Journal of Optoelectronic and Biomedical Materials Vol. 13, No. 3, July - September 2021, p. 89 - 94

Sol-gel Synthesis of Nanoscaled Spinels using 1, 2-ethanediol as a Gelation Agent

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In the present work sodium chromite ($NaCr_2O_4$) based pigment was synthesized using sol gel technique. From XRD analysis, it is clear that all samples manufactured by sol gel technique have spinel structure crystallization. Also chromites with a chromium concentration (max) shows black color and Na- substituted shows green color. The samples were annealed at different temperature from 600˚C to 700˚C. The obtained nano particles were characterized by other different techniques as well such as Scanning electron microscopy, Raman spectroscopy, Photoluminence and Energy dispersive spectroscopy. The particle size of parent compound is ranging from 4.4nm to 11nm determined from SEM. The tendency of particles to form the aggregates with the increasing annealing temperature has been observed. The optical characterization of the compound shows that the sol gel attained material is strongly persuasive sodium chromite.

(Received March 27, 2021; Accepted July 3, 2021)

Keywords: Spinel-chromite, Sol-gel, Structural characterization, Optical properties

1. Introduction

Oxides (mixed) with Spinel structure ($NaCr_2O_4$) widely used as catalysts are influential inorganic metalloid materials [1], heat-resistant pigments [2] and cathode materials [3], etc. With low surface area, spinel particles are usually synthesized with maximum temperature [4]. For spinel synthetization with maximum surface area, there are different methods of wet chemistry undertaken like co precipitation [5], polymeric gel method [6], heterogeneous precipitation [9], hydrothermal method [7], micro emulsion method [8], method of sonochemical [10], combustion method [11], sol-gel method [12], etc. Minimizing those methods is useful for reduction of the temperature therefore, the undesired collection of the particles obtained during calcinations. Mainly in experiments, sol-gel method of (mixed oxides) shows promising potential, great chemical homogeneity, Minimum calcinations temperature, owed high purity, etc. To attain homogeneous mixed oxides with determined compositions, the difference in reactivity has been reduced by controlled prehydrolysis of the less reactive precursor [13], by chemical moderation of the parent [14], by using single-source hetero bimetallic alkoxide predecessor [15], or by non-hydrolytic sol-gel techniques [16]. Sol-gel process concerns the usage of an epoxide such as gelation agent. In this procedural setup it demands approximately some techniques to attain oxides of metal at low temperature with minimum cost. This reaction promotes hydrolyze and condensation of complex that gives result in the formation of gel. By this process, few metal oxide gels [17– 20] and nano particle have been prepared [21–23]. T. M. Tillotson et al [24] synthesized lanthanide and lanthanide-silicate aerogels using two-

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step sol-gel method and shows surface area reduction with an increase in lanthanide concentration. Hongtao Cu et al [25] worked on both chromites and aluminites $CoCr_2O_4$, $CuCr_2O_4$, $ZnFe_2O_4$ and $CoAl_2O_4$ using sol-gel method. Results shows its novelty for mixed oxide nanoparticles with charge less than +3. The main purpose of our work is to prepare spinel nanoparticles through sol-gel epoxide route. To best of our knowledge, sodium chromite synthesis using 1-2 ethanediol is not reported yet.

2. Experimental Section

2.1. Sample synthesis

For this process, we use the material like sodium nitrate hexahydrate $[Na\ (NO_3)_2{\cdot}6H_2O]$ and chromium nitrate nanohydrate $Cr\ (NO_3\ )_3\ .9H_2O$. By the aqueous sol-gel process, we prepared the $(NaCr_2O_4)$ sodium chromium spinel. In this process, we take a beaker and dissolve $Na(NO_3)_2.6H_2O$ and $Cr\ (NO_3)_3.9H_2O$ in 100ml of distilled water at temperature ranging from 55ºC to 60ºC. We use hot plate and start stirring the mixture for 1 hour. To further proceed the experiment, 1, 2- Ethanediol (20ml) as a complexing agent is added with dropper in our solution. During stirring, Na-Cr-O nitrate-acetate-glycol sol which turned into a greenish transparent gel, after concentrated solutions which is evaporated at 65ºC .We then dry the obtained gel in oven at temperature of 105ºC for 10 hours. After 10 hours, we take the dry gel and grind the precursor gel with an agate mortar. After grinding, we placed it in furnace for 3 hours at 700ºC. We then again grind the gel in an agate mortar after calcination. Finally the desired nanomaterial is obtained.

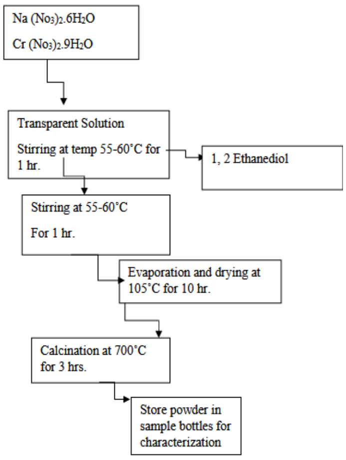

Fig. 1. Schematic diagram of synthesized sodium chromites sample.

3. Results and discussion

3.1. X-Ray diffraction

Crystallography of X-ray tells about molecular structutre of cryastal. Phase of a sample and structure is determined by Xrd. The value of 2θ starts from 20-70 in our sample. The main peaks of our sample are obtained with calcination temperatute of 700˚C are positioned at $2\theta=30$, 40, 45.5, 70. By using sol-gel method we obtain single phase of sodium chromite. Lattice constant a is 9.2181A˚ and c is 8.329A˚. Its c/a ratio is 0.8937A˚. Crystal structure of spinel is cubic that shows that sample has obtained high purity. The lattice parameters are closely related to reported ones. At 700˚C, sodium chromite spinel single phase has obtained with space group 141/amd.

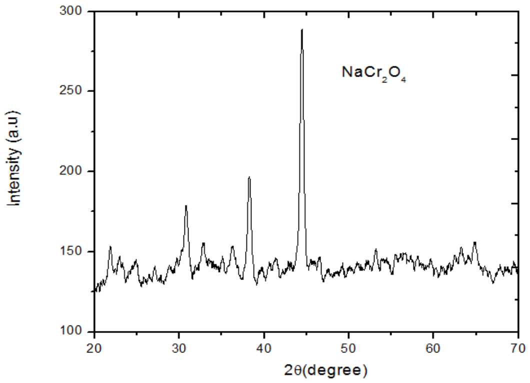

Fig. 1.2: X-ray pattern of $NaCr_2O_4$.

3.2. Raman spectroscopy

The Raman spectra for $NaCr_2O_4$ is shown in fig 1.3 with raman shift range 1200cm^{-1} to 1400 cm^{-1}. This spectra shows the collective features has a strong tip around 1465cm^{-1}.

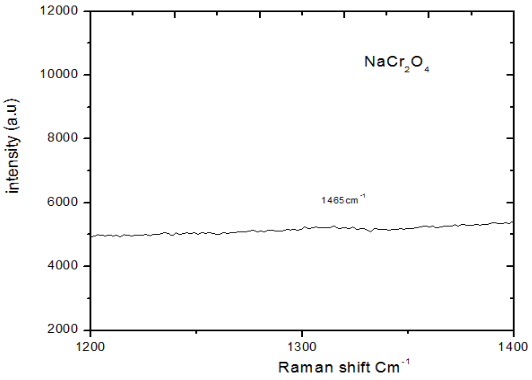

Fig. 1.3: Raman Spectra of Sodium Chromite.

3.3. Photoluminence spectra

Monitoring is appropriate by photoluminence and the physical properties of nano-particles changes with their dimensions and reduced in nanometer range measured called as quantum volume effect. From recombination of surface state photoluminence can be originated. The nano-particle photovoltaic tissues shows that the wavelength at room temperature is 347nm according to fig. 1.4. In this graph, spectrum describes emission peak available around (UV region) at 380nm corresponding to the excitonic release of the adjacent band space. Moreover, the spectrum also report luminance powder reduced size diffusion of nano-particles across entire width and only a few maximum in Nano-meters (FWHM). It is clear that nano structure possess the band gap of 3.771ev and when we increase temperature in it band difference is reduced and become 3.147ev, which is associated with the band gap transition.

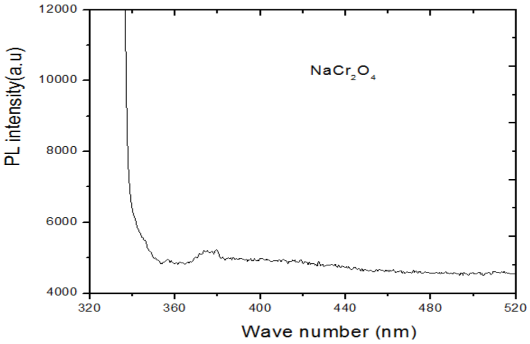

Fig. 1.4: PL spectra of sodium chromite.

3.4. Scanning electron microscopy

Surface morphology of manufactured Na-Cr-O nanoparticle has been investigated by using Scanning electron microscopy. It has been shown to be relatively small in size and fine particles obtained with increase in the temperature of spinel. Under altered situations, SEM phantasmagorias are designed as show in fig 1.5. With low consistency, the particles have semi-spherical structure, the results of which can be seen that can be particle have well separation good symmetry and spherical shape. Increase the temperature above 700˚C makes the particle more disorganized and less spherical between particles. It was also looked at that molar balance Na/Cr has a significant effect on the shape and size of the brush.

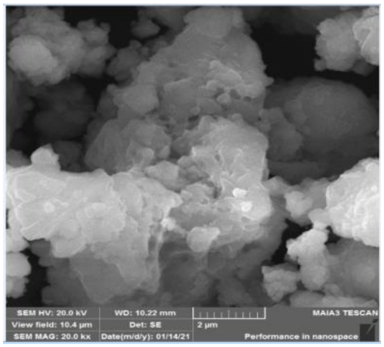

Fig. 1.5: Scanning Electron Microscopy of Sodium Chromite.

3.5. Energy dispersive spectroscopy

Energy dispersive analysis is also called "Energy Dispersive Spectroscopy". In this process, graph clearly shows that sodium chromite formed has single phase. In given table ratios of Na, Cr, and O are given according to their atomic ratios and weight. Through ED's graph, we can say that there are no extra impurity peaks. We have obtained single phase of sodium chromites. But here a peak of N is appear which was due to the impurity of beaker which is used in sample synthesis.

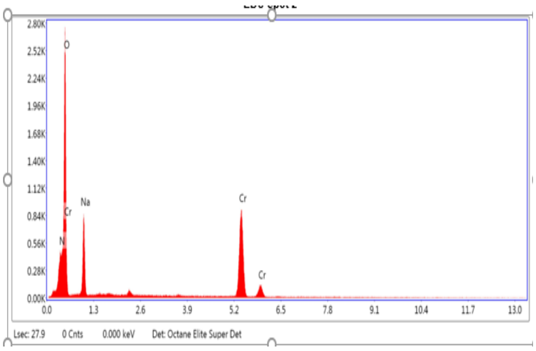

Fig. 1.6: EDS graph of Sodium chromite.

Table 1. Different compound ratios in EDS graph.

Element	Weight	Atomic %
Na	19.85	18.06
Cr	28.35	11.40
O	36.53	47.73

4. Conclusion

The results showed that the sodium chromite spinel structure was wonderfully synthesized by the predicted sol-gel method using chromium nitrate and sodium nitrate as the ancestors under thermal decomposition. Sample Xrd data confirmed nano-fusion formation of $NaCr_2O_4$ at calcination temperature of 700˚C. Band gap with temperature increase also reduces significantly. This proves that this method demonstrates the genius potential in the production of $NaCr_2O_4$ for mass production.

Acknowledgements

We are thankful for this project which is supported by NRPU grant from the Higher Education Commission of Pakistan and CPD grant from The Women University Multan. We are thankful to NILOP Islamabad for characterization facility of our synthesized materials.

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