

Synthesis and Processing of SnO₂, CaSnO₃ and Ca₂SnO₄ Nanopowders by Solid-State Reaction Technique

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ABSTRACT: *The nanopowders of SnO₂, CaSnO₃ and Ca₂SnO₄ in the size rang of 5-70 nm have been prepared using solid-state reaction technique. The technique is convenient and inexpensive in comparison to the conventional routes of compound prepared and processing where, many steps of mixing and annealing are involved. Formation of resultant compounds was explained on the basis of reaction taken place between SnCl₄. 5H₂O, CaCl₂ and Ca(OH)₂. It was found that Tin oxide, calcium stannate and calcium orto stannate have been prepared at calcinations temperature 400 °C/4 h by weight ratio of (Sn:Ca) 2:1, 1:1 and 1:2, respectively. Characterization of species was carried out using X-ray diffraction, SEM and TGA analysis. Investigation of samples revealed that, agglomerations of well connected, small grains lumped together with large number of pores have been formed. The XRD pattern analysis has shown that the change in crystalline sizes after calcining at various temperatures. Due to change in weight ratio of Sn:Ca from 2:1 to 1:1, the crystal structure has been changed from tetragonal rutile to perovskite.*

KEY WORDS: *Nanopowder, Tin oxide, Orto-stannate, Calcium-stannate, Solid- state reaction.*

INTRODUCTION

Alkaline earth stannates have gained considerable attraction in recent years because of thermal stability in air, and strong physical and chemical interaction with absorbed species. The materials have a variety of applications in ceramic dielectrics [1,2], gas-sensing materials [3] and battery electrode bodies [4]. Due to this fact that oxygen atoms absorbed on the surface of the metal oxide, particle influences its electrical properties by producing an electron-depleted space-charge layer in the space-charge region of the species.

It is therefore, interested to study materials in details. Among the metal oxides, SnO₂ acts as an important base material for gas sensing devices. Similarly, Calcium stannate in a pure and in doped form has been shown a gas sensing materials [5-7]. In literature survey, we find many articles about properties and behaviour of these materials, but no thoroughly and reliable studies are available on synthesis and thermodynamic stability of them in the CaO, SnO₂, CaSnO₃ and Ca₂SnO₄ configurations. According to JCPDS standard cards,

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compounds such as $\text{Ca}_3\text{Sn}_2\text{O}_3$ and Ca_2SnO_4 with a given ratio of Sn : Ca have been reported. However, detailed information on processing and micro structural characteristics of these compounds has not been given. Varieties of techniques are given for preparation of SnO_2 material. For example sol-gel method [8]. One-step solid-state reaction [9]. Also, for CaO-SnO_2 compound, the methods such as hydro thermal synthesis and wet-chemical are reported [10]. In this work, the solid-state reaction technique was employed to prepare, SnO_2 , CaSnO_3 and Ca_2SnO_4 through different weight ratio Sn : Ca to obtain nano-crystalline powders at ambient temperature in air to give nanocrystals with narrow size distribution. Solid-state reactions were found to give spherical products of uniform size and shape in over 90 % yields. Nanocrystals of many oxides, oxalates, carbonates and hydrated metal salts have also been prepared at ambient temperature in air through this technique [3,9].

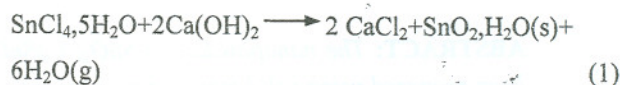
The solid state reaction is a kind of mechanochemical technique in which a chemical reaction takes place during grinding solid precursors namely, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, CaCl_2 , Ca(OH)_2 . The formation of salt by-product (CaCl_2), provide an effective driving force for the small particles. The growth of the particles is inhibited by the salts produced in the solid-solid state reaction. In other words, CaCl_2 and several water molecules are produced in the current reaction. In general, the water in hydrated metal salts apparently play a critical role in forming these nano crystals. The exact role of water is not clear. But the presence of water may also lower the activation energy and the reaction temperatures. Most hydrated metal salts have defects and relatively lower lattice energies. Presence of water could either increase the number of defects or interfacial diffusion, or reducing the activation energy and increasing reaction rates [10]. Thus, the structures of products by solid-state reaction depend on nucleation and growth of the reaction products. Furthermore, diffusion of solid particles of reactants at ambient temperature is often short-range, and thus helps yield nano-sized products.

Although the solid-state route is inexpensive and seems to be simple, but the important point is to establish correlation between the main parameters like synthesis, processing and micro structural of these materials. The role of calcium dopant as crystallite growth inhibitor in the resultant compounds was studied by considering different weight ratio of Sn to Ca.

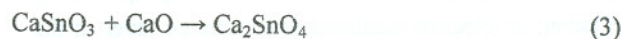
EXPERIMENTAL

Preparation of SnO_2 , CaSnO_3 and Ca_2SnO_4 nanopowders

The powders of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.01 mol, 3.5 g), Ca(OH)_2 (0.04 mol, 2.96 g) and CaCl_2 with 99.995 % purity supplied by Aldrich, were used as starting solid materials. The initial powder sizes were in sub- micron range. The powders were accurately weighed and dry mixed in three different preparative categories with Sn:Ca weight ratio of 1:1, 1:2 and 2:1 to yield CaSnO_3 , Ca_2SnO_4 and SnO_2 , respectively. Each of this preparative mixture was individually ball-milled at room temperature for 30 minutes in air-tight polystyrene bottle using zirconia's balls as a milling medium. The formation of SnO_2 nanopowder via solid-state reaction takes place according to following formula:



The reaction started readily during the mixing process accompanied by emission of water vapor from the surface. And precipitation of the salts leads to formation of walls surrounding the nanoparticles to keep them from growing. The product was washed thoroughly with hot distilled water, treated in an ultrasonic bath for ten minutes and then centrifuged (8000 rpm) for about 15 minutes. The operation was repeated many times until no Cl^- anion could be detected in the solution containing AgNO_3 (0.10 mol). The yield was calcined at different temperatures between 200 °C to 1000 °C for different times. It was found that four hours calcinations led to better performance, where, the powder sizes of SnO_2 , CaSnO_3 and Ca_2SnO_4 were obtained in the range of 4 to 70 nanometers. Thus, four hours calcinations time was kept constant throughout the experiments. Under above mentioned experimental condition, the white SnO_2 powders are prepared, its yield was 93 %. Tin oxide subsequently reacted with CaO produced under experimental condition to form CaSnO_3 and Ca_2SnO_4 , as shown below:



Where, CaO acts as inhibitor [11]. Their yields were 92 % and 91 %, respectively. The table 1 summarizes the composition legends of products.

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Table 1: Compounds formation by different weight ratio.

Nanopowder	Weight (mol)	Chemical formula	Weight ratio
CaSnO ₃	3.5g (0.04mol)	SnCl ₄ .5H ₂ O	1:1
	1.11g (0.04mol)	CaCl ₂	
	2.96g (0.01mol)	Ca(OH) ₂	
Ca ₂ SnO ₄	3.5g (0.01mol)	SnCl ₄ .5H ₂ O	1:2
	2.22g (0.02mol)	CaCl ₂	
	5.92g (0.08mol)	Ca(OH) ₂	
SnO ₂	7g (0.02mol)	SnCl ₄ .5H ₂ O	2:1
	1.11g (0.01mol)	CaCl ₂	
	2.96g (0.04mol)	Ca(OH) ₂	

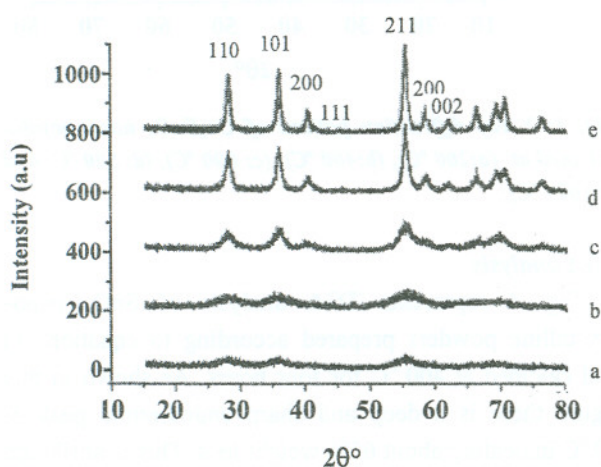


Fig. 1: X-ray diffraction pattern of tin oxide nanopowder calcined at: (a: 200 °C), (b: 400 °C), (c: 600 °C), (d: 800 °C) and (e: 1000 °C).

Measurements and characterization

The characterization of products was carried out by means of X-ray diffractometry (XRD), model PW1800 Philips using monochromatic CuK α radiation ($\lambda=0.154$ nm and θ from 10 to 80) and the diameters of the resultant nanopowders were determined from XRD line-broadening measurement from the Scherrer's equation:

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

Where λ is the wave length (Cu K α), β the full width at the half maximum line and θ is the diffraction angle.

The micro structural feature of nanopowders was studied by means of SEM, model XL-30 Philips. In the case of powders, the specimen was evenly sprinkled on the glued surface of an Al stub. In case of solid target a uniform thin film of gold was evaporated on the surface to avoid electrostatic charging during microscopic viewing. TGA of nanopowders was examined in O₂ on a TA-Int.2100 thermal analyzer at a heating rate 20°C min⁻¹ from room temperature to 1000 °C.

RESULTS AND DISCUSSION

Crystalline structure

Fig. 1 shows XRD pattern of nano tin oxide samples as prepared with 2:1 Sn to Ca ratio and calcined at temperature range of 200 °C to 1000 °C. It is obvious from the figure that, the peaks are sharpened with increase of temperature, indicating bigger crystal size of SnO₂ powders comparatively. This figure also confirms phase purity and tetragonal rutile crystalline structure of SnO₂ produced from solid-state reaction with various degree of crystallinity. The mean diameter of SnO₂ nanopowders was determined from the width of the (211) diffraction peak. Li *et al.* [3] and Min, B. K., Choi, S. D., [11] have also employed the same relation to evaluate nanoparticle size of SnO₂ prepared by two steps solid-state reaction and chemical growth technique, respectively. The effect of calcinations temperature on powder size of the samples is summarized in table 2. By comparing the intensities of XRD peaks in the Fig. 1, also, referring to table 2, it is realized that, the powder diameters at 200 °C is much smaller than the other elevated temperatures. Moreover, our further investigation on the gas sensor properties of the SnO₂ species prepared under the above mentioned condition revealed that, very good sensing response was obtained at 400 °C calcinations temperature. On account of this fact, calcinations temperature of 400 °C was adopted for further studies.

Figs. 2 and 3 illustrate X-ray diffraction patterns of CaSnO₃ and Ca₂SnO₄ nanopowders prepared from SnCl₄.5H₂O and CaCl₂ with Sn : Ca weight ratio of 1:1 and 1:2, respectively. Variation of crystalline powder diameters with calcinations temperature are summarized in the table 2. The effect of temperature on the both samples is very much similar to that of SnO₂ sample. This means that, yields are in single phase, matching with standard

Table 2: Effect of calcinations temperature on the nanopowder diameters.

Calcinations temperature (°C)	200	400	600	800	1000
d_{SnO_2} (nm)	3.36	6.99	14.23	28.00	32.00
d_{CaSnO_3} (nm)	16.59	35.60	49.80	66.35	66.37
$d_{\text{Ca}_2\text{SnO}_4}$ (nm)	14.00	24.00	39.00	49.80	36.17

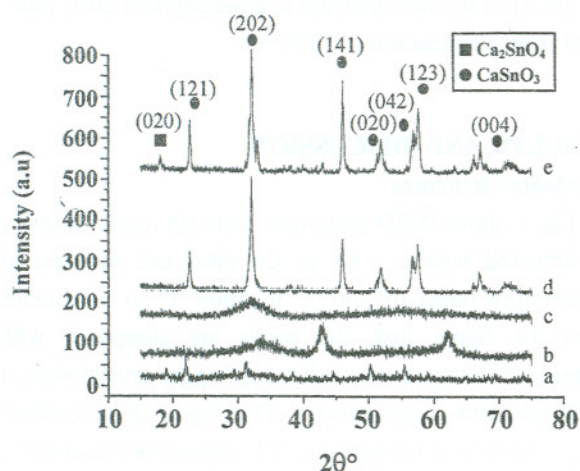


Fig. 2: X-ray diffraction pattern of CaSnO_3 nano powder calcined at: (a: 200 °C), (b: 400 °C), (c: 600 °C), (d: 800 °C) and (e: 1000 °C).

JCPDS cards and their grain diameters are significantly depended on calcining temperature. It was inferred from the results that, preparation of resultant powders via solid-state reaction route according to equation (1) is carried out at relatively lower calcined temperature. This is encouraging in the case of solid-state reaction comparing to the other technique, where usually larger grain are formed due to the use of higher temperature and several repetitions of annealing and mixing steps. For example, Mandal *et al.* [12], and Parkash *et al.* [13] have reported that solid-state synthesis of Ca, Sr and BaSnO_3 by mixing respective metal carbonate and dioxide in acetone medium, calcining at 1200 °C /4h and sintering at 1300 °C /12h, repeating the process several times. On the contrary, it was found in this work, that SnO_2 , CaSnO_3 and Ca_2SnO_4 could be easily reached with inexpensive and simple procedure. We attribute this achievement in the present case to the use of metal nitrate as one of the precursors rather than the conventionally employed carbonate. The metal nitrates have more favorite decomposition kinetics compared to their carbonate counter-parts.

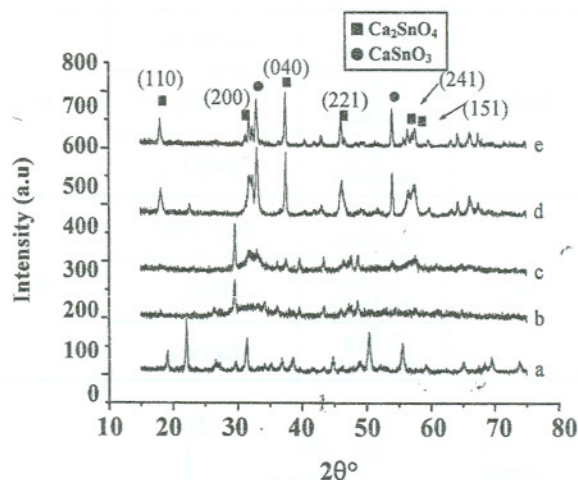


Fig. 3: X ray diffraction pattern of Ca_2SnO_4 nano powder calcined at: (a:200 °C), (b:400 °C), (c: 600 °C), (d: 800 °C) and (e:1000 °C).

TGA analysis

Fig. 4 represents TGA analysis of SnO_2 nanocrystalline powders prepared according to equation (1) and calcined at 400 °C for four hours. As shown in this figure there is a deep and sharp endothermic peak at 70 °C indicating about 65% weight loss. This is attributed to the evaporation of water from the surface of sample. Also, a continues weight loss occurred at Ca. 300 °C onwards could be assigned to exothermic effect in reaction (1), has resulted in decomposition of $\text{Sn}(\text{OH})_2$ in the preparation process. This was accompanied by a weight loss 4 % from 70 °C to 300 °C temperature shift. As a result, the total weight loss of 70% consistence with calculated 69 % of removing H_2O from SnO_2 . And finally, at 400 °C, the status becomes steady state, where SnO_2 nanopowder would appear. On set growth of SnO_2 from XRD pattern of Fig.1 is in good agreement with TGA studies.

Morphology of nano powders

The scanning electron microscopy (SEM) images of SnO_2 , sample prepared under above mentioned condition

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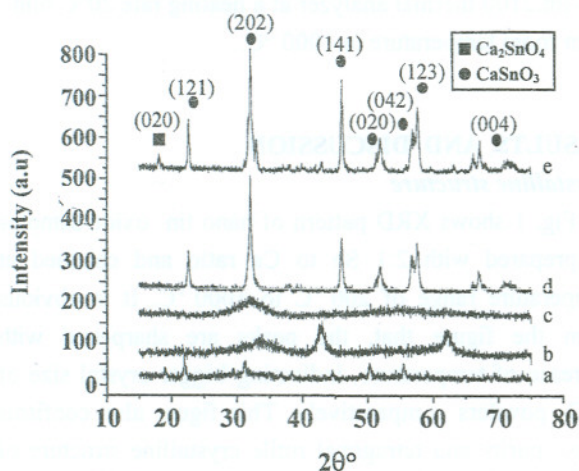


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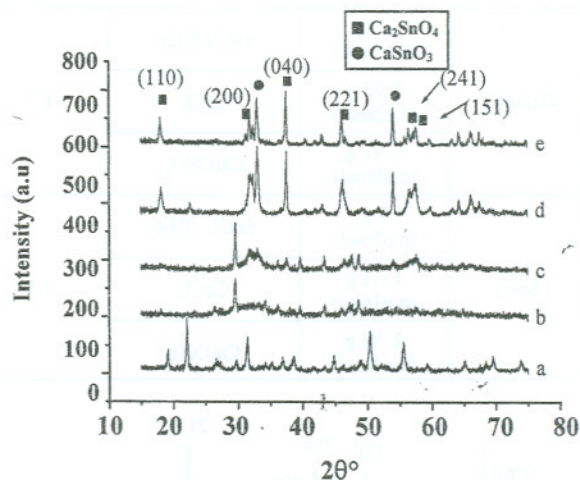


Fig. 3: X ray diffraction pattern of Ca_2SnO_4 nano powder calcined at: (a:200 °C), (b:400 °C), (c: 600 °C), (d: 800 °C) and (e:1000 °C).

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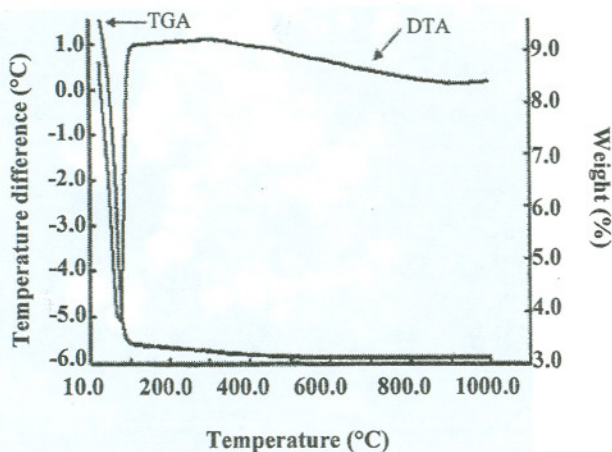
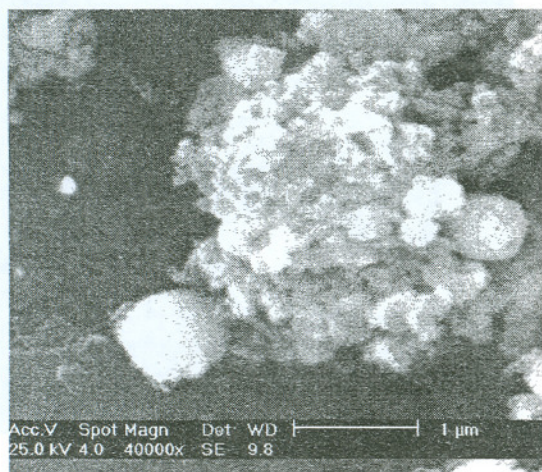
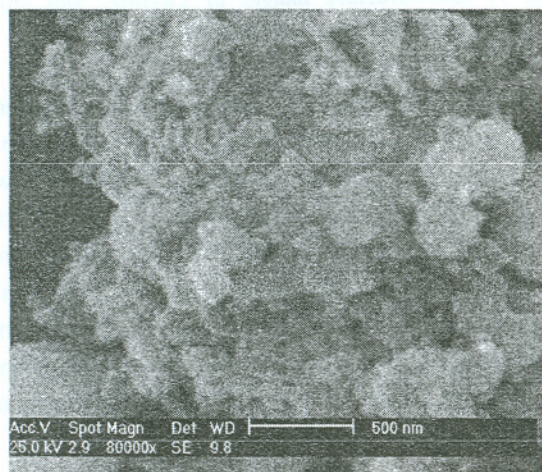


Fig. 4: TGA diagram of tin oxide nanopowder calcined at 400 °C.



(a)



(b)

Fig. 5: Microstructure images of SnO_2 with different magnifications: a: 40000x and b: 80000x.

is given in Fig. 5 (a, b) with different magnifications. The agglomeration of 50-70 (nm) connected grains lumped together with large number of pores, and very few individual grains could be observed. It may also be noted that diameter of the nanopowders calculated from x-ray analysis is different than the diameter obtained from SEM measurement. This could be due to picture taken by choosing a selected area in SEM image.

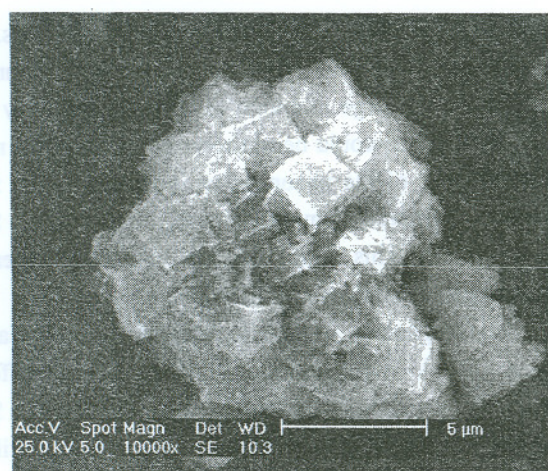
The morphology of CaSnO_3 sample obtained via 1:1, Sn to Ca ratio is presented in Fig. 6 (a, b) with different magnifications. Deficiency of Sn with compare to SnO_2 sample is led to change particle shape from rutile to provskite structured cubes Fig. 6 (a). Coalescence of small grains together with their subsequent densification without much grain growth is seen in Fig. 6 (b). It should be noted that due to loss of tin as volatile SnO_2 from the surface of the sample, the porosity of CaSnO_3 , is interesting in the sense that, it contains well-connected porosity and still smaller grains. It has been documented that such structures with

Small crystalline size, well-formed intergranular connectivity and open channels are desired features of gas-sensing devices. This is also important to remark that, if an electrical device such as capacitors is to be fabricated from these materials, whose instantaneous and long-term performance is influenced by the remnant porosity in the bulk, very high degree of densification with zero porosity is required.

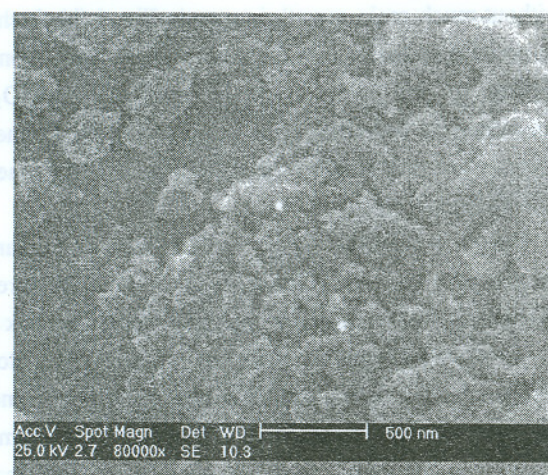
Fig. 7 (a, b) shows the SEM micro structural images of Ca_2SnO_4 prepared by 1:2 Sn, Ca ratio with two different resolutions. Strong agglomeration accompanied with spherically shaped grains was formed. However, further grain growth was not seen. This restricted grain growth is attributed to the rather smaller particle size in the powder obtained via solid-state reaction route and sustained the experimental condition. Unlike the CaSnO_3 , particle shape was not cubes, but they were spherical. According to our observations, the material obtained after calcinations (400 °C) revealed that the raw powder derived from solid-state reaction route were of very small (sub-micron) particles size .

CONCLUSIONS

In material synthesis and processing it is well known that, each of individual components such as the bulk, grain, grain boundary, phase purity, inclusions and etc.



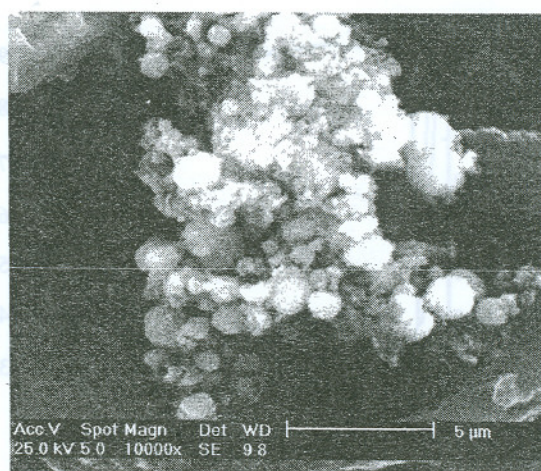
(a)



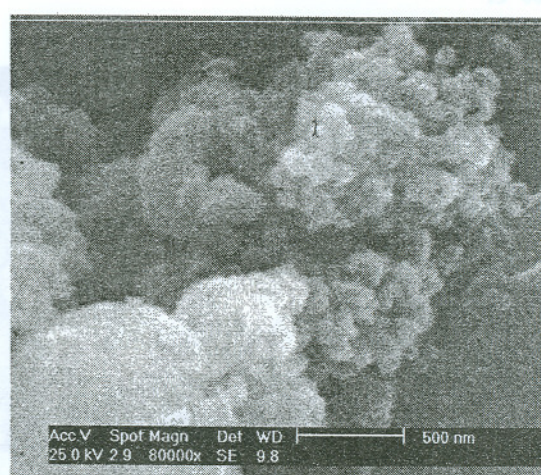
(b)

Fig. 6: Microstructure images of CaSnO_3 with different magnifications: a: 1000x and b: 80000x.

act as remarkable parameter in imparting an overall behavior. On the bases of this fact, and to meet the requirements, the preparation technique and study of micro structural become an important function of processing. In the light of foregoing discussion, it can be said that, solid - state reaction route is simple, convenient and inexpensive to obtain polycrystalline materials. For this purpose, by controlling of Sn:Ca weight ratio, nanopowders of SnO_2 , CaSnO_3 and Ca_2SnO_4 prepared by the ratio of 2:1, 1:1 and 1:2 were extensively studied. As a result of this work it can be said that, inhabitation effects on crystallite growth, geometry shape and the salt by- product could be studied by means of XRD, SEM and TGA.



(a)



(b)

Fig. 7: Microstructure images of Ca_2SnO_4 with different magnifications: a: 1000x and b: 80000x.

It was found that SnO_2 nano-crystalline powder has rutile-tetragonal structure with (211) crystal plane. Whereas, CaSnO_3 and Ca_2SnO_4 crystalline powders possessing perovskite structure. The calcining temperature $400^\circ\text{C}/4\text{h}$ was determined to be optimum and kept constant throughout the experiments. In all samples coalescence of well connected small grains lumped together are formed in high yield. Geometric shape of SnO_2 , CaSnO_3 and Ca_2SnO_4 are controlled by variation of Sn to Ca weight ratio.

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