

ECONOMICAL METHOD FOR SYNTHESIS A NANOCRYSTALLINE CHROMIA DOPED ALUMINA BASED ALUMINUM FOIL WASTE.

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ABSTRACT

This study aims to synthesize a nanocrystalline alumina doped with chromia by using aluminum foil waste as a source of alumina and chromium nitrate non-hydrate as a source of chromia. Chromia doped alumina was prepared by co-precipitation method and fired at different temperatures. The co-precipitated powder formed thereby has been examined by XRD, FTIR and TEM techniques. X-Ray diffraction patterns show a good crystalline of the powder with very sharp and neat peaks at high temperatures more than 1000°C. The results of FTIR analysis confirmed the getting of solid solution of alumina chromia. TEM photographs show the good distribution of the particles, which have an average particle size of 1-3 nm at low temperature.

Key Words: Chromia doped alumina, aluminum foil waste, coprecipitation, TEM.

1. INTRODUCTION

Ceramics based Al_2O_3 are widely used by modern industry as a construction materials with several unique properties such as high mechanical strength, hardness, heat resistance, chemical inertness, and insulation characteristics. Another important application of materials based Al_2O_3 is the creation of various catalytically active complexes for the oil industry and cleaning of industrial emissions [1,2]. According to the arrangement of oxygen anions, this interesting ceramic material exists in two broad categories, including a face-centered cubic (fcc), and a hexagonal close-packed (hcp) arrangement.

The Al_2O_3 structures based fcc lattice include γ , η (cubic), Θ (monoclinic), and δ (either tetragonal or orthorhombic), whereas the Al_2O_3 structures based hcp packing are α (trigonal), κ (orthorhombic) and χ (hexagonal). However, γ and α -alumina that are thermally stable, the other phases are unstable at room temperature and called transition phases [3]. γ -alumina is one of technological important materials in industrial applications. It is widely used as absorbent, catalyst supports, and catalysts in form of nanopowder or thin-film coatings due to its high specific surface area. Common methods to prepare γ -alumina nanopowders are mechanical synthesis, vapor phase reaction, precipitation, combustion, and sol-gel methods. Precipitation method is a simple and fast chemical route, which is used for synthesis of γ -alumina nanopowders [4,5]. In addition, the α -alumina has been conventionally produced by annealing aluminum hydroxide derived from aluminum salts or minerals at temperatures higher than 1000°C. The α -alumina can be also produced by fabricating amorphous alumina with methods using liquid phase such as precipitation and sol-gel process and then

annealing it at high temperature. These methods need high temperatures, which bring about much consumption of energy [6].

On the other hand, in the past decade the development of methods for comminuting various substances and materials to a nanodimensional level has received much attention in material science and technology. Specially, in ceramic materials, the trend is always to prepare fine powder for the ultimate processing and better sintering to achieve dense material with dense fine-grained microstructure and better properties for various applications. The fineness can reach up to 1-100 nm, by special processing technique. More in the fineness more is the surface area. Therefore, the densification occurs very well at low temperature than that of conventional ceramic system. Nanocomposite materials are complex of nanophase material and other materials, which optimize the performance of traditional material. Various nanocomposites have been synthesized using a wide range of processes such as deposition [7], self-propagating high-temperature [8], sputtering [9], coprecipitation [10] and sol-gel [11]. Nanomaterials, particularly transition-metal oxides play an important role in many areas of chemistry, physics and materials science. In technological applications, metal oxides have traditionally been used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species. Metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites. Among metal oxides, special attention has been focused on the formation and properties of chromia (Cr_2O_3) which is important as heterogeneous catalyst, coating material, wear resistance, advanced colorant, pigment and solar energy collector [12].

No doubt, chromia (Cr_2O_3) is one the many additives potentially able to improve the physical properties of alumina. When chromia is added into an alumina system, isovalent solid solution will form over full range of compositions because both chromia and alumina are sesquioxide and have the same corundum crystal structure (approximately hexagonal close-packed oxide ions with the Al^{+3} and sites). In reactions at high temperature "($T > 1000^\circ\text{C}$)", complete range of substitution solid solution happens when an atom or ion replaces an atom or ion of the same charge in the parent structure [13].

$\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ (alumina-chromia) is a simple binary system, which exhibits a complete substitutional solid solution at high temperature without formation of any eutectic over the entire range of composition. This system is well known for application in numerous fields such as fiberglass furnace, coal gasifiers, carbon black reactor, and different solid waste vetrification processes as corrosion resistance refractory. Currently, alumina-chromia distinctive with high resistance to chemical corrosion at high temperature due to low solubility in molten slags and salts [14-15]. On the other hand, aluminum recycling has a number of key environmental and economic benefits. Furthermore, the recycling of aluminum scrap reduces waste, saves energy, conserves natural resources, and lessens use of municipalities with considerable revenue [16].

The primary objective of this study is to synthesize a nanocrystalline alumina doped with chromia from aluminum foil waste. Where, a great amount of aluminum scrap is produced worldwide, of which a major part is recovered by recycling, but in this study an alternative way of using the aluminum scrap is to transform it directly into alumina, which finds several uses (in catalysts, in soft abrasives, in coating and in adsorbents). Thereafter, studying the effect of doping with different ratios of chromia to obtain a solid solution of alumina chromia by coprecipitation technique and characterized produced powders after firing between 500-1500°C.

2. EXPERIMENTAL WORK

Figure 1 shows the flow chart of experimental procedure in this study.

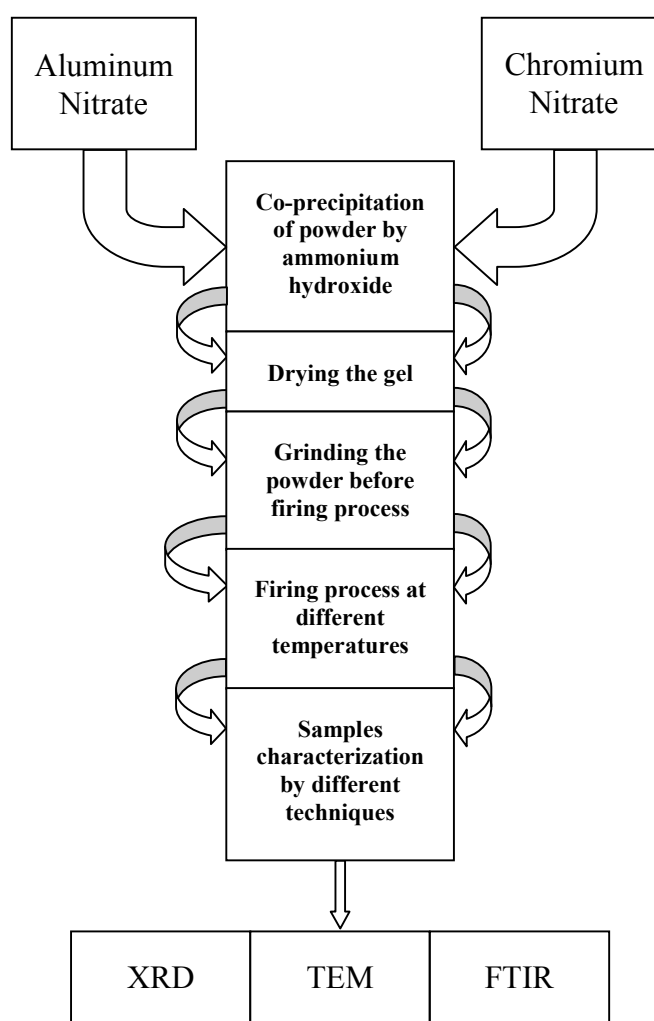


Fig. 1: shows the flow chart of the experimental procedure.

2.1. Materials

Materials used in this study are Aluminum foil waste (aluminum scrap) and Chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} > 98\%$ purity Oxford Laboratory). Nitric acid (68%), Hydrochloric acid (36.5%) and Ammonium hydroxide (32%) were also used.

2.2. Experimental Procedure

Aluminum nitrate solution is prepared by adding aqua regia to aluminum foil waste. Different batches of alumina chromia mixtures were prepared by adding different ratios of aqueous chromium nitrate non-hydrate, of the proposed concentrations, and aluminum nitrate solutions as shown in table 1. To obtain the co-precipitated powder of aluminum hydroxide and chromium hydroxide, the ammonium hydroxide solution was added to the above chromium nitrate and aluminum nitrate solution at pH~9. The produced co-precipitated powder (gel) was washed by hot distilled water for four times to remove the impurities, and then dried at 120°C for 24 h to get rid of humidity. Finally, the dried gels were fired at different temperatures (500, 700, 900, 1100, 1300, 1500°C) for 2 hrs with a heating rate of 5°C/min for all batches.

Table (1): Shows all the batches for alumina chromia mixtures.

Batch No.	Aluminum scrap	Chromium nitrate
1	100 g	0 g
2	95 g	5 g
3	90 g	10 g
4	85 g	15 g
5	80 g	20 g
6	75 g	25 g

2.3. Characterization

The fired mixtures were studied using different techniques to explain the nature of interaction between the two oxides as follows:

- X-ray diffraction instrument (Ni-filtered Cu K α radiation) was used to assess the phase formation of each composition and to measure the crystallite size of each phase.
- FTIR (SHIMADZU IR affinity-1) technique was used to detect the functional groups, in addition to identify bonds found in each composition.
- Transmission electron microscope (JEM-2100ELECTRON-MICROSCOPE) was used to investigate the different batches with a spatial resolution much better than the light-optical microscope in addition to studying the particle morphology, size and shape agglomeration.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

Figure 2 shows the X-ray diffraction patterns of different batches fired at 500°C. γ -alumina which is the only identified phase observed in X-ray diffraction for all batches at 500°C according to the diffraction peaks at 2θ , 46.00° for (400) and 66.80° for (440) matched to γ -Al₂O₃ (Card.No#10-0425) and there are no other peaks for new phases of chromia which would indicate solid solution of γ -Cr₂O₃ in the γ -Al₂O₃. Furthermore, The increase of the firing temperature from 500 to 900°C, which did not lead to any change in the result of XRD, that's mean obtaining solid solution of γ -Cr₂O₃ in the γ -Al₂O₃ at the temperature range of 500-900°C. The crystallite size of γ -Cr₂O₃ in the γ -Al₂O₃ was calculated from X-ray line broadening using Scherrer's formula ($D = 0.9 \lambda/B$

$\cos \theta$), where, D is the crystallite size, λ is the wavelength of the radiation, θ is the Bragg's angle and B is the full width at half maximum [18].

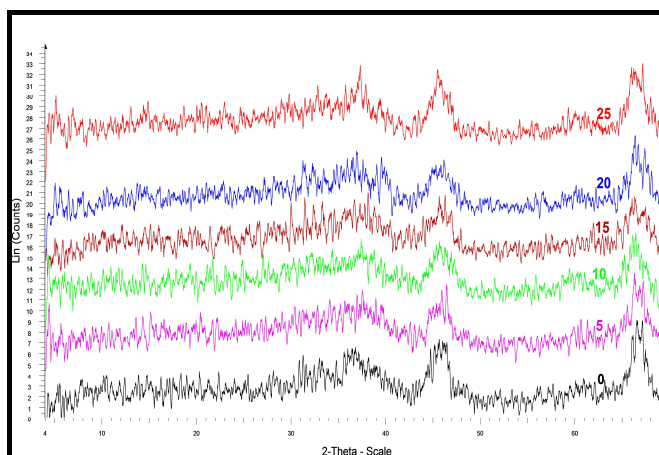


Fig. 2: XRD of the fired batches at 500°C.

The average crystallite size of $\gamma\text{-Cr}_2\text{O}_3$ in the $\gamma\text{-Al}_2\text{O}_3$ showed a value of 1-3 nm. The X-ray diffraction patterns of alumina chromia mixtures after firing at 1100°C are shown in figure 3. In this case, all diffraction patterns due to $\alpha\text{-Al}_2\text{O}_3$ were faintly observed at 35.2, 43.4 and 57.5 degrees, This indicated that the crystallization to $\alpha\text{-Al}_2\text{O}_3$ matching (Card.No#81-2267), these peaks became strong with an increase in annealing temperature and also there are no other peaks for new phases of chromia. This can also be explained because of the formation of solid solution of $\alpha\text{-Cr}_2\text{O}_3$ in the $\alpha\text{-Al}_2\text{O}_3$. Furthermore, the diffraction peaks of the fired mixtures show sharp intensive peak and clean profiles, indicating that the obtained nano powders of $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ have high crystallinity. The same results were found for the batches fired at (1300, 1500°C) [19].

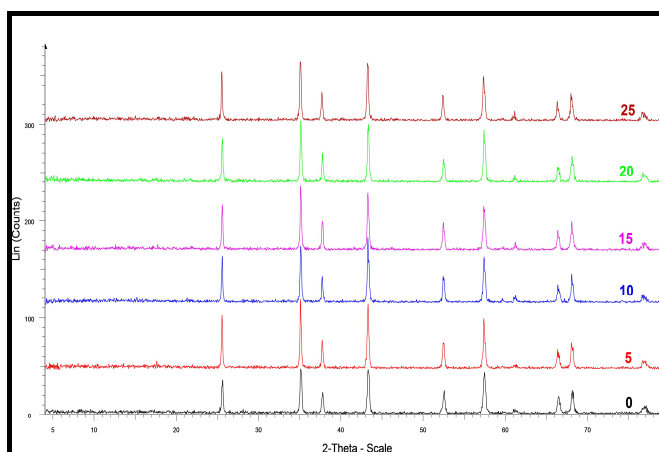


Fig. 3: XRD of the fired batches at 1100°C.

3.2. FTIR Analysis

To support our conclusion drawn from XRD results that fired mixtures at low temperatures are $\gamma\text{-Al}_2\text{O}_3$ and that at higher temperatures above 1000°C yielded $\alpha\text{-}$

Al_2O_3 , FTIR studies were performed and the results are given in (see figures 4-5). Both figures show an intense band centered around 3,500 cm^{-1} and another one around 1,600 cm^{-1} . These peaks are assigned to O–H stretching and bending modes of adsorbed water. For the wide band appearing between 500 and 900 cm^{-1} corresponds to the vibrational frequencies of co-ordinate O–Al–O bond, showing nano amorphous Al_2O_3 . This wide band is divided into two peaks. The peaks in the region 500–750 cm^{-1} are assigned to $\nu\text{-AlO}_6$, and the other at 800 cm^{-1} is assigned to $\nu\text{-AlO}_4$, indicating tetrahedral and octahedral coordination existence in $\gamma\text{-Al}_2\text{O}_3$. For the mixtures fired at 1100°C two significant spectroscopic bands near 600-650 and 450 cm^{-1} appear, which are identified to the characteristic absorption band of $\alpha\text{-Al}_2\text{O}_3$ with a corundum structure [20,21,22].

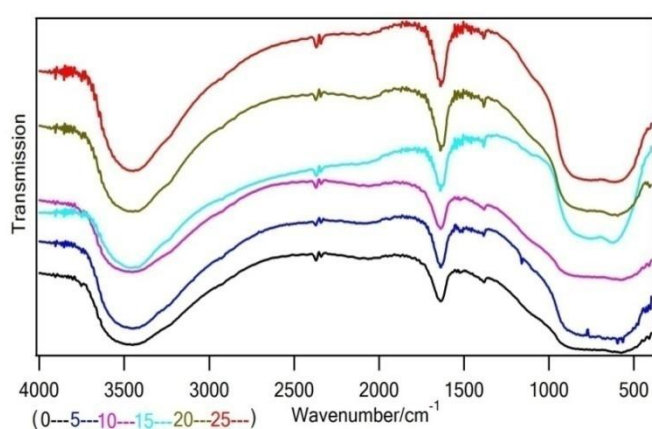


Fig. 4: FTIR of the fired batches at 500°C.

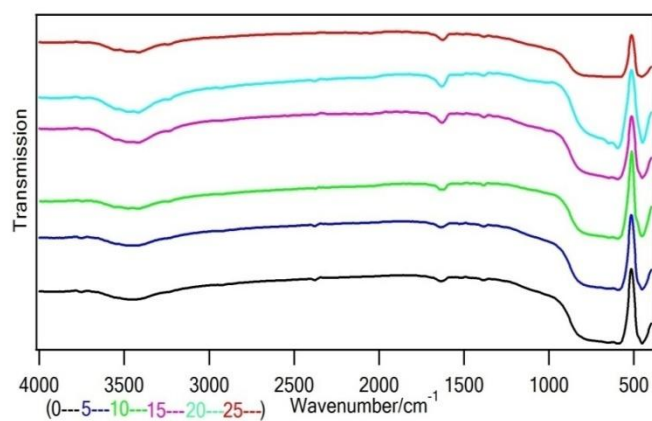


Fig. 5: FTIR of the fired batches at 1100°C.

3.3. TEM Analysis

The TEM micrographs of the sample annealed at 700°C (batch no 4) for $\gamma\text{-Al}_2\text{O}_3$ is shown in figure 6(a). TEM micrographs reveal the nanocrystalline nature of the products. These results are in close agreement with the crystallite size estimated by X-ray line broadening for the same sample. On the other hand, most of the researches using one of the components of the composites or the reinforced materials in the range of nanoparticle. Our work is too different from those, where both the components are in

nanosized particle. TEM photograph shows the powder has a good distribution of the particles, which has a mean particle size of 1-3 nm. Figure 6(b) shows the TEM image of α -Al₂O₃ annealed at 1100°C for the same batch. Transformation of all pure Al₂O₃ into the single α phase was observed at temperature of 1100°C, as indicated by figures 6(a) and (b). The sharp peaks of α phase indicate the relatively large grain sizes and well-defined long-range order in corundum. It can be seen that all these powders clearly appear to be in agglomerated form, which is often observed by combustion route. The selected area diffraction (SAD) pattern shown in figures 6(c) and (d) demonstrate that the particles are crystalline in nature [23].

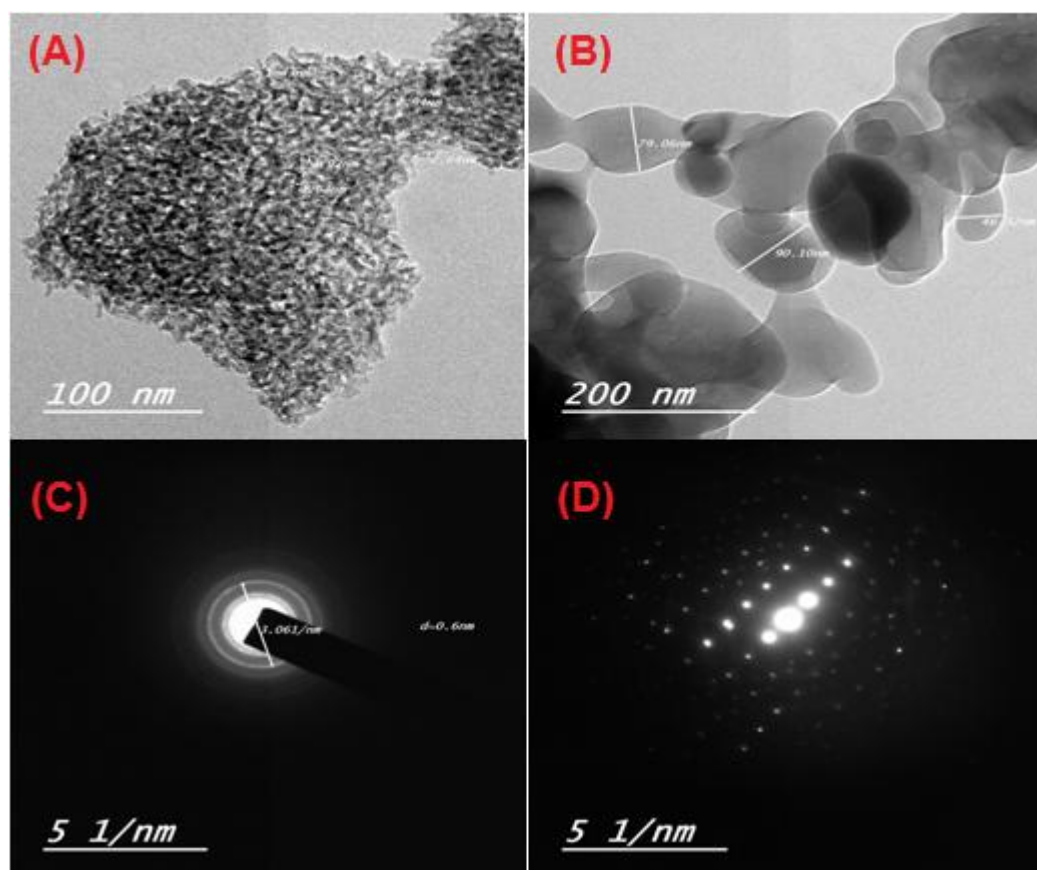


Fig. 6: TEM, SAED micrographs of nanocrystalline chromia doped alumina powders at different annealing condition: (a), (c) 700°C and (b), (d) at 1100°C for (batch no 4).

4. CONCLUSIONS

- Aluminum nitrate was synthesized by the precipitation method from inexpensive materials such as an aluminum foil waste. The phase transition $\gamma \rightarrow \alpha$ -Al₂O₃ occurs in two steps, as seen from X-ray diffraction (XRD), and transmission electronic microscopy (TEM) techniques. The first step, at the temperature range of 500–900°C, alumina is constituted of γ -Al₂O₃ as seen from XRD patterns, with cubic crystal of structure and particle size less than 4 nm. In the second step, in the temperature range of 1100–1500°C, it converted into α -Al₂O₃ as seen from XRD patterns, with corundum crystal of structure. It can also be concluded that the crystallite size calculated by XRD

results is closely related to the phase transition, i.e., crystallite size increases according to the phase transition variation and consequently, with the increase in temperature. Therefore, co-precipitation method was successfully used to prepare a substitutional solid solution of chromia-doped alumina at different temperatures.

5. REFERENCES

- [1] Smovzh, D. V.; Kalyuzhny, N. A.; Zaikovskiy, A. V. and Novopashin, S. A.: "Synthesis of hollow nanoparticles γ -Al₂O₃". *Advances in nanoparticles*, 2, pp. 120-124, (2013).
- [2] Kim, B.; Hirage, K.; Morita, K.; Yoshida, H.; Miyazaki, T. and Kawaga, Y.: "Microstructure and optical properties of transparent alumina". *ActaMaterialia* 57, pp. 1319-1326, (2009).
- [3] Rajaaeiyan, A. and Mahagheghi, M.: "Comparison of sol-gel and co-precipitation methods on the structural properties and phase transformation of γ and α -Al₂O₃ nanoparticles". *Adv. Manuf.*, 1, pp. 176-182, (2013).
- [4] Shayesteh, M.; Afarani, M. S.; Samimia, A. and Khorram, M.: "Preparation of γ -Al₂O₃ and prioritization of affecting factors on the crystallite size using Taguchi method". *Trans. phenom. nano micro scales*, 1(1): pp. 45-52, Winter-spring (2013).
- [5] Cava, S.; Tebcherani, S. M.; Souza, I. A.; Pianaro, S. A.; Paskocimas, C. A.; Longo, E. and Varela, J. A.: "Structural characterization of phase transition of Al₂O₃ nanopowders obtained by polymeric precursor method". *Materials chemistry and physics* 103, pp. 394-399, (2007).
- [6] Inouse, K.; Hama, M.; Kobayashi, Y.; Yasuda, Y. and Morita, T.: "Low temperature synthesis of α -alumina with a seeding technique". *Hindawi publishing corporation ISRN ceramics*, Article ID 317830, 5 pages, Volume (2013).
- [7] Didenko, L. P.; Kolesnikova, A. M.; Voronetskii, M. S.; Savchenko, V. I.; Domashnev, I. A. and Sementsova, L. A.: "Chromia-alumina catalysts for the dehydrogenation of propane prepared by a modified method of co-deposition". *Catalysis in industry*, vol. 3, No. 2, (2011).
- [8] Tarasov, A. G.; Gorshkov, V. A. and Yuxhvid, V. I.: "Phase composition and microstructure of Al₂O₃-Cr₂O₃ solid solutions prepared by self-propagating high-temperature synthesis". *Inorganic materials*, vol. 43, No. 7, (2007).
- [9] Witthaut, M.; Cremer, R.; Reichert, K. and Neuschütz, D.: "Preparation of Cr₂O₃-Al₂O₃ solid solutions by reactive magnetron sputtering". *Mikrochim. Acta* 133, pp. 191-196, (2000).
- [10] Bondioli, F.; Ferrari, A. M.; Leonelli, C. and Manfredini, T.: "Reaction mechanism in alumina/chromia (Al₂O₃-Cr₂O₃) solid solutions obtained by co-precipitation". *J. Am. Ceram. Soc.*, 83 [8], 2036-40, (2000).
- [11] Fujita, M.; Inukai, K.; Sakida, S.; Nanba, T.; Ommyoji, J.; Yamaguchi, A. and Miura, Y.: "Sintering of Al₂O₃-Cr₂O₃ powder prepared by sol-gel process". *Journal of the society of materials science, Japan*, vol. 56, No. 6, pp. 526-530, June (2007).
- [12] Garicamf and Rodriguez, J. A.: "Metal oxide nanoparticles". *Brookhaven national laboratory BNL-79479-2007-BC*.
- [13] Azhar, A. Z. A.; Mohamed, H.; Ratnam, M. M. and Ahmed, Z. A.: "The effects of Cr₂O₃ addition on microstructure and toughness of ZTA ceramics composite". *Journal of nuclear and related technologies*, volume 10, No. 2, December (2013).
- [14] Tripathi, H. S. and Nath, M.: "Thermo-mechanical behavior of Al₂O₃-Cr₂O₃ refractories: Effect of TiO₂". *Ceramics international* 41, pp. 3109-3115, (2015).

- [15] Kim, H. E.; Riu, D. H. and Kong, Y. M.: "Effect of Cr_2O_3 addition on microstructural evolution and mechanical properties of Al_2O_3 ". Journal of the European ceramic society 20, pp. 1475-1481, (2000).
- [16] Rabah, M. A. "Preparation of aluminum-magnesium alloys and some valuable salts from used beverage cans". Waste management 23, pp. 173-182, (2003).
- [17] Poole, C. P.; Kehl, W. L. and Maciver, D. S.: "Physical properties of co-precipitated chromia-alumina catalysts". Journal of catalysis 1, pp. 407-415, (1962).
- [18] Cullity, B. D.: "Elements of x-ray diffraction". Addison-Wesley, 1: 110, (1956).
- [19] Bondioli, F.; Ferrari, A. M.; Leonelli, C. and Manfredini, T.: "Reaction mechanism in alumina/chromia (Al_2O_3 - Cr_2O_3) solid solution by co-precipitation". J. Am. Ceram. Soc., 83 [8], 2036-40, (2000).
- [20] Rajaaeyan, A. and Mahagheghi, M.: "Comparison of sol-gel and co-precipitation methods on the structural properties and phase transformation of γ and α - Al_2O_3 nanoparticles". Adv. Manuf., 1, pp. 176-182, (2013).
- [21] Saha, S.: "Preparation of alumina by sol-gel process, its structures and properties". Journal of sol-gel science and technology, 3, pp. 117-126, (1994).
- [22] Varghese, N.; Hariharan, M.; Cherian, A. B.; Sreenivasan, P. V.; Paul, J. and Asmy Antony, K. A.: "PVA-assisted synthesis and characterization of nano α -alumina". International journal of scientific and research publications, Volume 4, Issue 10, ISSN 2250-3153, October (2014).
- [23] Sathyaseelan, B.; Baskaran, I. and Sivakumar, K.: "Phase transition behavior of nanocrystalline Al_2O_3 powders". Soft nanoscience letters, 3, pp. 69-74, (2013).