesis methods are have already described to synthesize the phosphates, by using solid-state reactions [4]; melt techniques, flux methods, ball milling and other technique and other famous techniques like carbothermal synthesis method [5], mechanochemical activation method [6], microwave heating technique [7], hydrothermal

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synthesis process [8], microwave-solvothermal synthesis method [9], sol-gel synthesis technique [10], spray pyrolysis technique [11], co-precipitation technique [12], carbothermal reduction technique [13] and many more techniques [14].

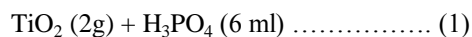
Between the above these preparation techniques, hydrothermal process is very easy, economical and good purity with uniform materials and also this technique is a better method, because synthesis can be carried out at relatively moderate temperatures. Moreover, since synthesis technique occurs in a packed system, gas fugacity plays an important role in the synthesis method. However, there is relatively less number of reports in the literature on the synthesis of these groups by hydrothermal techniques.

In our previously published papers of our research group we have already synthesized a few new group of alkali such as ortho, pyro/condensed phosphate and phosphides in the form of single crystals using hydrothermal techniques, which seems to be prospective solid electrolytes and magnetic materials [15-20]. However still there is a wide scope to develop new group of Titanate and phosphate crystalline material and hence in this research investigation, we prepared doped Titanate and Lithium Titanate phosphate through hydrothermal technique at different low pressure and Moderate temperature conditions.

Experimental:-

Synthesis:-

A series of TiP_2O_7 and LiTiP_2O_7 crystals were synthesized by soft hydrothermal technique at adequate pressure and temperature conditions. The reagents of annular grade (99.99 % purity) from Merck Chemicals were used without further purification. The starting reactance were thoroughly mixed at room temperature to get a homogenous, relatively less viscous mixture and were transferred to a Teflon lined stainless steel autoclaves of 50 mL capacity. The synthesis of TiP_2O_7 and LiTiP_2O_7 crystals were carried out at temperature range of 250°C . The nucleation was spontaneous and it was minimized through slow rate of heating. At this temperature, the experiments were run continuously and followed by instant quenching to ambient conditions. The resultant product was in semisolid condition. The product was thoroughly washed several times with double distilled water and ethanol using ultrasonic cleaner and final product was filtered and dried under vacuum at 90°C for 2 hours. The crystals were obtained under following molar ratios in grams shown in the Equation (1) and (2).



The synthesis of TiP_2O_7 and LiTiP_2O_7 materials to confirmed the reproducibility of the crystals.

Characterization:-

Powder X-Ray Diffraction Studies:-

X-Ray studies were carried out using a high-resolution X-ray Diffractometer Maxima-7000 (Shimadzu) at a scanning rate of 2°min^{-1} using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 30 mA.

SEM:-

Scanning Electronic Microscopy (SEM) studies were carried out using SEM (SU-1500, HITACHI). The accelerating potential was 15 kV, and the beam current was 20 mA to understand the micro to macro structural surface morphology, growth fractures of fine crystalline materials to access the quality and applications. Here electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

EDAX:-

EDAX analysis was carried out using SEM (JSM-5600LV, JEOL) equipped with an EDAX detector of Solid State and Structural Chemistry Unit to obtain the elemental composition of the group of phosphate samples.

FTIR Studies:-

The FTIR spectrum was recorded on Perkin Elmer FTIR 1600. Spectrophotometer at ambient temperature using a KBr disk method. The disk containing 0.0010 g of the sample and 0.3 g of fine grade KBr was scanned with 16 scans at wave number range of 400-4000 cm^{-2} .

TGA:-

TGA was carried out using Universal V4.5A TA Instrument, by measuring the weight loss of the samples as a function of temperature. The samples were heated from 25°C to 800°C at a heating rate of 10°C/min in nitrogen atmosphere with a nitrogen flow rate of 20 mL/min., which are essential to understand the thermal behaviors of the starting components and resultant products, to unravel first and second order structural phase transitions, chemical decomposition accompanied by absorption (endothermic) or evolution (exothermic) of heat by a compound. It also provides more information on the crystallization temperature of the compound.

Electrical Properties:-

The electromagnetic interaction between constituent phases is key point to change dielectric behavior of material. The dc conductance of sample was measured by Wayne Kerr 6500B impedance analyzer with computer interface, where the signal frequency varied from 1 kHz to 10 MHz, equivalent circuit in series and bias voltage set at 1V.

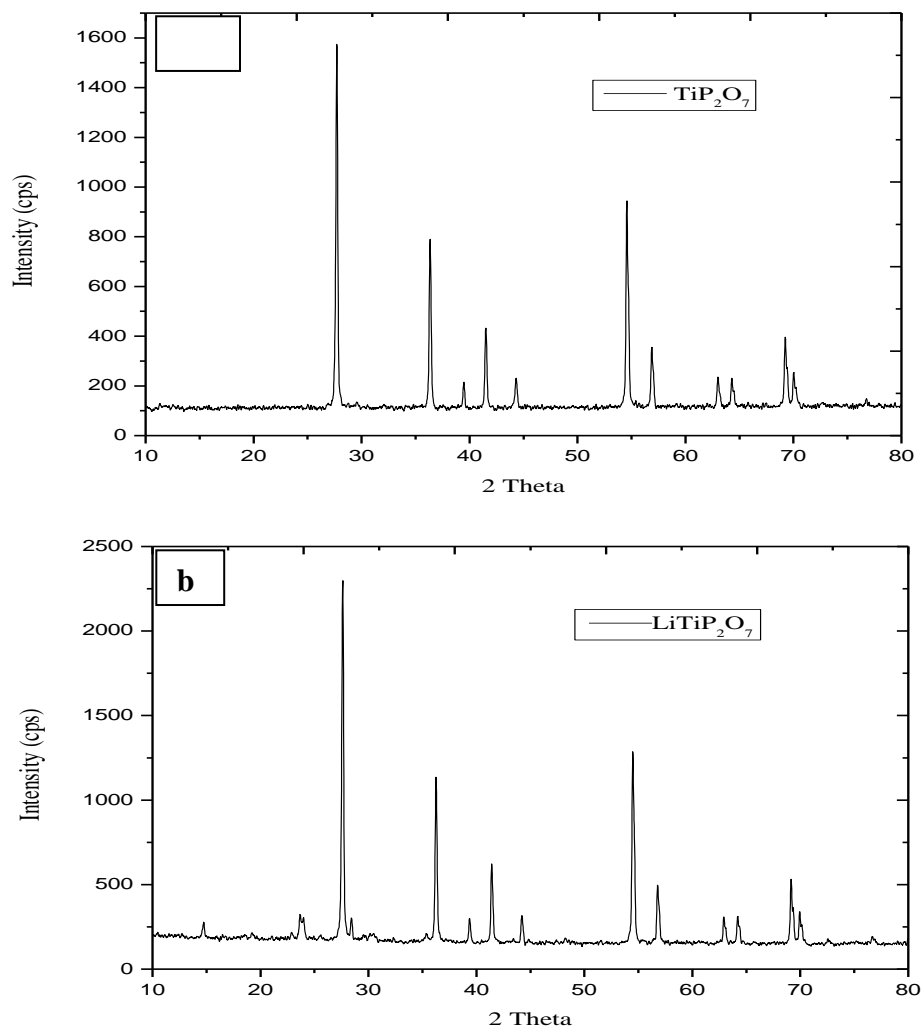
Results and Discussion:-**X-Ray Diffraction Studies:-**

Fig. 1:-XRD Patterns of a) TiP_2O_7 and b) LiTiP_2O_7

The Fig. 1. Confirms the well crystalline rhombohedral phase for the prepared phosphates and all the peaks are characteristic of the LiTiP_2O_7 compound. The absence of secondary peaks confirms the formation of purely crystallized single phase. The average crystallite size was estimated from Scherrer's formula and was found to be in the range below 50 nm, which consist of tetrahedral PO_4 to make infinite channels for Li ions to reside in. Moreover, the intensity of the peaks becomes stronger and narrower, indicating a better structural quality of materials. In addition, as the calcination temperature increased, the intensity of the diffraction peaks of the samples increased, which indicated that the increase in the calcination temperature of the LiTiP_2O_7 -materials is advantageous for improving the crystallinity of the samples.

Scanning Electron Microscopy (SEM) Studies:-

The crystals obtained by the soft hydrothermal method were of good quality and exhibited smooth surface, sub transparent and sub vitreous lustre as shown in Fig. 2 (a-d). It was found that as the TiP_2O_7 concentration materials has not yielded any considerable change either in the morphology or in the size and shows agglomerations. After addition of Li to TiP_2O_7 (Fig. 2c-2d), the concentration of morphology exhibited homogeneous particles with nano size irregular spherical morphologies like structure and uniform distribution of fine particles with less agglomeration compared to that of TiP_2O_7 . Composition analysis of LiTiP_2O_7 -samples shows that the grains are uniform and roundish in shape having a size in the range below 100 nm respectively, which was also confirmed by XRD results.

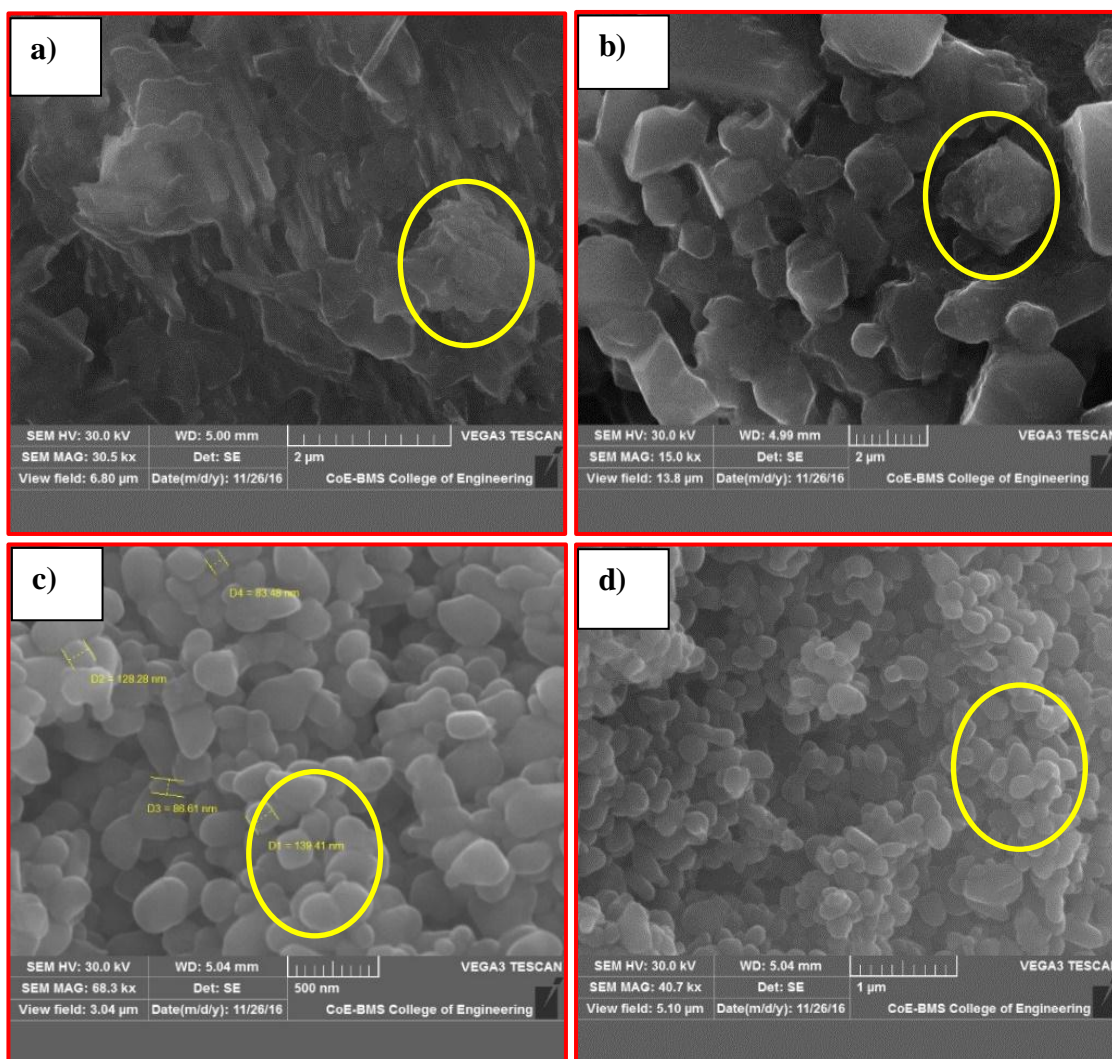


Fig.2 SEM micrographs of a& b) TiP_2O_7 and c & d) LiTiP_2O_7

Energy dispersive X-Ray analysis (EDAX):-

The EDAX pattern recorded were shown in Fig. 3, was also distinctively different from those of any titanium phosphate reported. Elemental analysis revealed a composition of 48.55 wt. % Ti and 4.91 wt. % P which agreed well with the values calculated for TiP_2O_7 . These results confirmed the existence of TiP_2O_7 . The amount of elements added in the reaction mixture of TiP_2O_7 as shown in Table 1.

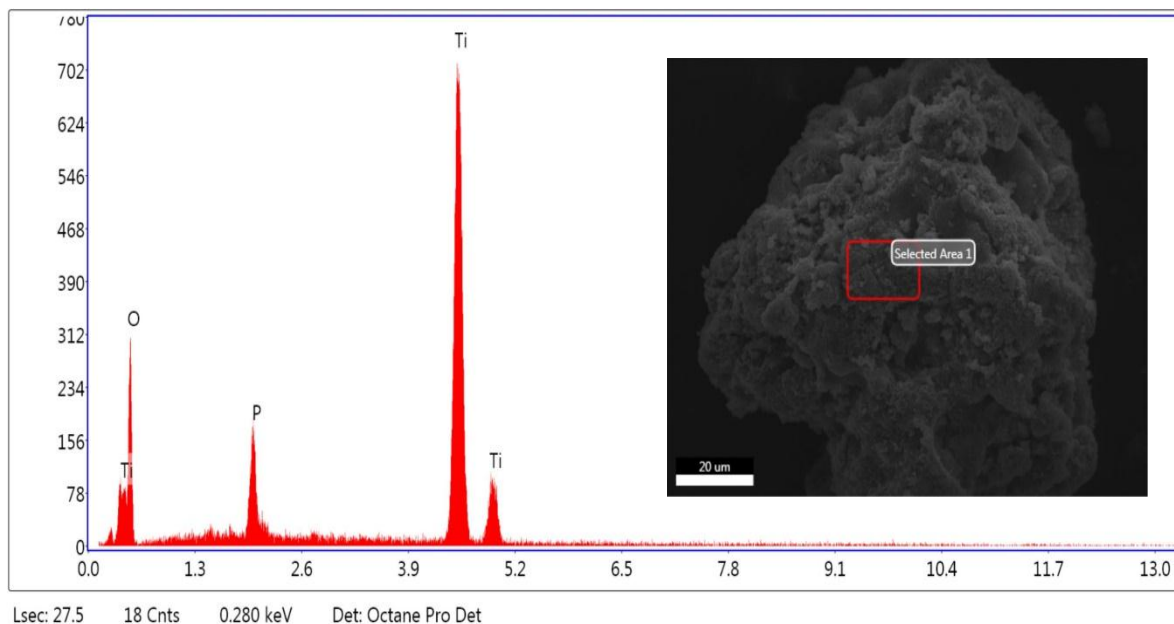


Fig.3. EDAX analysis of TiP_2O_7

Table 1:-Comparison of the amount of elements added in the reaction mixture of TiP_2O_7 with that estimated in the reaction product by EDX.

Element	Weight %	Atomic %	Net Int.	Error %	K ratio
O K	46.53	71.27	104.48	11.75	0.0626
P K	4.91	3.89	94.86	6.23	0.0383
Ti K	48.55	24.84	599.78	2.29	0.4340

Fourier transfer infrared spectra (FTIR) Analysis:-

Fig.4 show the spectrum in the infrared region of TiP_2O_7 and $LiTiP_2O_7$ as shown in Fig.4a-Fig. 4b, it was detected a broad band in the region of 3437 cm^{-1} and 3412 cm^{-1} which was attributed to symmetrical and asymmetrical -OH stretch, there is also a narrow and medium band in 1645 cm^{-1} that was assigned to H -O -H bond of water and a strong absorption at 1052 cm^{-1} which was attributed to $\nu(P=O)$ stretching. The band observed at 1400 cm^{-1} was attributed to δ (POH) stretching. The bands presented with values of $518, 532, 630$ and 663 cm^{-1} correspond to links O-Ti-O.

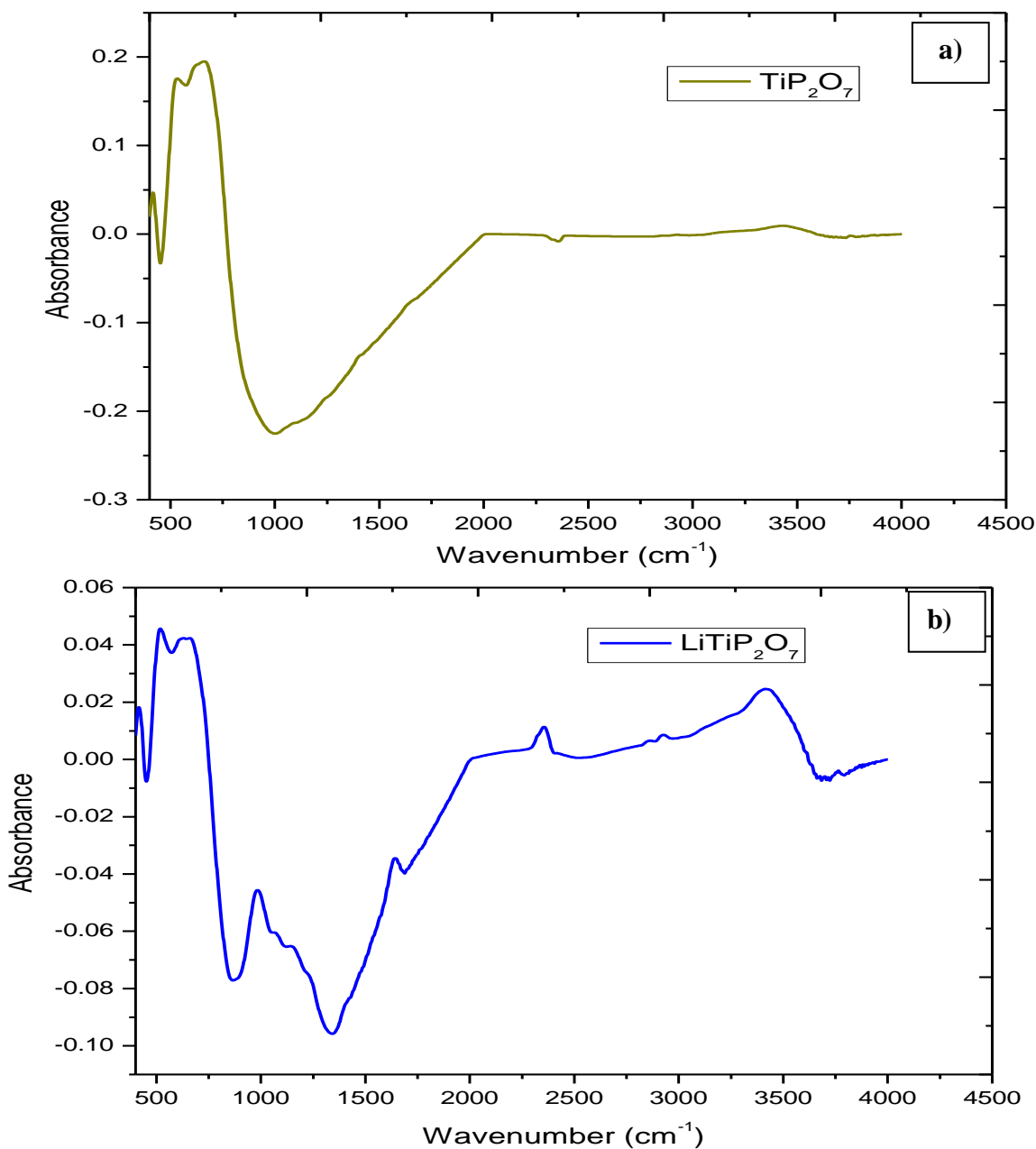
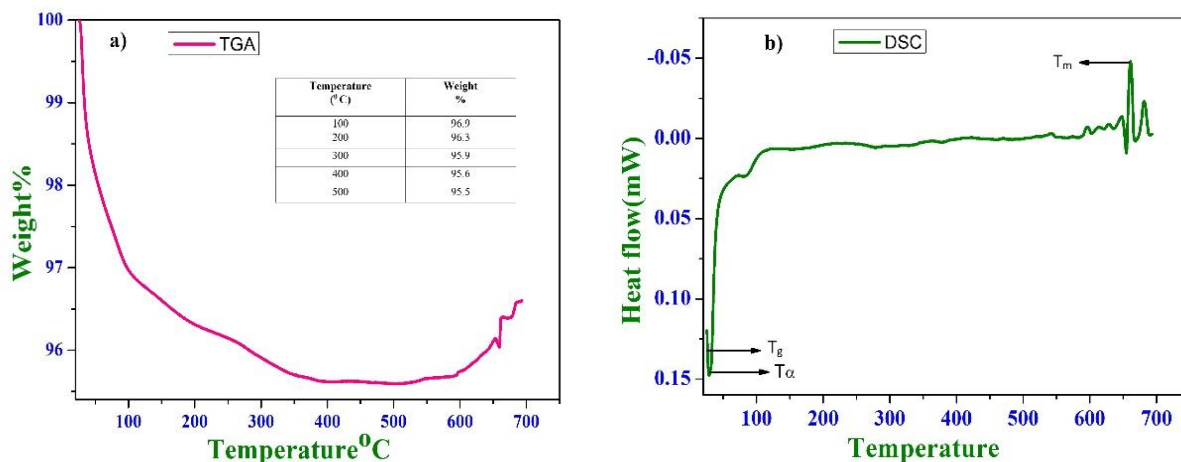
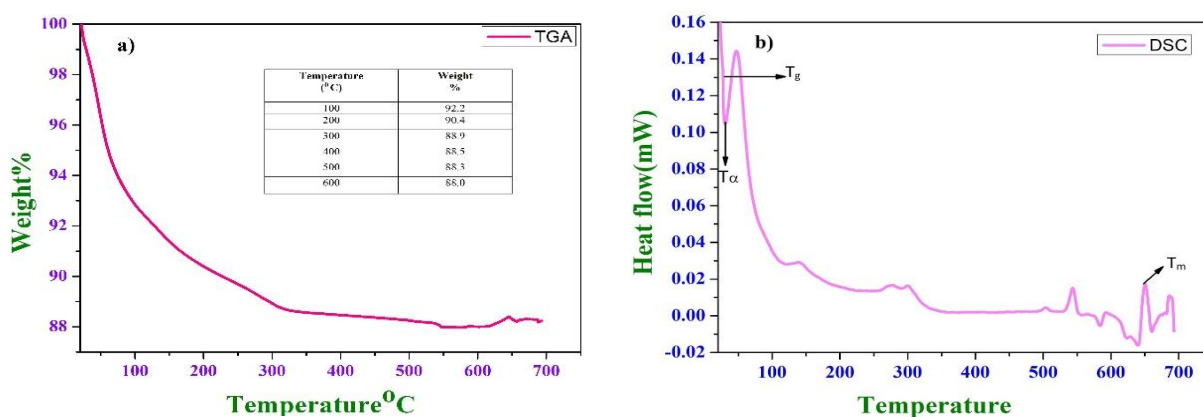


Fig. 4:-FTIR of a) TiP_2O_7 and b) LiTiP_2O_7

TGA and DSC analysis:-

TiP_2O_7 and LiTiP_2O_7 are very important to soft magnetic materials due to these materials are high magnetic permeability. The TGA thermo grams of TiP_2O_7 and LiTiP_2O_7 as shown in Fig.5a-5b. In Fig.5a-5b, the graph temperature v/s weight % loss decreases with increasing the temperature as mentioned in the graph. In this way, the LiTiP_2O_7 was thermally stable, so it is used as some opto-electronic device applications as compared to TiP_2O_7 . The thermal properties of the TiP_2O_7 and LiTiP_2O_7 was studied using differential scanning calorimetry (DSC) from room temperature to 800°C and the observed thermo grams are shown in the Fig.6a-6b. In Fig. 6a-6b, the melting temperature (T_m) of LiTiP_2O_7 identified more than 600°C. Thus, the thermal properties of LiTiP_2O_7 material gives a more information for opto-electronic applications compared to TiP_2O_7 which shows 500°C.

Fig. 5:- TGA and DSC studies of TiP_2O_7 Fig. 6:-TGA and DSC studies of LiTiP_2O_7

Electrical Properties:-

The Fig.7a-7d. Plots it can be seen that the conductivity increases slowly. This conduction can be attributed to localized charge carriers. According to localized model the electronics are strongly localized on cations. Theoretical work by several over the years has provided some understanding of conduction in oxides and transition metal compounds. For these materials, the interaction between electrons and optical phonons is strong and conduction is explained on the basis of polarons. It is observed that with increase in substitution of cations, the resistivity at room temperature decreases with decrease in porosity. This may be due to the fact that, as with decrease in porosity the conducting paths get available for charge carriers to jump from grain to grain. There may be a several factors responsible for relatively high value of resistivity including the formation of other secondary phases and relatively large values of porosity. The increase in porosity causes the separation between the grains. This separation may lead to difficulty in the conduction of free electrons across the grain boundaries. This type of behavior was observed [21]. The large value of dielectric constant ϵ' for small frequency due to polarization in dielectric structure, porosity, grain boundaries [22]. Better dc conductivity increases the performance of LiTiP_2O_7 as shown in Fig. 7b in various device application than compared to that of TiP_2O_7 (Fig. 7d) [23].

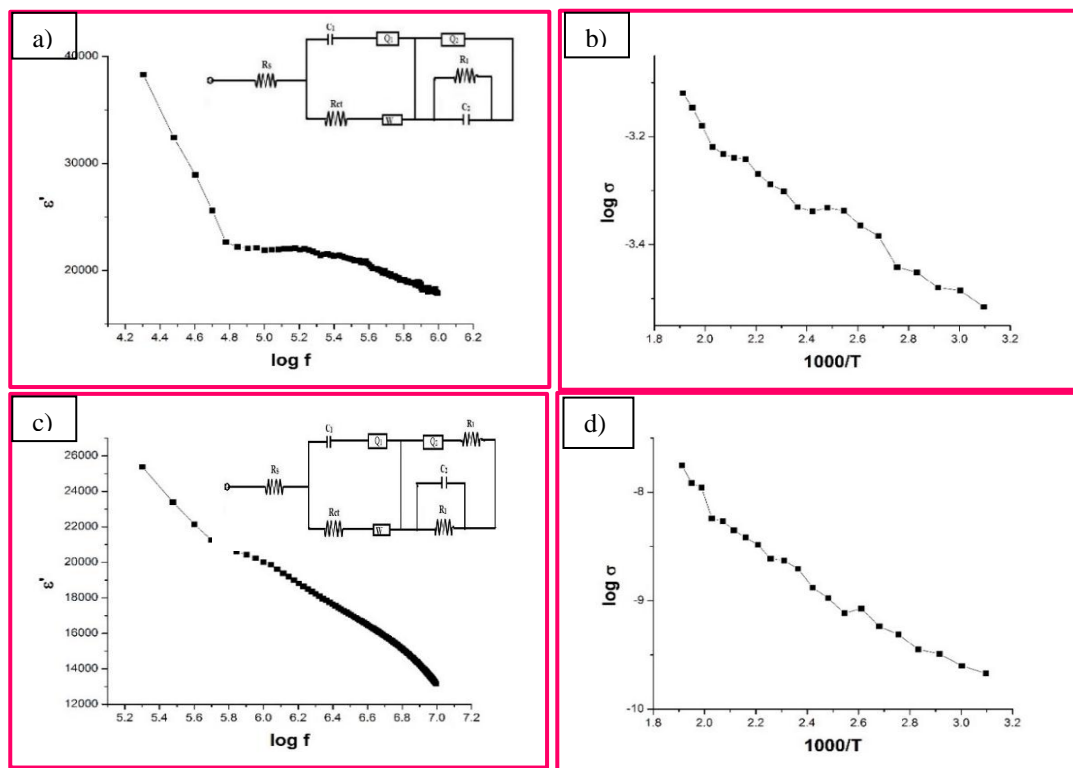


Fig.7 a) Nyquist with Equivalent circuit of TiP_2O_7 , b) Conductivity of TiP_2O_7 c) Nyquist with Equivalent circuit d) Conductivity of LiTiP_2O_7

Conclusion:-

Based on the experimental studies of TiP_2O_7 and LiTiP_2O_7 materials were synthesized by using soft hydrothermal method at moderate pressure and temperature conditions. From the P-XRD, Confirms the well crystalline rhombohedral phase for the prepared phosphates and all the peaks are characteristic of the LiTiP_2O_7 compound. SEM shows composition analysis of LiTiP_2O_7 samples shows that the grains are uniform and roundish in shape having a size in the range below 100 nm. FTIR spectra indicated that there is an increase in the degree of splitting and stretching of the vibration bands, whereas the splitting of vibration bands and polymerization of $[\text{PO}_4]$ decreased as the Li ions concentration increased. The TGA/DSC studies revealed that these materials display endothermic reactions due to the liberation of ligands and diffusion. The LiTiP_2O_7 was thermally stable, so it can be used for some opto-electronic device applications. The melting temperature (T_m) of LiTiP_2O_7 identified more than 600°C whereas TiP_2O_7 showed below 500°C . Better dc conductivity increases the performance of LiTiP_2O_7 as compared to that of TiP_2O_7 .

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