



A Brief Review on Prospect and Applicability of Perovskite Oxide based Nonmaterial

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Abstract

A brief review on the prospect and applicability of perovskite oxide nanocrystal has been carried out here in this work by first of all considering different forms of perovskite oxide nanocrystal materials which often appear in powder form or as thin film form deposited on a substrate. Different deposition techniques available for use to achieve the deposition in both cases depending on the form of the material were also considered with some of these deposition methods outlined and found to be unique in its procedural approach. In this case, it was observed that some of these techniques were found to be preferred to others because of the processes involved which are often seen to offer a better atmosphere for growth of perovskite oxide material with unique structural size and morphological pattern that creates room for a better critical size and dimensions of the material that were often seen to enhance the growth of the perovskite oxide nanocrystal especially with that which possesses optimal properties that are desired for various device applications. Also, some of these applications were highlighted with the structural properties of the materials that would offer the best quality in realizing a particular application.

Keywords: Review; Analysis; Prospect; Applications; Perovskite Oxide Nanocrystal; Deposition Technique; Characterization; Morphological Structure; Size Effect

Abbreviations: MRAM: Magnetic Random Access Memory; MLCC: Multilayered Ceramic Capacitors; DRAM: Dynamic Random Access Memory.

Introduction

Perovskite material based nanocrystals are material films with crystal structure in the form of cube with space group, the structure associated with this kinds of material is derived from the prototype CaTiO_3 perovskite oxide which is general a metal oxide with the formula in which B is a small transition metal cation and A is a layer s-,d- or f- block cation. Such materials can be classified into alkaline metal halide,

inorganic oxide and metal halide perovskites [1-3]. There are basically three groups of perovskite oxide based nanocrystal materials that may appear as binary, TiO_3 , ZnO , Al_2O_3 etc: ternary, CaTiO_3 , BaTiO_3 , CaSiO_3 or SrTiO_3 etc. Also they may be in different forms with various types of properties and as a result they have a wide range of applications and this is more reasons and rational behind there are lots of eyes and interest on perovskite nanocrystal [4]. This is due to the numerous area of applications of the materials towards technological and energy harnessing especially in recent dispensation. These and other used of the materials had drawn the attention of the material science researchers over decades coupled with the vulnerability in manipulating

growth materials into various application or so many other domestic usages. For instance the applications of ferroelectric, BaTiO_3 , PbTiO_3 , dielectric $(\text{Ba,Sr})\text{TiO}_3$, Piezoelectric $(\text{Pb}(\text{ZrTi})\text{O}_3)$, electrostrictive $(\text{Pb}(\text{MgNb})\text{O}_3)$, magnetoresistant, $(\text{LaCa})\text{MnO}_3$ and multiferric, (BiFeO_3) [5-7]. had been well known especially when it comes to areas of applications with computers, memories and electronic appliances such for long such as in ferroelectric random access memories, multilayer ceramic capacitor, transducers, sensors and actuators, magnetic random access memories and other potential new types of multiple – state memories and spintronics devices that are typically controlled by electric and magnetic fields [1-8]. All these varieties of applications have created quest for advancement in probing into perovskite oxide nanoscale based electronic devices that are amenable to miniaturization of conventional CMOS, complementary metal oxide semiconductor devices. These and many other reasons had led researchers in nanoscience to have the urge to focus more on the area of production and development of high volume (MLCCs) with good purity and uniform shape that would be useful in fabrication of next generation of the same MLCCs which will be of tens of nanometers for enhancement of miniaturization of the aforementioned devices.

Therefore in our review, we have observed some major challenges that were being encountered in producing these kind of materials when it comes to processing qualitative perovskite oxide on based nanocrystal materials with reliable and functional reproducible properties [9-14], due to the complexity nature involved in the evolution processes that yields perovskite oxide materials with stoichiometry and desired properties and based on this, the fabrication and synthesis of high quality, purity, ultrafine, and agglomerated free perovskite materials with fine controlled particle size and morphology that will enhance the desired properties of the materials involve critical steps and processes would be considered, although it is clear that whichever process is used to produce the perovskite oxide material the produced material formed is found to be either in powdered form or in the form of thin film deposited on the substrate. This implies that whichever form, a specific deposition mechanism must be used. Therefore based on observed dual state in which perovskite oxide based materials can exist in and the multiple growth techniques that can be used to synthesis it, depending on state or form, the applications are enticing and as such we are poised to review its prospect and applicability.

And based on these, it is obvious that the choice of the growth mechanisms is dependent on the choice of the techniques desired which of course may be invariably determined by the availability of the equipment couple with the simplicity of the instrumental operation and control that will lead to the achievement of the necessary optimized

properties which will lead to production of the perovskite nanocrystal material that would have a wide range of prospect and applicability.

Generally, the two major issues that are required to be in mind while synthesizing perovskite oxide based nanomaterials in order to achieve a desired result are (i) control of particle size and composition and (ii) the control of the interfaces and distribution of the structural blocks within the perovskite materials. However, it should be noted that the growth processes may lead to the growth of perovskite oxide nanocrystal in powder form or perovskite oxide nanocrystal in thin film form deposited on a substrate depending on the technique used. Some of these methods that may lead to grow the material either in powder or thin film form to mention but a few of them are physical vapour deposition, chemical vapour deposition electro-deposition, pulse laser, vacuum thermal, sputter deposition, successive ionic layer adsorption, hydrothermal deposition, Sol-Gel etc.

Deposition of Perovskite Oxide Nonmaterial

Since it is certain had been made known that all perovskite oxide base nonmaterial formed may be in powdered form or thin film form deposited on substrate is solely determined by the growth mechanism, there is need to highlight some growth mechanism that could be used to grow perovskite materials, therefore in this section a consideration is given to the process and growth mechanisms of perovskite oxide based nanomaterials, the growth which found to dependent on some conditions that would yield optimum results such as simplicity, cost effectiveness, and availability of equipments and materials. Some of these processes, their basic principle and effectiveness will be highlighted here in this section.

Deposition of Perovskite Oxide Based Nanomaterial in form of Powder

Some of these techniques are based on solid- state reaction methods, molten-salt technique which involves production of powder form of perovskite material.

The first one that is solid- state method involves weighting starting materials (the corresponding oxides or oxides and carbonates), mixing, milling and calcining them at elevated temperature to form perovskite phase. For instant, in growing BaTiO_3 material by solid –state reaction technique, the process involves three stages and also hinges on the diffusion of Ba^{2+} ions into TiO_2 [15]. The first stage is the reaction with the outer surface region of TiO_2 form a surface layer of BaTiO_3 on the grains of TiO individually and the diffusion of Ba^{2+} which culminates in the formation of Ba_2TiO_4 between and BaCO_3 that has not been involved in

reaction and the BaTiO_2 as previously formed. This is followed by a prolonged sintering periods to enable the intermediate Ba rich phase Ba_2TiO_3 to react with the remnant of the TiO_2 in the core-region of its grain to finally form BaTiO_3 . However, with high calcinations temperature, the agglomerated produced perovskite particle size of the powder seems to be coarse that may require further milling which may invariably result in contamination and undesirable features and defect of material.

The second one is type that uses molten salt as a medium by making use of (oxides and carbonates) [16]. The basic principle here is that it utilizes the melt-solid reaction which involves small diffusion distance with high mobility of oxides in the melt. This method is advantageous over the former one because it has one step after another; it is rapid and more environmental friendliness as regards synthesis of perovskite oxide functional materials. During the processes, it is observed that the melt increases with the rate of reaction due to small diffusion distances and high mobility of oxides in it thereby maintaining the medium of the reaction, the choice of molten salt system is variable. For instant, alkali chlorides, sulphates, carbonates, and hydroxides are the probable choices though other choices do exist. It is important to note that the feature of this technique is simple, versatile and cost effective when it comes to obtaining pure powdered perovskite materials at low temperature within a short time lapse of soaking. However the principal procedure involved in this method is heating the raw materials which includes the reactants and the salt system above melting temperature of the salt in order to enhance the synthesis of the particle at the melted salt solvent that would invariably formation of perovskite oxide powder that can be controlled by turning the heating temperature and period and after which it is allowed to cool to room temperature naturally and then it is washed with de-ionized water and then subsequently dried for it to be in complex perovskite oxide powder. This method is known to be a popular method that has been used to produce SrFeO_3 nonmaterial [17] that depends on metal precursor and salt medium [18] as explained earlier.

The third technique is wet chemical methods that constitute two different techniques (a) Sol-gel colloidal process and (b) hydrothermal processes. The basic principle invoked in the main sol-gel process is formation of a sol by dissolution of metal aioxide, metal-organic, or metal-inorganic salt precursors in a suitable solvent unlike the conventional solid-state reaction, one of the examples that are capped under this method is sol-gel colloidal process [19-21] and the other one is Hydrothermal process [22-24]. Due to its unique mechanism which involves chemical wetting solution, the dopant ions like paramagnetic or rare-earth ions can be introduced during the preparation of the solution of the precursor that will go a long way to enhances

the control of the stoichiometry that invariably leads to production of narrow sized distributed perovskite materials at a low crystallization temperature. This is due to the mix at the quasi-atomic level in the solution system. One of the key concept that is imbibe this method of sol-gel is that it involves technical formation of a sol by the dissolution of the metal aioxide, meta-organic, or metal inorganic salt precursor in a suitable solvent with subsequent drying of the gel followed by calcinations and sintering at an elevated temperature to grow to perovskite crystal material. Based on these involved processes, there is homogenization at the atomic level which culminates in the considerable reduction of the diffusion distance as compared to the former methods and as such the properties of the developed crystal grown using this so-gel method has unique properties coupled with the fact that it can be used to grow the material at much lower temperatures than the former [21,25,26]. Optimization of developed perovskite nanocrystal can carried out by post annealing in order to affect the grain sizes of the formed perovskite oxide powder nonmaterial [27-29]. (b) In the case of hydrothermal process which is made up of two categories, conventional and microwave hydrothermal process, the process is the same although the microwave process is advantageous over conventional process due its cost effectiveness and rapid internal heating that enables the synthesis to be rapid which results from the formation of the tetragonal phase and quick increase in particle size with reaction time. However basic principle for the synthesis as applied for the duo is the same because the method involves is similar, heating an aqueous suspension of insoluble salts in an autoclave at a moderate temperature and pressure to facilitate desired phase crystallization so as to enable formation of fine and homogeneous perovskite oxide powder with good size distribution and morphology [27,29,30]. It has been confirmed that BaTiO_3 produce using this technique has been found to formed good size distribution and morphology when it was analyzed using high resolution TEM [27].

Deposition of Perovskite Oxide Based Thin Film on Substrate

The deposition in these categories can be classified broadly into twos

(i) Chemical deposition (ii) Physical deposition; the former one involves a process in which (a) the chemical precursor are directed to form on a substrate surface with the product layer growth on the surface during which the reaction is kick started. In this case the growth of the film involves heterogeneous nucleation and growth while (b) the materials are meant to dispersed into solvent either as molecular precursor or nanoparticles "ink", or are deposited and coating formed up on the solvent evaporation and potentially annealing) and its own case, viscous fluid is deposited on the substrate. In the case of physical deposition, precipitation of

vaporized material on the substrate under reduced pressure (vacuum) is first process with the formation involving heterogeneous nucleation and growth of thin film.

Chemical Deposition Techniques includes; Chemical vapor (CVD), anodization, electroless deposition, Chemical bath deposition, CBD. Successive Ionic Layer Adsorption and reaction, SILAR, Spin/Dip Spray coating or ink jet printing of sol-gel solution or nanoparticle ink [13-24] and atomic layer deposition, ALD [18-37]. The principle of chemical bath deposition is based in the utilization of controlled chemical reaction by ligand to induce the formation of thin film layer of a material by means of heterogeneous precipitation [38] formed from an aqueous solution of a metal salt acting as a bath for the substrate with the addition of counterion in the form of for oxides/hydroxides or for sulfides being governed by the solubility product of the target compound, and then the coating is deposited on the surface of the substrate with the required ligand to facilitated easy deposition processes [5,2,38]. SILAR for depositing thin film layer on the substrates operates within the combined ALD and CBD mechanism as it makes use of physically separated layer approach similar to ALD in combination with some flexibility features and CBD in conjunction with the ambient deposition technique from aqueous solutions of metal salts without the need of high-vacuum equipment [31-38]. Though in contrast to CBD, it require the application of alternating baths of chemical precursors and also additional features of pure solvent in between the deposition cycles in order enable removal of excessive precursor molecules which makes its process unique such that it has the ability to deposit ultra-thin film of highly conformal coatings on a desired substrate [39-42]. On the other hand it is worth mentioning here all the chemical deposition processes especially CBD and SILAR deposition techniques have a unique inherent simplicity, low cost, effectiveness and above its ability to operate in an ambient environment which the characteristics that placed them advantageous over all the techniques used for deposition of

perovskite oxide nanomaterials that are mentioned here.

Characterization of Perovskite Oxide based Nanocrystals

The structural characterization of the nanocrystals was carried out using TEM, HTEM, SEM and XRD. The structural features of perovskite oxide based nanocrystals in either powder form or thin film form deposited on substrate were analyzed where it was revealed that the structure of some of them like BaTiO_3 powder has internal pores of various sizes have invariably effect the density of the crystals and the morphological structure of nanocrystals. However, these observed pores were seen to disappear as the material is annealed at particular temperature with formation of small particle sizes on the structure which stabilized in a cubic phase at room temperature [33-42], a factor that is suspected to be the cause of high strain within the crystals and the reason behind the existence of structural defect within the particles (lattice defect) because it would make the unit cell distortion ratio c/a very small than it suppose to be as that inhibits the completion of the structural transition. These are the reasons behind the variation in the contrast in the images of the morphological structure as depicted in the TEM image as shown in Figures 1-4 for powder perovskite materials while the SEM images for thin film form of the perovskite materials are shown in Figures 5-10. From the observation, there is an indication that there is a contrast variation across particles is an due to the existence of high strain in the structure must have affected the diffraction behaviour of the electrons which suggested that there might be abnormal crystallographic behaviour during the growth of the materials as indicated in the XRD pattern this may be related to the presence of strain in crystals as manifested on the morphological contrast is as shown on Figure 4 for powdered perovskite materials.

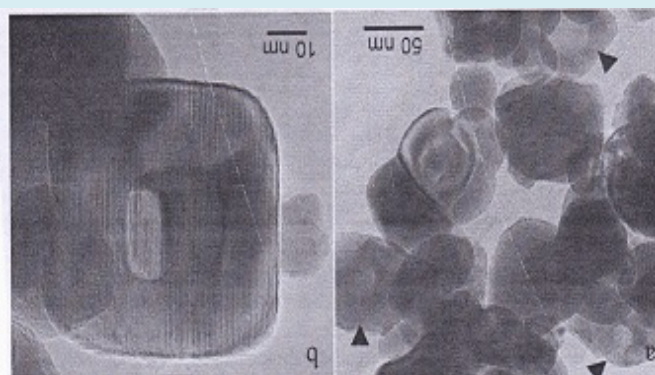
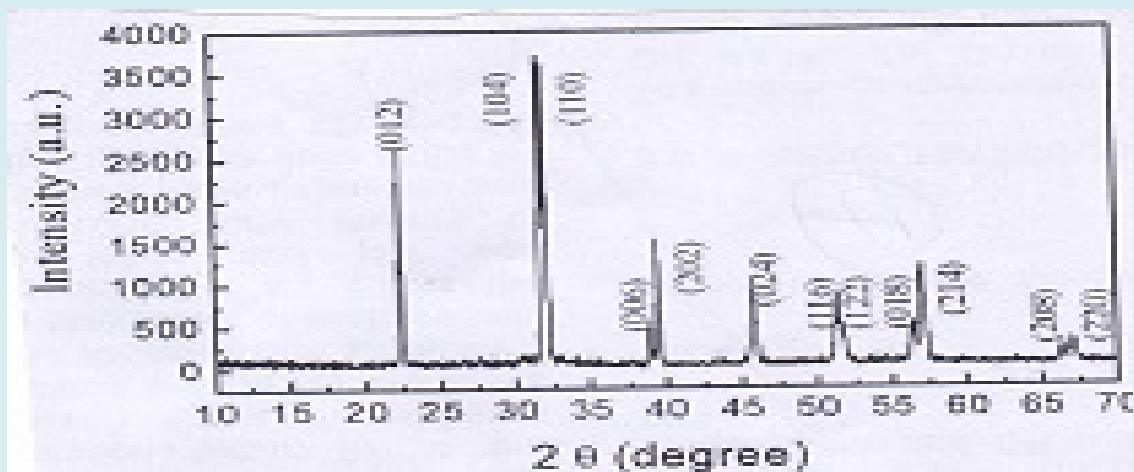
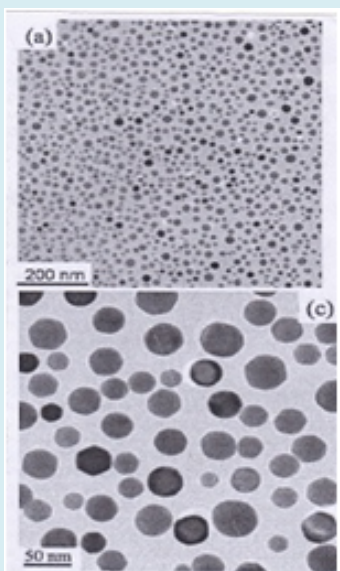
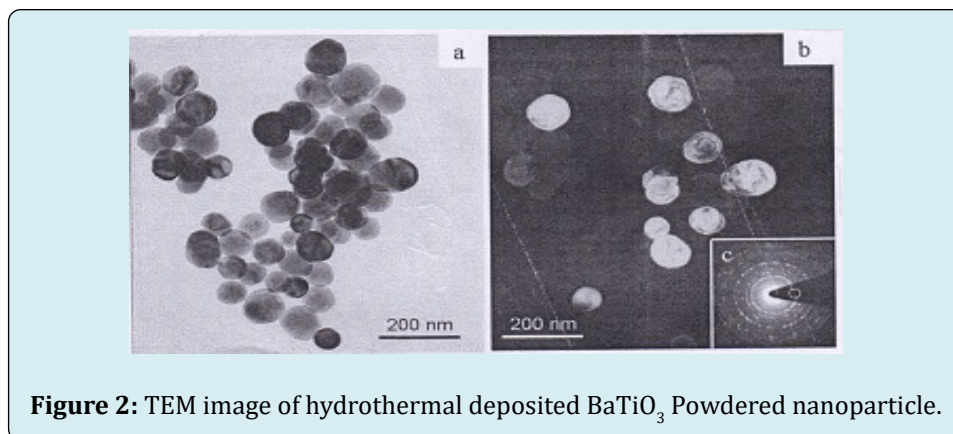


Figure 1: TEM image of BaTiO_3 Powder Perovskite Oxide nanoparticle; (a) Un-annealed, (b) Annealed at 673K.



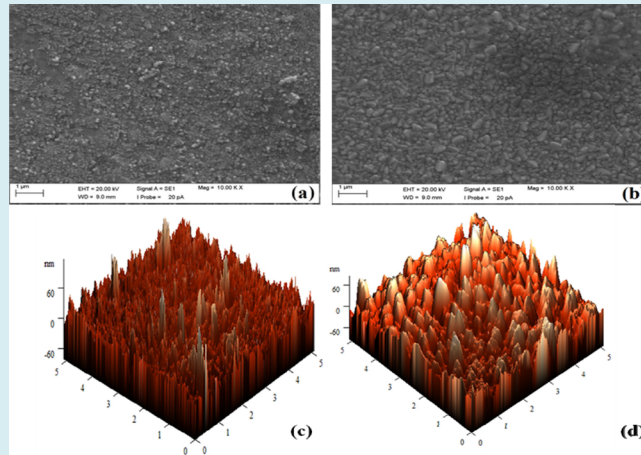


Figure 5: SEM morphological structures of as deposited and TeZnO thin Film (a and b) Un-annealed and annealed.

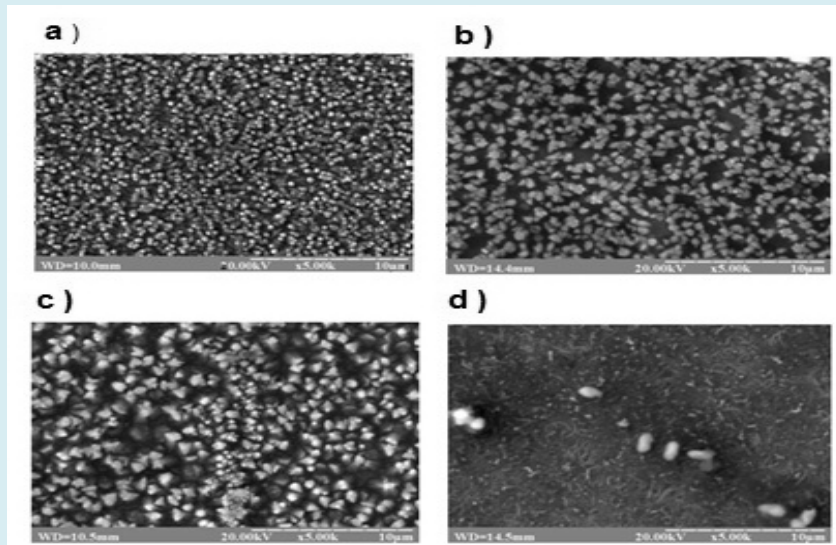


Figure 6: SEM morphological Structure of Cu ZnO thin film [a, b, c and d] as- deposited and annealed at temperature; 500°C, 700°C and 850°C.

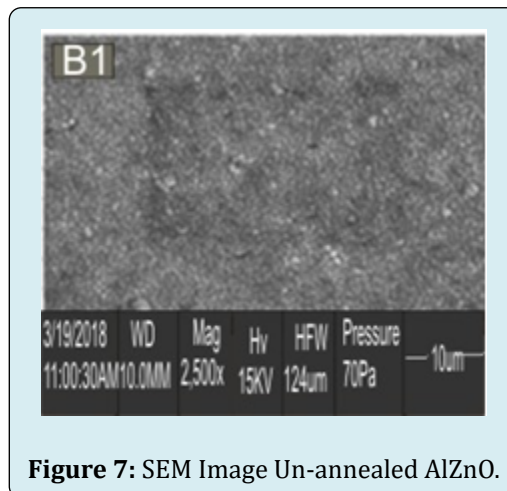


Figure 7: SEM Image Un-annealed AlZnO.

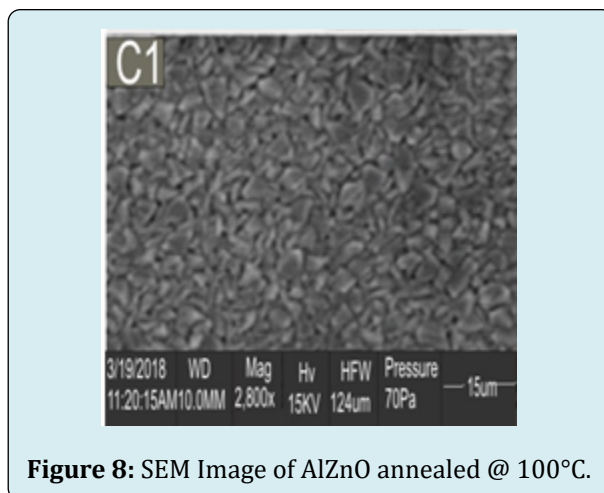


Figure 8: SEM Image of AlZnO annealed @ 100°C.

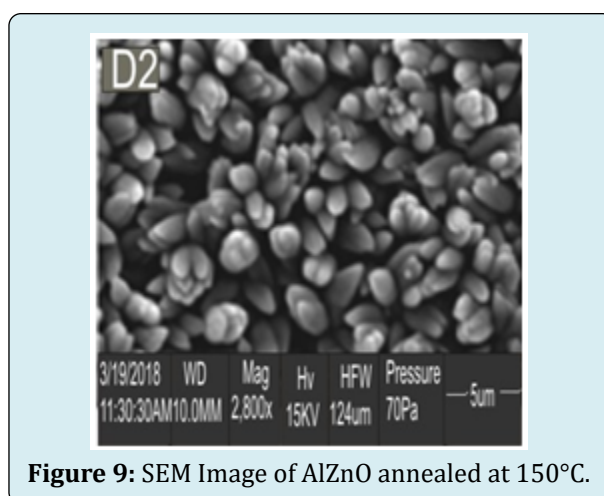


Figure 9: SEM Image of AlZnO annealed at 150°C.

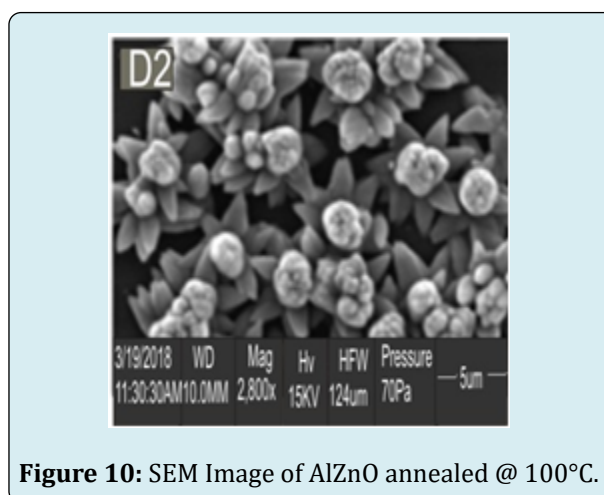


Figure 10: SEM Image of AlZnO annealed @ 100°C.

The XRD of microwave hydrothermally powdered perovskite materials, the intensity occurred at the planes; (012), (104) and (112) while the (308) and (220) plane

experienced lowest intensity as in Figure 4, but for thin film type, the highest intensity occurred at (101), (002) and (100) planes respectively as Figures 11 & 12.

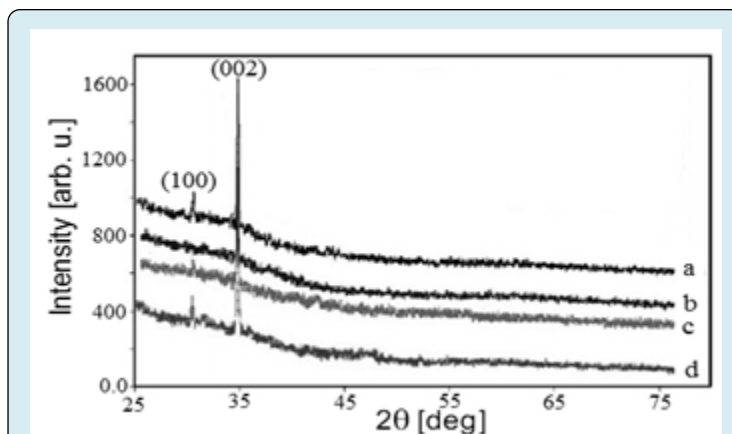


Figure 11: XRD Spectra for ZnO [1,3,5] % Al ZnO thin films.

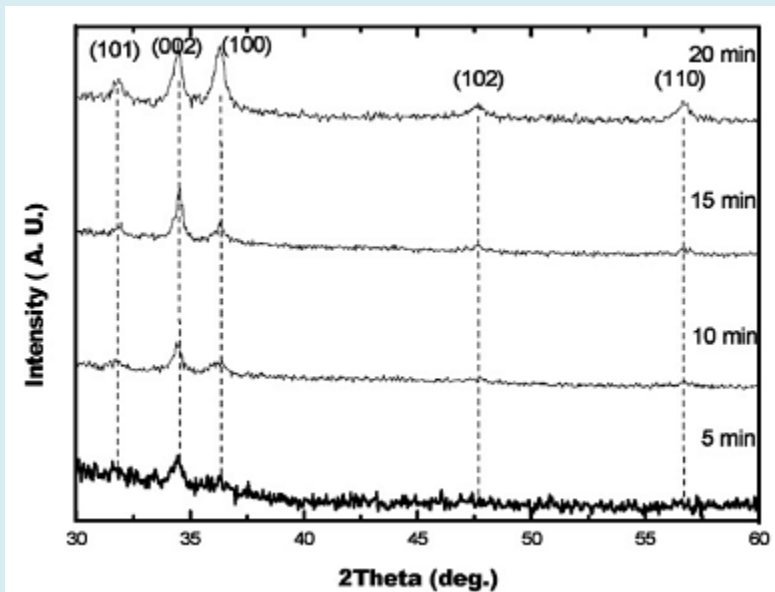


Figure12: XRD Spectra of pure and CuZnO thin film annealed at Temperatures; 500°C, 700°C and 850°C.

Recent Advances in Applications of Perovskite Oxide based Nonmaterial

Perovskite oxide based nonmaterial have been in recent time found to be indispensable essentially in modern days for some technological devices especially due to their functional properties which include Ferroelectric, Piezoelectric, Ferromagnetic dielectric, magnetoresistance, multiferroic properties that are vital to the desired optimum performance in application in various areas such as electronics, sensing, catalysis, energy harvesting, conversion and storage, optics and optoelectronics couple with the fact that some are good for passivation of layers of metals which make them to act as corrosion protection on metal surface just to mention but a few of these. It is based on this that there is now veracious quest for research on various forms and types of perovskite

oxide nonmaterial using different approaches and growth mechanisms in order to ascertain the one that would enhance the improvement in optimization of the material's applicability in industries and sciences as outlined below.

Ferroelectric and Dielectric Properties

Ferroelectric characteristics of some perovskite oxide nanomaterial such as BaTiO_2 makes promising candidate for applications in thin film capacitance [42-46], when the structured texture and then grain sizes formed with controlled aggregation and crystal densities which lead to uniform nanocrystalline grain texture sizes while BaTiO_3 can be manipulated under a condition at a room temperature to possess a ferroelectric property with spontaneous electric polarization which could be reoriented by an external electric

field with anticipated application on ferroelectric memories.

Magnetic Properties

The perovskite oxide nanocrystals such as BiFeO_3 material hinges on its particle size with emphasis on Curie temperature above room temperature for to be amenable for applications in most biomedical and magnetofluidic analysis [47-49].

Multiferroic Properties

Multiferroic characteristic of Perovskite nanocrystal is based on the coexistence of spin, orbital, and/or electric dipole order and cross-term effects between the corresponding different degrees of freedom (102,103) multiferroic and magnetoelectric characteristics of materials involve combining simultaneously ferromagnetic and ferroelectric in the same phase, with coupling between the two orders induce on it properties of spontaneous magnetization which can be reorientated by application of external electric field which is applied in magnetoelectric memory effects and magnetic switching of ferroelectric domain which is the base of in magnetic random access memory (MRAM) cell [50].

Nanoelectronics and Information Devices

Perovskite oxide nanocrystals have been of use electronic devices such as video camera, cell phone, laptop computers and automobiles because of they have a special feature in the process of multilayered ceramic capacitors (MLCC) that is very useful due to its efficiency in synthesis of electronic devices more especially for printed circuit board and hybrid circuits on ceramic substrates.

Also ferroelectric materials possess an inherent electric dielectric dipole moment in absence of an external electric field there found to have spontaneous polarization which is feature that makes such a material good candidate for random access memory, known as FeRAM (ferroelectric random access memory that could simply realized by the use of ferroelectric capacitors, in two states are normally "1" or "0" as in binary logic are represented by the manifestation of the spontaneous polarization which play vital role in electronic information. While some with good dielectric characteristics can be applied in dynamic random access memory (DRAM) which is the working medium block for information storage in the microelectronic devices that constitute the entire litany of the electronic systems.

Solar and Energy Harnessing

Optically, perovskite oxide based materials have good and effective absorption co-efficient within the visible range

which is dependent on the thickness of the materials. It has been observed that within the range of some thickness, there is complete absorption of light and this makes perovskite oxide materials to exhibit good charge transfer [26-27], which is one of the major factors that makes it favorable in solar energy harnessing and thereby indicating its prospect in solar cells conversion.

High efficiency of perovskite solar cells devices has been of interest in recent years as it efficiency is not limited only to small devices but also to large cells though the fabrication of the material with good stable and selective charge carriers extraction layers in solar cells is yet to be optimized [51-53].

Summery

In this work, we have been able to carry out a brief review of the prospect and applicability of perovskite oxide nanomaterial with consideration given to various deposition techniques that can be used to grow the materials either in powder or thin film form on a given substrate [54-57]. From the review and the assessment, it was revealed that some of these deposition techniques were meant to undergoes certain unique processes during the formation of the materials that may often impact on the structural and morphological properties, especially as it concerns structural size effect of material which is found to be influential to the structural and other important properties of the materials that are discovered to be associated with a particular growth mechanisms. Also it was observed that some of these growth techniques have some added advantage over other in formation of a suitable perovskite oxide nanomaterials and then based on this it will be worthy to note that the for knowledge of this would an added advantage in making a choice in the growth mechanisms to be adopted that would help in optimizing and achieving the right critical size and dimension for the purpose of production of perovskite nanomaterials suitable for various applications while growing the material. It is clear that a better understanding of the size effects in perovskite oxide nanocrystal will be highly appreciable in making choice of the growth mechanisms that will be helpful in implementing the development of the materials amenable for various device applications. Hence, this brief review has made an attempt to assess succinctly the prospect and development of the perovskite oxide nanocrystal materials and their possible applications especially in nanoelectronics, information storage devices, and other potential application in industries. Based on these, the research on perovskite oxide based nanocrystal had found to spread like wide bush fire with thereby becoming very extensive and has thus prompting the desire to review the prospect in research of the material and their possible applications I various areas.

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