CHAPTER 5

Synthesis and characterisation of lithium tin oxide and vanadium tin oxide

5.1 Synthesis of lithium tin oxide

The tin dioxide and tin monoxide that have been prepared by soft chemistry and whereby conditions for their synthesis have been described (chapter. 3) are further reacted with lithium salts oxide to form lithium tin oxide. Lithium tin oxide was prepared using starting material $SnO_2.1.6H_2O$ and $SnO.9H_2O$ obtained at room temperature.

A mixture of tin dioxide (0.3 g) and lithium hydroxide (0.142 g) was ground in the mortar and then placed in a crucible, which was heated in the furnace at 650°C for 10 hours. The experiment was repeated with lithium nitrate in the place of lithium hydroxide.

In the third experiment, a ground mixture of lithium hydroxide (0.134 g) and tin monoxide (0.2 g) was put in ceramic crucible and heated in the furnace at 650°C for 10 hours.

The reaction at room temperature of both tin dioxide and tin monoxide with lithium hydroxide has been investigated using XRD. The mixture was put in the mortar, first was mixed by soft mixing by spatula and recorded with XRD and then was ground in the mortar

and recorded by XRD too.

5.2 Characterisation of lithium tin oxide obtained from tin dioxide and lithium hydroxide

5.2.1 X-ray diffraction

Fig. (5.1) shows the X-ray diffractogram of lithium tin oxide obtained using (a) lithium hydroxide and (b) lithium nitrate as the co-reactant. The X-ray diffraction peaks correlate well with those of JCPDS:31-0761 of dilithium stannate(IV), Li_2SnO_3. The results show that the use of tin dioxide $SnO_2.1.6H_2O$, prepared by the soft chemistry route that does not use commercial dihydride SnO_2, decreases the sintering temperature of preparation from 1000°C to 650°C. The tin dioxide is of a smaller particle size and therefore a larger surface area-to-volume ratio that should increase its reactivity.

In Fig. (5.1), the X-ray diffractogram shows that the lithium tin oxide prepared from $LiOH.H_2O$ presents better crystallinity than the lithium tin oxide prepared from $LiNO_3$. Hence in the following experiments only lithium tin oxide prepared using $LiOH.H_2O$ was used for characterisation.

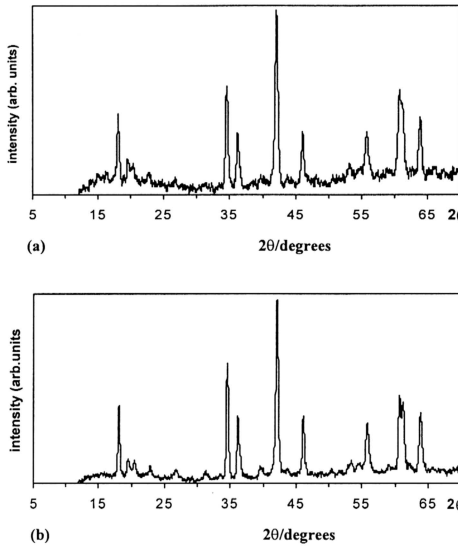


Fig. (5.1): XRD pattern of lithium tin oxide prepared (a) using $LiNO_3$, (b) using $LiOH.H_2O$

Fig. (5.2) shows the X-ray diffractogram of lithium tin dioxide prepared by $SnO_2.1.6H_2O$ and $LiOH.H_2O$ at 550°C for 5 hours. Some peaks are observed in the diffractogram, which indicates that the reaction has already commenced even at a lower temperature and shorter heating time.

Fig (5.3) shows the X-ray diffractogram of the physical mixture of tin dioxide and lithium hydroxide (a) when they are mixed by using a spatula (soft mixing); (b) when they are ground and kept at room temperature for three days. Fig. (5.3, a) shows the broad peaks of tin dioxide as well as other few sharp, intense peaks. The latter peaks do not correlate with those of $LiOH.H_2O$ and Li_2O, Fig. (5.4). Fig. (5.3, b) shows other different peaks, which can not be assigned to either tin dioxide or lithium hydroxide. This observation proves that by merely mixing tin dioxide with lithium hydroxide, a spontaneous reaction has occurred; when the mixture is well ground and kept for three days new peaks appear that must be a consequence of reaction between the two materials (Melghit et al, 1999; Idota et al, 1995; Genrts et al, 1984).

5.2.2 SEM photograph

The photograph Fig. (5.5) shows that the sample is composed of agglomerates of small spherical particles having approximately 1μm diameters.

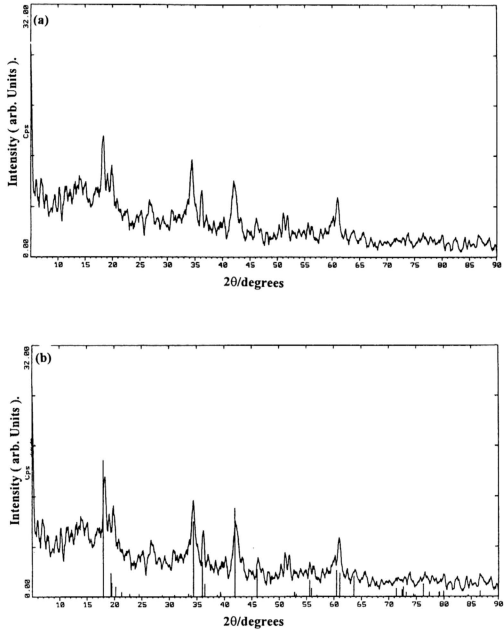


Fig. (5.2): XRD pattern of (a) tin dioxide mixed with lithium hydroxide heated at 550°C for 5 hours (b) Superimposed with JCPDS reference

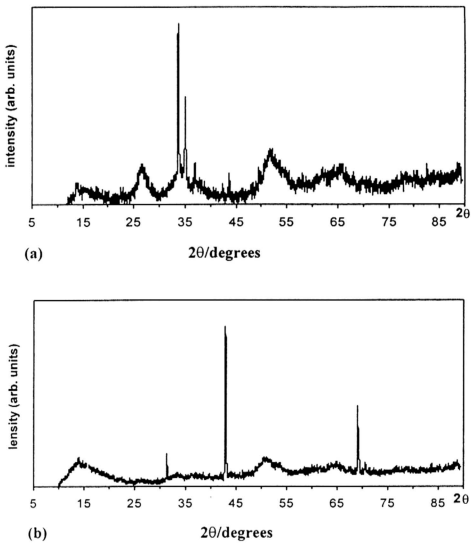
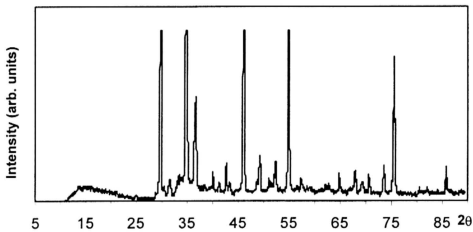
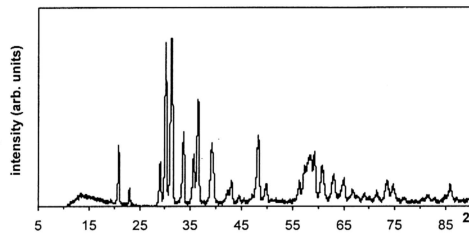


Fig (5.3): XRD pattern of tin dioxide mixed with lithium hydroxide (a) by mixing with spatula, (b) by grinding after three days



(a)



(b) 2θ/degrees

Fig. (5.4): XRD pattern of (a) $LiOH.H_2O$, and (b) Li_2O

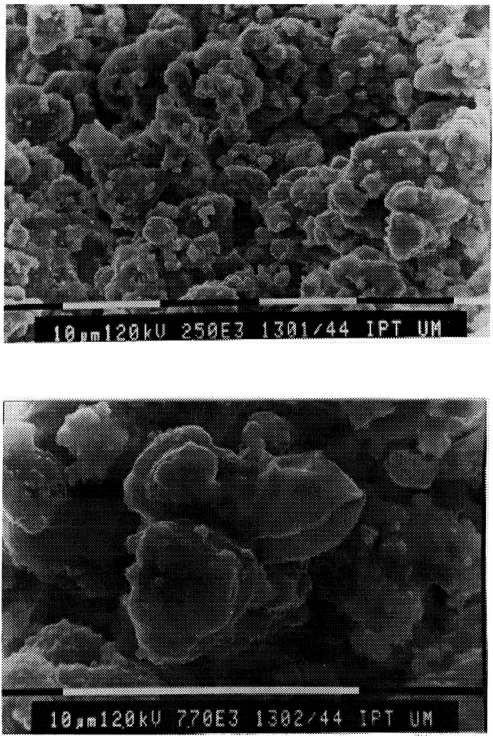


Fig. (5.5): SEM Photographs of lithium tin oxide.

5.2.3 Thermal analysis

Fig. (5.6) shows DSC thermograms (under nitrogen gas) of (a) lithium hydroxide, (b) tin dioxide and (c) a physical mixture of tin dioxide with lithium hydroxide. The DSC curve of lithium hydroxide shows two valleys at about 90°C and 420°C. The first valley corresponds to the loss of the lattice water and the second to the loss of coordinated water accompanied with the decomposition of LiOH to Li_2O. The DSC curve of tin dioxide shows only a single valley at about 80°C, which corresponds to the loss of lattice water. The DSC curve of the physical mixture tin dioxide-lithium hydroxide shows two peaks at 80°C and 370°C. The first valley correlates well with the signal of $SnO_2.1.6H_2O$ and $LiOH.H_2O$. The second peak is due to melting of the mixture. The peak at 420°C in the lithium hydroxide curve is absent, since the melting point has been reduced to 370°C on addition of tin oxide. The DTA curve Fig. (5.6), performed between room temperature and 800°C in air does not show any other peaks above 450°C.

After heating the mixture at 550°C, the new phases have disappeared and lithium tin oxide is formed.

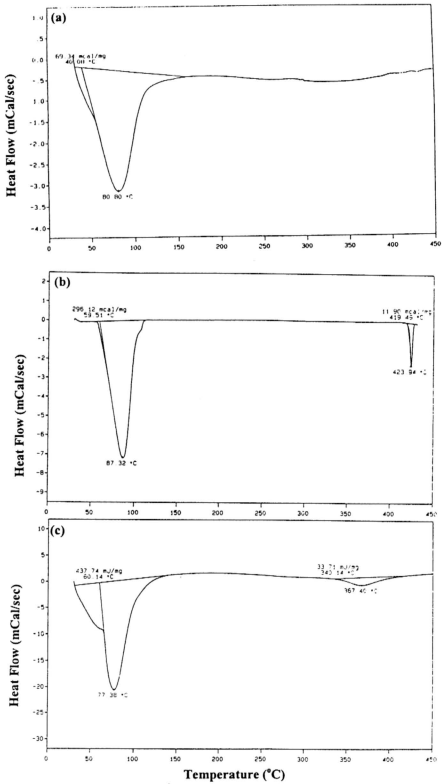


Fig. (5.6): DSC curves of (a) tin dioxide, (b) lithium hydroxide and (c) tin dioxide mixed with lithium hydroxide.

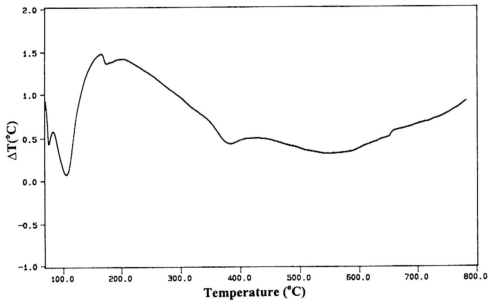


Fig. (5.7): DTA curve of tin dioxide mixed with lithium hydroxide.

5.2.4 FTIR

Fig. (5.8) depicts the FTIR spectrum of (a) tin dioxide, (b) lithium hydroxide and (c) tin dioxide mixed with lithium hydroxide at room temperature before heating, and (d) tin dioxide mixed with lithium hydroxide after heating at 650°C for 10 hours. The IR of tin dioxide shows a broad absorption band characteristic of water at 3400 cm^{-1}. The IR of lithium hydroxide shows, beside the water band, several bands at about 1150, 1006, 865, 600 (Sn-O vibration) and 500 cm^{-1}. The IR spectrum of tin dioxide mixed with lithium hydroxide, before heating Fig. (5.8, c), shows a mixture of the absorption bands that are found in both tin dioxide and lithium hydroxide spectra. The IR spectrum of the mixture after heating Fig (5.8, d) shows approximately the same peaks as before heating; the intensities of some peaks are more enhanced (e.g., the peak at 860 cm^{-1}).

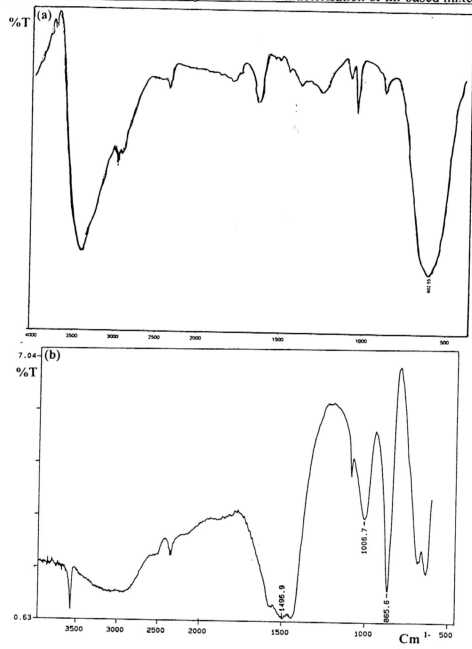


Fig. (5.8): FTIR spectra of (a) tin dioxide $SnO_2.1.6H_2O$, (b) lithium hydroxide $LiOH.H_2O$.

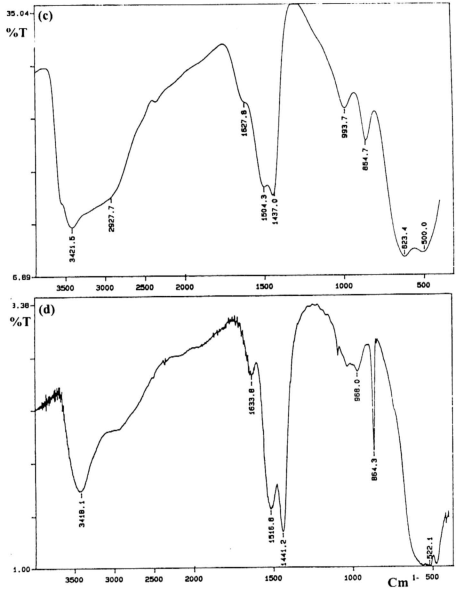


Fig. (5.8): FTIR spectra of tin dioxide mixed with lithium (c) before heating, (d) after heating at 650°C

5.3 Characterisation of Lithium tin oxide obtained from tin monoxide and lithium hydroxide

5.3.1 X-ray diffraction

Fig. (5.9) depicts the X-ray diffractogram of lithium tin oxide prepared from tin monoxide (SnO. $9H_2O$) as reactant. The material shows slightly better crystallinity than the lithium tin oxide prepared from tin dioxide ($SnO_2.1.6H_2O$).

Fig. (5.10) shows the X-ray diffractogram of tin monoxide mixed with lithium hydroxide; (a) when they are mixed softly; (b) when they are ground and kept at room temperature for three days. Fig. (5.10, a) presents new sharp peaks that can not be attributed to either tin monoxide or lithium hydroxide. Also Fig. (5.10, b) shows peaks different from those of Fig. (5.10, a). The differences in the diffractograms suggest that by merely mixing lithium hydroxide with tin monoxide, a spontaneous reaction occurs. Such a spontaneous reaction has also been observed (Wang et al, 1998; Barrett et al, 1971; Goldstein and Tok, 1971) in the reaction between stannous halides and cesium halides. The starting reagents are colourless, but upon mixing, orange to black compounds are obtained that show a diffraction pattern identical to those of perovskites.

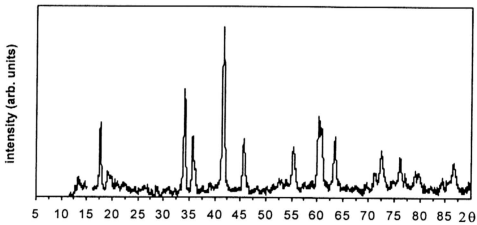


Fig. (5.9): XRD pattern of lithium tin oxide obtained by using tin monoxide and lithium hydroxide

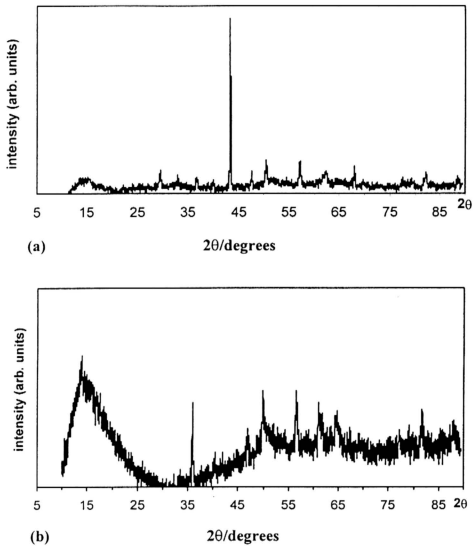


Fig. (5.10): XRD pattern of (a) tin monoxide mixed with lithium hydroxide. by mixing with spatula, (b) by grinding.

5.3.2 Thermal analysis

Fig. (5.11) shows the DSC thermograms (under nitrogen gas) of (a) lithium hydroxide and (b) tin monoxide mixed with lithium hydroxide. The thermogram of lithium hydroxide shows two valleys at about 90°C and 420°C whereas that of tin monoxide mixed with lithium hydroxide Fig. (5.11, b) shows two valleys at about 70°C and 200°C. Peaks at 50°C in the DTA Fig. (5.11, c) of tin monoxide and at 420°C in the thermogram of lithium hydroxide are absent in the DSC thermogram of the mixture.

Fig. (5.12) shows the DTA thermogram of the mixture performed between room temperature and 700°C. Besides the two peaks at about 100°C and 220°C, a small peak at about 190°C is the result of the oxidation of tin monoxide.

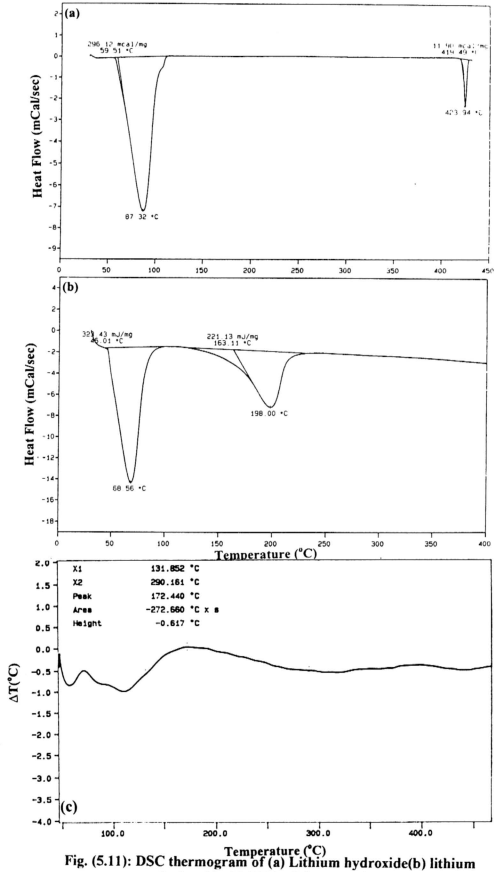


Fig. (5.11): DSC thermogram of (a) Lithium hydroxide(b) lithium hydroxide (c) DTA of tin monoxide

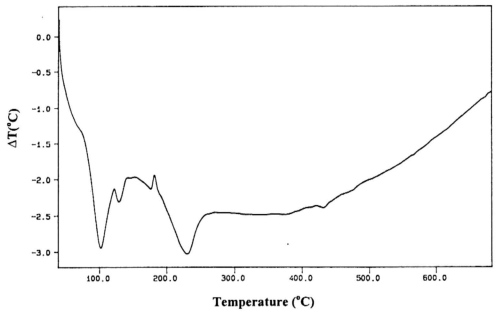


Fig. (5.12): DTA of tin monoxide mixed with lithium hydroxide.

5.3.2 FTIR

Fig. (5.13) depicts the IR spectrum of (a) tin monoxide; (b) lithium hydroxide; (c) tin monoxide mixed with lithium hydroxide at room temperature, and (d) tin monoxide mixed with lithium hydroxide and heated at 650°C for 10 hours. The IR spectrum of tin monoxide Fig. (5.13, a) is similar to that of tin dioxide Fig. (5.8, a) but with some extra bands at 1024 cm^{-1} and 1245 cm^{-1}; The IR spectrum of the mixture Fig. (5.13, c) shows other than the water and lithium hydroxide bands new bands at about 1830, 910, 750, 660 and 440 cm^{-1}. These new peaks disappear after heating the mixture. This implies the formation of lithium tin oxide Fig. (5.13, d). The IR spectrum of the mixture after heating corresponds to that of lithium tin oxide, and it is similar to the spectrum obtained using tin dioxide as reagent Fig. (5.8, d). The new absorption bands in IR spectra disappear after heating, and the presence of a new compound is supported by the X-ray diffractograms, which shows the formation of new phases.

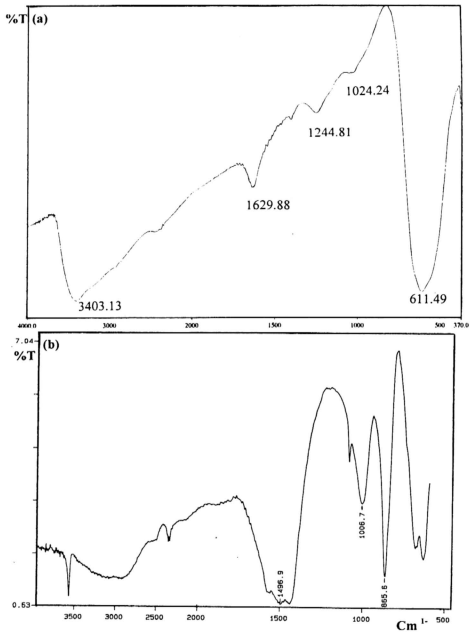


Fig. (5.13): FTIR spectra of (a) tin monoxide, (b) lithium hydroxide

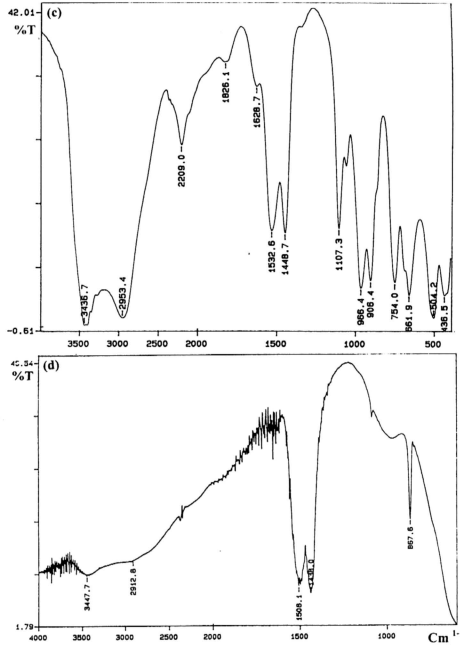


Fig. (5.13): FTIR spectra of (c) tin monoxide mixed with lithium hydroxide before heating, (d) after heating at 650°C.

5.4 Alternative method for the preparation of lithium tin oxide and X-Ray characterisation

The tin dioxide that was prepared in (chap 3) was suspended in boiling water (0.3 g) and a weighed amount of lithium hydroxide (0.142 g) added to this suspension. After stirring the mixture for 10 hours, the water was evaporated, and then the product was put in the ceramic crucible in the furnace for 650°C for 10 hours.

The X-ray diffractogram of the dried product, Fig. (5.14, a) shows only broad peaks assigned to tin dioxide, which indicates that this solid phase is composed essentially of amorphous lithium hydroxide and semi amorphous tin dioxide. After heating at 650°C for 10 hours, lithium tin oxide is obtained Fig. (5.14, b). The direct preparation of lithium tin oxide by the above method was not quite successful.

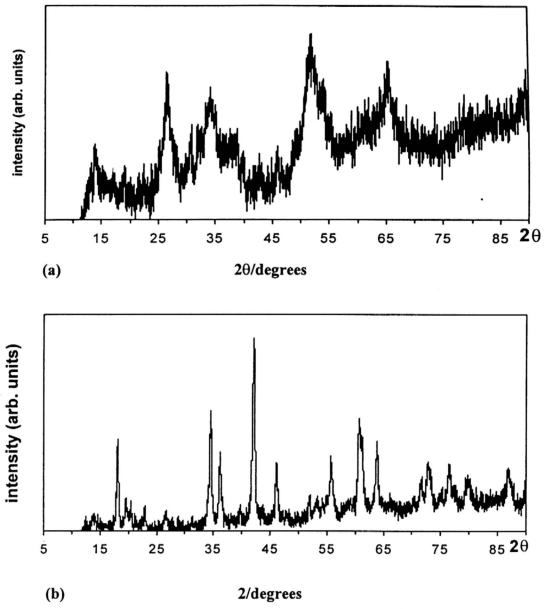


Fig. (5.14): XRD pattern of lithium tin oxide obtained by using a solution method (a) after evaporation of water (b) after heating at 650°C.

5.5 Synthesis of vanadium tin oxide

Wen and Huggins, (1980) have prepared vanadium pentoxide using the sol-gel method. The synthesis of V_2O_5. xH_2O process is based on the acidification of a vanadium salt solution by passing it through an ion-exchange resin. (Courtney and Dahn, 1997).

Recently, Melghit et al, (1999), have prepared vanadium tin oxide using tin metal and vanadium oxide, their work revealed that, the solid solution of vanadium tin oxide contains only a small amount of vanadium. This was also observed by Volkov and Buldakova, (1994). XRD and chemical analysis have shown that 18mol % vanadium can be incorporated into the tin oxide lattice

In this work the vanadium tin oxide has been prepared using the "home-made" tin dioxide and vanadium pentoxide prepared using soft chemistry method.

The vanadium pentoxide was prepared by the sol-gel method. A solution of sodium metavanadate is passed through an ion-exchange column to give an acidic solution that forms a brown gel (vanadium oxide) after 48 hours. The method employed is same as that of Znaidi et al, (1989) and Aldebert et al, (1991). However the concentration of sodium meta-vanadate is half of that used by the former and the latter produced the vanadium pentoxide gel by polymerization of decavanadic acid. The mixture of vanadium oxide xerogel and semi-amorphous tin dioxide in the weight ratio of 5:95 was placed in ceramic crucible and

heated in the furnace at 500°C for 5 hours. A yellow material was obtained. Fig. (5.15) schematically shows the process leading to vanadium tin oxide. Starting from $NaVO_3$ to the final material including the thermal treatment of tin dioxide and vanadium pentoxide.

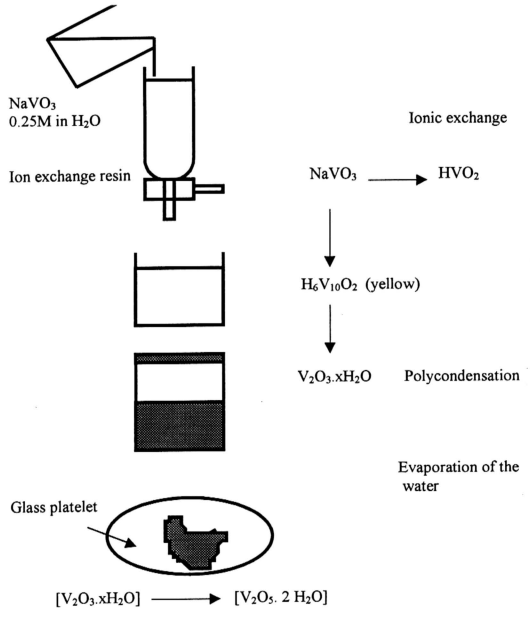


Fig. (5.15): Vanadium synthesis through the sol-gel process

5.6 Characterisation of vanadium tin oxide

Fig. (5.16, a) shows the X-ray diffractogram of vanadium pentoixde superimposed with JCPDS data: 41-1206 and t Fig. (5.16, b) shows the X-ray diffractogram of vanadium tin oxide; the sharpness of the peaks implies that the compound exists in the crystalline phase. The peaks are slightly shifted compared with those of tin dioxide (section 3.2.1). This is attributed to the incorporation of vanadium in tin dioxide.

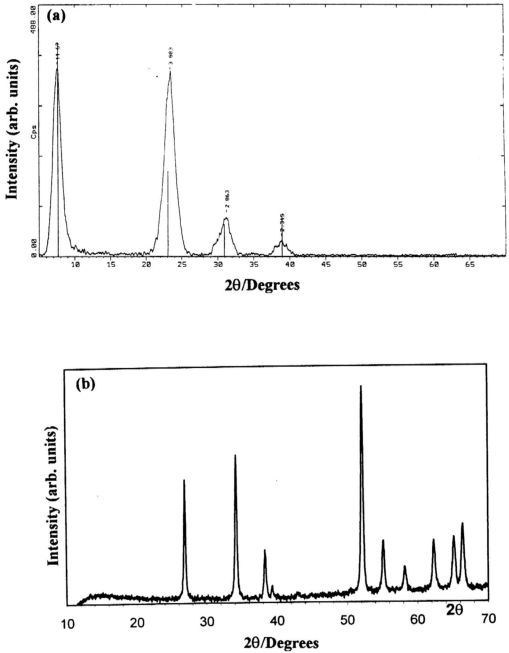


Fig. (5.16): XRD pattern of (a) vanadium pentoxide superimposed with JCPDS , (b) vanadium tin oxide