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Study of Zinc Oxide Varistors by Incorporating Alkaline-Earth and Rare-Earth Metal Nanofillers

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This paper investigates recent developments in the field of zinc oxide varistors' development using nanocomposite materials. In addition, the materials under discussion have attracted academic and industrial interests due to their dramatic improvement in characteristics at nanofiller contents. Moreover, the varieties and forms of zinc oxide varistors, as well as the structure and properties of zinc oxide varistors, are discussed in this article. Zinc oxide varistors have traditionally been filled with synthetic or natural inorganic compounds to improve their properties or simply to save cost. In addition, this paper investigates the performance evaluation of zinc oxide varistors by incorporating alkaline-earth and rare-earth metal nanofillers. These applications require multifunctionality in a single material, which is rare in zinc oxide varistors. Zinc oxide varistors incorporating with other materials is a cost-effective technique to create multifunctional materials. The property improvement in nanocomposite systems, where the fillers typically have nanometre-scale dimensions, probably occurs with a tradeoff.

У даній роботі досліджуються останні результати в області розробки варисторів оксиду Цинку з використанням нанокомпозитних матеріялів. Крім того, обговорювані матеріяли привернули академічні та промислові інтереси завдяки різкому поліпшенню їхніх характеристик із вмістом нанонаповнювачів. Крім того, різновиди та форми варисторів оксиду Цинку, а також будова та властивості варисторів оксиду Цинку розглянуто в даній статті. Варистори оксиду Цинку традиційно заповнюються синтетичними або природніми неорганічними сполуками для поліпшення їхніх властивостей або просто для економії витрат. Крім того, в даній роботі досліджується оцінка ефективности варисторів оксиду Цинку шляхом включення лужноземельних і рідкісноземельних металевих нанонаповнювачів. Ці застосування вимагають багатофункціональности в одному матеріялі, що рідко зустрічається у варисторах оксиду Цинку. Варистори оксиду Цинку, що входять до складу з іншими матеріялами, є економічно вигідною технікою для створення багатофункціональних матеріялів. Поліпшення властивостей у нанокомпозитних системах, де наповнювачі зазвичай мають розміри в нанометровому масштабі, ймовірно, відбувається з компромісним розв'язанням.

Key words: alkaline-earth metal, rare-earth metal, nanofillers, zinc oxide varistors.

Ключові слова: лужноземельний метал, рідкісноземельний метал, нанонаповнювачі, варистори оксиду Цинку.

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1. INTRODUCTION

Metal oxide varistors are ceramic semiconductor devices based on ZnO, which have highly nonlinear current–voltage characteristics akin to back-to-back Zener diodes. These varistors' devices have been the dominant method of shielding electronic, electrical, and power distribution and transmission circuits from the damaging voltage levels caused by lightning impulses or switching surges over the last 30 years [1]. The varistors are made via a ceramic sintering method, which results in a structure that is mostly made up of conductive ZnO grains surrounded by thin electrically insulating barriers.

As a semiconductor ceramic resistor with nonlinear volt-ampere characteristics, ZnO varistor has several advantages, including low raw material costs, a simple manufacturing process, adjustable potential gradients, a high nonlinear coefficient, low leakage current, and excellent energy absorption [2]. Many research efforts have been devoted to the application of ZnO varistor in high/low voltage power systems and semiconductor industries due to its unique functionality. The instantaneous overvoltage in the circuit is limited by the ZnO varistor to a range that the equipment or system can withstand, potentially protecting the system from surge impact and damage [3]. Considering the current application and manufacturing method of zinc oxide varistor, this new kind of varistor is separated into two categories: high-voltage varistor and high-energy type pressure, both of which are irreplaceable in terms of formulation and performance.

To improve its electrical properties, the ZnO varistor is commonly doped with a tiny amount of metal oxides as additions [4]. The microstructure and phase composition of the material, as well as the distribution of dopants, all play a significant role in its overall performance. The considerable variance in particle sizes of these dopants, on the other hand, may reduce the varistors' microstructure uniformity. As a result, increasing the homogeneity of mixed oxides is a significant component in improving the overall performance of ZnO varistors. The significant nonlinearity of the current-voltage characteristics of ZnO varistors is their distinguishing feature. The microstructure, composition, additive distribution, and homogeneity of ZnO varistors determine their electrical properties.

Doped ZnO grains, intergranular, and spinel phases are three the major phases seen in varistors [5]. If the varistor is made the traditional way, these phases are generated during the reactive sintering of ZnO powder with a small number of additives like Bi, Sb, Co, Mn, Cr, Al, Ni, and other oxides. The spinel phase may dissolve almost all other elements in the system [6]. Its basic formula in ZnO varistors is $Zn_{2.33}Sb_{0.67}O_4$ [7]. Its exact formula is determined by the composition of the initial varistor mixture and the sintering circumstances. Although many different features of ZnO varistors have been studied (microstructural, chemical, electrical), there are just a few studies that deal with the spinel phase, its composition, and its influence on varistor characteristics. Spinel is thought to operate as a ZnO grain development inhibitor and, as a result, influences the breakdown voltage, which is dependent on ZnO grain size [8]. Catalysts, phosphors, and polishing compounds are all made from rare earths. These are employed in air pollution control, electronic device lighted screens and optical-quality glass polishing. Demand for all of these items is expected to increase. Other compounds can be used in place of rare-earth elements in their most essential applications, but they are usually less effective and more expensive.

According to previous research, adding fine-particle raw materials to the varistors might considerably improve their microstructure and electrical performance [9]. During the sintering process, all types of additive materials should be refined in advance to provide a homogeneous reaction between the additives and the main material-ZnO with an average particle size of roughly 500 nm. At the moment, chemical and mechanical milling processes are used to make the ZnO varistors' precursor powder. Apart from military applications, beryllium is employed as a dopant in semiconductors, an electrical insulator, and a heat conductor. Magnesium is used in pyrotechnics, signalling, flares, in the aviation sector, to prevent iron pipes from corroding. Chemical approaches that can increase additive distribution homogeneity include the gas phase method, sol–gel method [10], co-precipitation method [11], a wet chemical method [12], and microemulsion method [13]. Chemical approaches, on the other hand, are challenging to apply in the large-scale industry due to their high cost and the fact that dopants are prone to separate precipitation and segregation in complicated multi-component systems. In the following chapter, we discussed 5 different topics related to zinc oxide varistors by incorporating alkaline-earth and rare-earth metal nanofillers.

2. LITERATURE SURVEY

Various approaches in zinc oxide varistors by incorporating alkaline-earth and rare-earth metal nanofillers are discussed in the following sections. In addition, the advantages and disadvantages of zinc oxide varistors are described in the succeeding section.

2.1. Review on Micro- and Nanovaristors

Liu *et al.* [14]. The chemical vapour deposition method was used to produce nano-ZnO in this experiment. Then, to generate a suspension, ZnO nanoparticles were combined with deionized water. In which, impurities were removed by heat treatment and then a different amount of water was added to obtain a nano-ZnO electrode under the action of a micromechanical stirrer. The nano-ZnO electrode conductive process and electrochemical properties were investigated and analysed. The results show that after adding nano-ZnO, the varistor pressure ratio increases significantly.

Xin Ren *et al.* [15]. This paper demonstrated a quick refining approach using ball milling and sand milling that significantly increased milling efficiency, suspension dispersion, and ZnO varistors' electrical properties. The effects of the refining methods on the size of the doping additive oxides, the microstructure, and the overall electrical properties, especially the ZnO varistors' degradation behaviours, were investigated.

Rohini *et al.* [16]. Varistor samples are prepared using a sequential process that includes ball milling, calcination (700°C), compression (340 kg/cm^2), moulding, and sintering (1150°C) in this paper. The prepared samples are then characterized with a scanning electron microscope (SEM) and experimentation is conducted to determine various parameters such as non-linearity, permittivity, dielectric loss, and thermal conductivity. Sample 3 and 4 had better surge arrester characteristics since SrO was used as a primary additive component instead of bismuth oxide.

Miranda-López *et al.* [17]. A comparison of the incorporation of Co_3O_4 micro- and nanoparticles as a densifying dopant in a SnO_2 based varistor process is carried performed. With $x = 0$, 0.5, 1.0, 2.0, and 4.0 mol. percent, the ceramic composition was $(99.9 - x)$ percent SnO_{2-x}, percent $Co_3O_{4-0.05}$, percent $Cr_2O_{3-0.05}$, percent Nb_2O_5. Co_3O_4 was employed in two particle sizes (5 m and 50 nm). The inclusion of 0.5 mol.% Co_3O_4 nanoparticles resulted in a grain size increase of 7.9 m in sintered samples, which is the greatest value among all variations. Further research will be conducted to confirm this assumption and to improve the non-linear behaviour.

Aljaafari *et al.* [18]. The effect of nanocrystal fraction in bulk-ZnO varistors was analysed in this paper. X-ray diffraction (XRD) and field-emission scanning electron microscopy have been used to investigate the structure of ZnO nanocrystals (FE-SEM). The nanocrystals were indexed with the hexagonal wurtzite structure of ZnO nanostructures, according to XRD investigations. The average crystallite size determined by XRD analysis was 135–273 nm, which was eight times smaller than the nanoparticles shown in FE-SEM micrographs (1151–2214 nm). The number of nanocrystals applied to the ZnO varistor was increased from 0% to 100%.

Bao-hui Chen *et al.* [19]. X-ray diffraction, infrared, x-ray photoelectron spectroscopy, scanning electron microscopy, an electric field–current density, capacitance–voltage, mechanical, and thermal expansion measurements were used to investigate the effect of raw particle size and the annealing process on the compositions, microstructure, mechanical, thermal, and electrical properties of ZnO varistors in this paper. In addition, the mechanism of ZnO grain development during the annealing process was thoroughly explored. The produced ZnO-based varistors had outstanding mechanical, thermal, and electrical properties when the raw particle size was 90 nm and sintering was performed at 1100°C for 2 hours.

Yan *et al.* [20]. The effects of different additive sizes on the dispersion of mixed suspensions, microstructures, and general electrical properties of ZnO varistors were examined. To determine the effect of the additive sizes on the dispersion of the metal oxide particles, the particle size distribution, viscosity, and zeta potential of the suspension were measured. The influence of the additive sizes on the performance of the ZnO varistors was estimated using the potential gradient, leakage current, nonlinear coefficient, voltage ratio, and aging coefficient.

Kaufmann *et al.* [21]. This is the first detailed research of the electrical characteristics of electrode grain junctions in Pr-based ZnO varistor ceramics with Pd electrodes, namely, the I–V characteristics. On the microstructural scale, these connections were studied using a micro 4-point probe system. The Schottky barrier height was found to be 0.47±0.03 eV on average. A model based on an interfacial layer could describe the reverse current across the junctions. Furthermore, using electron backscatter diffraction and analysing etching patterns, the crystal orientations and polarities of grains about the electrode layers were determined, as well as a probable influence on the barrier height.

Wang *et al.* [22]. By using Ga_2O_3 doping and raw ZnO nanoparticles, ZnO-based varistors with a minimal concentration of Bi_2O_3, Sb_2O_3, Co_2O_3, SiO_2, and MnO_2 were created with high voltage gradient, outstanding mechanical and thermal performances. XRD, XPS, SEM, E–J, C–V, mechanical, and thermal expansion measurements were used to evaluate the varistors' compositions and microstructure, as well as their electrical, mechanical, and thermal properties. The effects of Ga_2O_3 addition on the electrical and mechanical properties of the varistors were also thoroughly discussed. The results showed that the added Ga_2O_3 initially occupied the lattice position of the ZnO crystal by forming a substitutional solid solution (donor doping), then occupied the void position by forming an interstitial solid solution (acceptor doping), with the residual Ga_2O_3 remaining in the grain boundary and representing as inversion boundaries.

Shaifudin *et al.* [23]. The impact of Pr_6O_{11} and Co_3O_4 on the electrical characteristics of ZnO–$BaTiO_3$ varistor ceramics was explored in this paper. The nonlinear coefficient, varistor voltage, and leakage current characteristics are all influenced by Pr_6O_{11} doping. A commercial varistor is often formed by blending ZnO powder with a variety of varistor-forming oxides, such as Bi_2O_3, transition metal oxide (V_2O_5), rare-earth oxide (Pr_6O_{11}), and alkaline-earth oxide (AEO).

Ref.	Technic used	Features	Challenges
[14]	The chemical vapour deposition method	For LD conductivity detection, the electrode of nano-ZnO varistor valve sheets maintains good stability.	It is not suitable for large scale production
[15]	The fast combinatorial method is a combination of both ball milling and sand milling	It significantly enhanced production efficiency and overall electrical performance, suggesting it has a lot of potential for achieving significant and low-cost industrial production of ZnO varistors.	Horizontal sanding has high production efficiency; however, the uniformity of additive particle size is still inadequate, because it is difficult to grind raw materials with sanding if their initial particle size is too large.

[16]	Energy dispersive spectroscopy method	The increase in capacitance and resistivity for Sample 4 at higher temperatures is due to a larger interfacial layer. Due to the overall increased quantity of ZnO grains between the electrodes, the threshold voltage for Sample 4 also has improved.	Internal and external transient overvoltage is effective in large voltage networks, causing damage to exposed terminal equipment.
[17]	X-ray diffraction technique and Scanning electron microscopy	The densification repeatability attribute was improved using nanoparticles.	As this creation of potential barriers is required to permit non-linear characteristics in ceramic materials, acquiring a dense material becomes important.
[18]	Field emission scanning electron microscopy (FE-SEM)	As a logical consequence, nanosize crystals at ZnO ceramic grain boundaries can fully deform the potential barriers of ZnO.	Due to the general potential barriers created at the intergrain interfaces, ZnO polycrystalline nanostructures exhibit nonlinear I–V characteristics.
[19]	X-ray diffraction method	The obtained ZnO-based varistors had excellent mechanical, thermal, and electrical properties when the raw particle size was 90 nm and sintering occurred at 1100°C for 2 hours.	Varistors constructed of ZnO are semiconductor ceramic devices with resistance that varies with applied voltage and have outstanding electrical qualities such as voltage gradient, high nonlinear coefficient, high energy-absorption capability, and low leakage current.
[20]	Effects of sizes of additive particles on suspensions	The potential gradient and nonlinear coefficient increased while decreasing, whereas leakage current, voltage ratio, and aging	The cost is high, purity is difficult to ensure, and the preparation process is more difficult.

		coefficient had a distinct pattern.	
[21]	A comprehensive study of the electrical behaviour of electrode grain junctions in Pr-based ZnO varistor ceramics with Pd electrodes, specifically the *I–V* characteristics	The *I–V* characteristic can only be determined accurately using the 4-point probe approach.	They have a relatively high electrical resistance below a critical voltage threshold.
[22]	The impact of introducing Ga_2O_3 on the varistors' electrical and mechanical properties	Increased IB concentration induced abnormal development of ZnO grains, resulting in a plate-like grain that improved mechanical and thermal performance.	Lower voltage gradient
[23]	The impact of Pr_6O_{11} and Co_3O_4 on the electrical characteristics of ZnO–$BaTiO_3$ varistor	Co_3O_4 had a lower leakage current density and varistor breakdown voltage than Pr_6O_{11}.	To these characteristics, a varistor is capable of promptly sensing and absorbing surge energies, preventing damage to electronic circuits and electric power systems.

Various studies are performed in these micro- and nanovaristors, in which comparison of the incorporation of Co_3O_4 micro- and nanoparticles as a densifying dopant in a SnO_2-based varistor process is carried out. Moreover, further research will be carried to improve the non-linear behaviour in this research.

2.2. Review on Synthesis Methods for ZnO Nanoparticles with Fillers

Fiedot-Toboła *et al.* [24]. Extrusion and injection moulding were used to create a series of nanocomposites comprised of high-density polyethylene (HDPE) with 10% zinc oxide nanoparticles (ZnO NPS). The nanoparticles were made in a green method, with pectin-based banana peel extract serving as a stabilizer and dispersion agent. The fillers were evenly distributed throughout the matrix, and the composites had better functional features such as higher thermal stability and mechanical properties. The inclusion of the pectin-organophilic filler influenced the crystallization of HDPE significantly.

Batra *et al.* [25]. Present the chemical co-precipitation synthesis of pure and Ba-doped ZnO nanoparticles to investigate the viability of Ba-doped ZnO nanoparticles as piezoelectric fillers in composite piezoelectric nanogenerators. The impact of Ba-doping on ZnO structural, ferroelectric, and piezoelectric properties has been thoroughly explored. Powder XRD structural analysis demonstrates that both pure and Ba-doped ZnO nanoparticles form a single hexagonal wurtzite phase. From field emission scanning electron microscopy, a hexagonal rod-like shape was detected in both samples.

Din *et al.* [26]. Semolina, which was used as biomass in this study, served as the polymer matrix, into which ZnO nanoparticles were inserted. To minimize any potentially harmful side effects, ZnO nanoparticles were biogenically produced using *Syzygium cumini* extract. The development of hydrogen bonds between the starch polymer matrix and nanoparticles was demonstrated by FTIR analysis of ZnO enhanced Semolina plastic blends. A moisture content test was conducted, which revealed a drop in moisture content with an increase in ZnO NPs concentration, with 9.7% serving as the lowest value by a 10% ZnO blend.

Sevcik *et al.* [27]. The focus of the research is on the power efficiency and brightness of polymer light-emitting diodes (PLEDs) made from a polymer matrix and nanoparticulate filler. Microwave-assisted polyol technique was used to make nanofillers, aluminium-doped ZnO nanoparticles, which were studied using XRD, SEM, and TEM. Colloids of nanoparticles were produced and blended with the dissolved polymer. UV–Vis absorption, photoluminescence, energy-resolved electrochemical impedance spectroscopy (ER-EIS), and I–V and luminance measurements were used to examine the optoelectronic and electric properties of nanocomposite materials, as well as the performance of PLED devices.

Alsayed *et al.* [28]. The microstructural, thermal, and mechanical properties of HDPE-based composites made utilizing the compression moulding technique are investigated in this work. HDPE was mixed with microsize zinc oxide (bulk ZnO) or zinc oxide nanoparticles (nano-ZnO) as fillers at 0, 10, 20, 30, and 40% wt.%. X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transforms infrared spectrophotometer (FTIR), and thermal gravimetric analysis was used to determine the structural, morphological, and thermal properties of the composites (TGA). At low weight percentages, the results demonstrated good dispersion and interaction mechanisms between HDPE and the fillers.

Dhatarwal *et al.* [29]. Polymer nanodielectrics (PNDs) are polymer nanocomposites (PNCs) with tailorable dielectric and optical properties for application in constructing flexible and stretchable-type advanced organ electronic devices. This paper examines the structural, dielectric, and optical properties of multiphase

PEO/PMMA/ZnO nanocomposites made up of poly(ethylene oxide) (PEO) blended with poly(methyl methacrylate) (PMMA) in equal proportions as a host matrix and zinc oxide (ZnO) nanoparticles in various concentrations (1–5 wt.%) as filler.

Alsulami *et al.* [30]. For the production of new multifunctional MWCNTs/$NiFe_2O_4$/ZnO (MNFZ) hybrid nanostructures, hydrothermal and co-precipitation procedures were applied. The MNFZ hybrid nanostructure development was confirmed using x-ray diffraction (XRD) and transmission electron microscopy (TEM) investigation. The MNFZ nanoparticle-doped poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO) were then prepared using the casting procedure with varied concentrations of MNFZ NPS as nanofiller. XRD measurements reveal that all polymer blend and nanocomposite films are semi-crystalline, with a decreasing degree of semi-crystallinity with the dopant.

Anand *et al.* [31]. A solution combustion approach was used to make zinc oxide nanoparticles. X-ray diffraction was used to determine the average particle size. A latex blending approach was used to create natural rubber and ZnO nanoparticle composites. The crosslinking agent pentane1,5-diylidenediamine was used to cure the matrix phase. The effects of crosslinking and nanoparticle inclusion on the tensile and solvent transport properties of natural rubber were thoroughly investigated. Scanning electron microscopy (SEM) and energy dispersive x-ray analysis were used to investigate the nature of the nanoparticles' dispersion (EDX).

Praseptiangga *et al.* [32]. The chemical surface of nanoparticles is particularly sensitive to Fourier transform infrared spectroscopy (FTIR). The functional groups in the substance were identified using FTIR spectra. The FTIR technique is effective for monitoring functional groups in a mixed suspension, as evidenced by a simple comparison of standard spectra and samples. FTIR spectroscopy with wavenumbers of 500–4000 cm^{-1} was used to examine the chemical interaction of silicon dioxide (SiO_2) and zinc oxide (ZnO) nanoparticles with SDS surfactant and water in this work. The nanoparticle suspension material and SiO_2–ZnO nanoparticle suspension with varied ratios (1:1, 1:2, and 1:3 percent w/w c) were FTIR analysed.

Ref.	Technic used	Features	Challenges
[24]	Nanocomposites of high-density polyethylene	The thermal properties of the materials were a maximum contribution to the use of inorganic filler.	There is a constant need to improve the mechanical and thermal properties of HDPE, such as low-density polyethylene and polypropylene.

[25]	X-ray diffraction	Due to the improved piezoelectric charge coefficient (41.28 p.m./V), the synthesized Ba–ZnO nanoparticles were used to fabricate piezoelectric nanogenerators, and the nanofiller concentration was optimized for best output.	Mechanical energy is the most abundant of these sustainable sources.
[26]	FTIR analysis of ZnO	Water-resistant, fully biodegradable.	When compared to commodity plastic films, these biopolymer-based packaging solutions have some drawbacks, such as poor barrier or mechanical qualities and high production costs.
[27]	Energy-resolved electrochemical impedance spectroscopy	The PLED devices were produced in a simple method with easy control of processing parameters using MEH-PPV and F8BT polymers.	Organic and polymer materials, in general, are delicate and fragile and can degrade when exposed to moisture and oxygen in the air.
[28]	High-density polyethylene	Due to its outstanding characteristics, lightness, and low manufacturing cost, high-density polyethylene (HDPE) is a commonly utilized polymer.	However, due to its limited thermal stability and mechanical and structural failure, its use is limited.
[29]	PEO/PMMA/ZnO nanocomposites comprising poly(ethylene oxide) (PEO) blended with poly(methyl methacrylate) (PMMA) in equal composition as a host matrix and zinc oxide (ZnO)	The amount of blended PEO greatly plasticizes the PMMA and so reduces its brittleness, whereas the amount of PMMA in the blend largely improves the thermal and mechanical stabilities of the PEO.	To these characteristics, a varistor is capable of promptly sensing and absorbing surge energies, preventing damage to electronic circuits and electric power systems.
[30]	Hydrothermal and coprecipitation method	The doping method improves the magnetic, electrical, and dielectric properties of the	When a modest amount of fillers was added to the polymer matrix, the charac-

		PVA/PEO.	teristics of the matrix altered substantially. The chemical cause of this alteration is still being investigated.
[31]	Thermogravimetry differential thermal analysis	At 600°C, the precursor was calcined and pyrolysed to produce a light-gray TiO_2/Sb–SnO_2 composite with good crystallinity.	During the pyrolysis process, waste gases will need to be collected and handled.
[32]	Solution combustion method	The highest ultimate tensile strength and EAB were found in cured NR with 0.02 percent ZnO.	Uncured NR, on either side, is unsuitable for industrial usage because it is sticky, deforms quickly when heated, becomes brittle when cooled, and has poor electrical conductivity.
[33]	Fourier transform infrared spectroscopy (FTIR)	Due to the use of SDS as a surfactant in aqueous media, formulations containing SiO_2–ZnO NPs promote new functional groups known as SiOH bonds.	The water vapour barrier and mechanical properties of the films generated by these polymers are poor.

A latex blending approach was used to create natural rubber and ZnO nanoparticle composites, which, uncured NR, on either side, is unsuitable for industrial usage because it is sticky, deforms quickly when heated, becomes brittle when cooled, and has poor electrical conductivity.

2.3. Review of Different Additives That Is a Composition

Hakeem *et al.* [34]. Metal oxides (MOs) in the nanosize range were used as additions in the oxynitride network to create a variety of sialon ceramics compositions. The present work included nanosize precursors such as Si_3N_4, SiO_2, AlN, Al_2O_3, and MO (MO = MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, CeO_2, Nd_2O_3, Eu_2O_3, Dy_2O_3, Er_2O_3, and Yb_2O_3). At a relatively low temperature of 1500°C, probe sonication and spark plasma sintering procedures were employed to mix the powder precursors and then synthesize sialon ceramics.

Zhang *et al.* [35]. Direct chemical extraction by acid, on the other hand, was able to achieve reasonable recovery rates, and the addition of leaching additives, alkaline pretreatment, and/or heat pretreatment significantly improved the process performance. These techniques, combined with appropriate solution purification technologies, have been successfully applied at two major pilot plants to generate continuously high-grade mixed rare-earth products (as high as +95 percent) from coal-based resources, according to the studies discussed in this article. This paper provides a thorough examination of the recovery methods, testing results, and separation mechanisms used in REE extraction from coal-related materials.

Pan *et al.* [36]. The majority of rare-earth elements (REEs) in coal fly ash (CFA) are associated with the aluminosilicate glassy phase, which makes them difficult to dissolve in acid. For the recovery of REEs from CFA, a sequential chemical roasting, water leaching, and acid leaching technique was established in this work. The impact of various roasting additives on the conversion of CFA phases into water or acid soluble phases was initially investigated. A thermodynamic analysis was used to choose the reaction parameters for chemical roasting. The chosen reaction conditions were then tested in the lab.

Honaker *et al.* [37]. The majority of rare-earth elements (REEs) present in coal preparation plant feed are transferred to coarse trash streams for permanent storage in confined piles. Based on laboratory test data, an integrated flowsheet combining physical separation, pyrite biooxidation, heap leaching, selective precipitation, and solvent extraction procedures was created in this work. The test data came from (1) the characterization of several natural leachates and solid samples taken from various preparation plants that process coal from a variety of coal seams, and (2) the results of laboratory acid leaching and selective precipitation tests.

Prudêncio *et al.* [38]. The attenuation mechanisms in a passive system for acid mine drainage treatment were assessed using rare-earth elements (REE) (Jales, Portugal). After summer and winter, hydrochemical parameters and REE contents in water, soils, and sediments were measured along with the treatment system. After summer, there is a reduction in REE content in the water due to interaction with limestone; in wetlands, soil particles release considerable amounts of REE into the water. Because REE contents drop along with the system during winter, higher water dynamics support AMD treatment effectiveness and performance.

Zhang *et al.* [39]. Acid mine leachate (AML) might be a major source of rare-earth and other essential elements required for innovative electronics and sustainable energy technologies. A thorough investigation was conducted on natural leachate collected from a coal preparation plant that handled bituminous coal with high pyrite levels. 1.96 ppm total REEs, 2.52 ppm Zn, 2.15 ppm Ni, 1.22 ppm Cu, 0.77 ppm Co, and 25 ppm Mn were found in the leachate. A preconcentrate comprising 0.82 percent total REEs, 1.08 percent Zn, 0.91 percent Ni, 0.50 percent Cu, 0.34 percent Co, and 7.1 percent Mn was produced by sequential precipitation with easy pH control. Redissolution of the preconcentrate in a 10M HNO_3 solving was used to treat it further.

Ziemkiewicz *et al.* [40]. Traditionally, the rare-earth element (REE) sector has attempted to develop ore deposits where geologic processes have formed mineralized zones with commercially appealing REE concentrations. These types of deposits are extremely rare, especially in the United States. Given the importance of these minerals and the necessity for a long-term domestic supply, the current study aims to use additional autogenous methods to produce concentrated REE resources. Acid mine drainage is one example of such a process (AMD). AMD is highly frequent in many coal-mining locations, and it is caused by pyrite exposure and oxidation.

Vass *et al.* [41]. Rare-earth elements (REEs) are used in many modern businesses to make goods that are critical in both civil and defence purposes. REE grades in acid mine drainage (AMD) and associated by-product precipitates from AMD treatment (AMDp) justify research as a feedstock for REE production, according to a previous study [1]. The current study expands on previous efforts by conducting a comprehensive survey of 141 AMD treatment centres in Northern and Central Appalachia. 185 raw AMD and 623 AMDp outdoor samples were collected and evaluated for REE and main metal concentrations in this investigation. The results demonstrate that REEs occur in AMD and AMDp at an average of 282 g/L and 724 g/tonne, respectively.

Claude *et al.* [42]. The effect of alkali, alkaline-earth or rare-earth dopant (*i.e.*, Ca, K, Mg, or Ce) addition in a 10 wt.% $Ni/-Al_2O_3$ catalyst on the material physicochemical parameters and catalytic activity was investigated in this study. In an aqueous solution, twelve doped $Ni/-Al_2O_3$ catalysts were produced using the sol-gel method. As a control, a $Ni/-Al_2O_3$ catalyst with no dopant was also produced. Due to limited interactions with the support, adding 1.5 wt.% alkali (*i.e.*, Ca, K, or Mg) did not affect the acido-basicity properties of the catalysts.

Rong *et al.* [43]. Rare-earth elements and their compounds can be employed as catalysts or promoters for the pyrolysis of organic matter, including coal; however, there have been few studies on the role of rare-earth materials in coal pyrolysis. Using gas chromatography, this study investigates the effects of cerium oxide (CeO_2) and lanthanum oxide (La_2O_3) on the generation of gaseous products from low-rank coal pyrolysis (GC). The mechanisms of two types of rare-earth oxides (REOs) that are involved in coal pyrolysis are also briefly reviewed.

Ref.	Technic used	Features	Challenges
[34]	X-ray diffractometry and field emission scanning electron microscopy	LEDs, cutting tools, seal rings, wear pads, airplane brakes, and bearing component components can all benefit from the diverse thermomechanical capabilities of RE and AE-doped sialon ceramics.	Low toughness and brittleness are significant drawbacks.
[35]	Recovery of rare-earth elements from coal-related materials	Can be used as a pre-concentration step to generate a better feed for downstream recovery.	Low recovery; ultrafine grinding is required if a significant enrichment ratio is to be achieved.
[36]	Direct acid leaching	When compared to physical beneficiation, provide a higher recovery.	The effectiveness of leaching is determined by the type of the examined samples; acid consumption is typically high.
[37]	Pre-leach calcination followed by acid leaching	Higher REE recovery; rapid leaching kinetics; mild leaching conditions; minimal chemical use	Contaminant ion recovery, such as Al^{3+}, is also improved.
[38]	Beneficiation through physical means	Can be used as a pre-concentration step to produce a higher-quality feed for downstream recovery.	Low recovery; ultrafine grinding is required if a significant enrichment ratio is to be obtained.
[39]	Acid Leaching	Higher REE recovery; rapid leaching kinetics; mild leaching conditions; little chemical use.	Contaminant ion recovery, such as Al^{3+}, has also improved.
[40]	Leaching after alkaline/hydrothermal treatment	Rapid leaching kinetics; high recovery.	Low selectivity and a lot of impurities are extracted along with REEs due to high alkali consumption.
[41]	Beneficiation physically	It can be used as a pre-concentration step to produce a higher-grade feed for downstream	No significant enrichment could be provided.

		recovery.	
[42]	Sol–gel method	Low recovery; expensive chemicals; difficult leaching conditions.	On the other hand, the sample doped with K+Ca displayed interesting toluene and methane conversions, which were linked to a minimal quantity of carbon deposit that was solely amorphous.
[43]	Gas chromatography	Rapid leaching kinetics; high recovery.	Low selectivity and a lot of impurities are extracted along with REEs due to high alkali consumption.

This research paper provides a thorough examination of the recovery methods, testing results, and separation mechanisms used in REE extraction from coal-related materials. In which, low toughness and brittleness are significant drawbacks.

2.4. Characterization of Alkaline-Earth and Rare-Earth Metals

Hakeem *et al.* [44]. The present work included nanosize precursors such as Si_3N_4, SiO_2, AlN, Al_2O_3, and *MO* (*MO* = MgO, CaO, SrO, BaO, Y_2O_3, La_2O_3, CeO_2, Nd_2O_3, Eu_2O_3, Dy_2O_3, Er_2O_3, and Yb_2O_3). The influence of the MOs on the microstructure and resultant densification, hardness, fracture toughness, thermal expansion, and thermal conductivity were studied using x-ray diffractometry and field emission scanning electron microscopy on the synthesized samples. The sialon samples synthesized with the specified MOs all had similar relative densities, ranging from 96 to 99 percent, and Vickers hardness (*HV* 10) values, ranging from 15 to 20.8 GPa, depending on the kind of MO.

Pothuganti *et al.* [45]. Melt quenching was used to make glasses having the composition $20BaO{-}10Bi_2O_3{-}(70-x)B_2O_3{-}x NiO$ with $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1 mol. percent. The amorphous nature of the produced samples was confirmed by x-ray diffraction (XRD) tests. Optical basicity (theoretical), metallization criterion, density, molar volume, molar refraction, electronegativity, polaron radius, and oxygen packing density (OPD) were all estimated. Because of the lower metallization criteria, the produced glass samples can be employed as amorphous semiconductors in electronic and memory switching devices.

Wu *et al.* [46]. A mild hydrothermal technique was used to make a novel alkali metal–rare-earth metal sulphate with the composition $NaY(SO_4)2H_2O$. Unit cell characteristics are $a = 6.8191(3)$, $b = 6.8191(3)$, $c = 12.7035(11)$, and $Z = 1$. It crystallizes in the non-centrosymmetric trigonal space group $P3121$ (No. 152) with $a = 6.8191(3)$, $b = 6.8191(3)$, $c = 12.7035(11)$ and $Z = 1$. It has isolated $[SO_4]$ groups in its structure, which extends to a three-dimensional (3*D*) framework linked by [YO9] and $[NaO_8]$ polyhedra. SHG experiments reveal that $NaY(SO_4)_2H_2O$ is phase matching, with an SHG response approximately 0.6 times that of KH_2PO_4 (KDP).

Zhang *et al.* [47]. The rare-earth element (REE) leachability and mineralogy of three segments of a core sample obtained from the Guxu coalfield (Sichuan Province, China) were investigated. The roof and floor strata contained as much as 2.087 ppm of total REEs, a figure substantially greater than other coal-based materials described in the literature, according to the elemental analysis of the three samples. Within 5 minutes of contact time with 1M mineral acid, 47 percent to 65 percent of the light REEs (LREEs) were leached from the floor samples, and continued contact, up to 120 minutes, boosted the LREE recovery to as high as 75 percent.

Akram *et al.* [48]. Using alternating current electrophoretic deposition, a hybrid coating was created on ZK60 magnesium (Mg) alloy (AC-EPD). Chitosan, gelatine (Type-B), bioactive glasses (BG(*a*, *b*)), and ZnO/CeO_2 nanoparticles made up the hybrid coating. The presence of the above-mentioned compounds on coated samples was confirmed by Fourier-transform infrared (FTIR) spectra. Coating morphology was homogeneous and covered the maximal surface area, according to scanning electron microscopy (SEM) images.

Sulaiman *et al.* [49]. The creation of novel transition metal oxide-modified CaO catalysts from eggshells for the transesterification of refined waste cooking oil is described in this research. CaO is a well-known transesterification base catalyst. Its catalytic performance has been limited by its modest basicity and low surface area. As a result, a fresh attempt was made to change the CaO catalyst using a simple wetness impregnation process with transition metal oxides such as Ni, Cu, and Zn oxides. The transesterification reaction with refined waste cooking oil was used to test the catalytic performance of the modified CaO-based catalysts.

Choi *et al.* [50]. A Zn(II)-based metal–organic framework (MOF) compound and MnO_2 were used to prepare ZnO_x–MOF@MnO_2 composites for selective Sr^{2+} removal in aqueous solutions. The ZnO_x–MOF@MnO_2 composites were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric analysis, and Brunauer–Emmett–Teller surface area analysis. The functional groups, morphologies, thermal stabilities, and specific surface areas of the composites were suitable for Sr^{2+} adsorption. A maximum adsorption capacity of 147.094 mg·g^{-1} was observed in batch adsorption experiments, and the sorption isotherms were fit well by the Freundlich model of multilayer adsorption.

2.5. Characterization with Different Sintering Temperatures

Chandekar *et al.* [51]. Several characterizations have been performed on the dielectric characteristics of pure and yttrium-doped PbS nanoparticles generated through the co-precipitation chemical synthesis technique. Using Williamson–Hall (W–H) plot analysis, crystallite sizes and intrinsic microstrains were estimated from x-ray diffraction patterns of materials. W–H plots were used to determine the crystallite size and intrinsic microstrain values in the ranges of 13.7–15.9 nm and 1.09 9 10–3–1.72 9 10–3, respectively. Scanning electron microscopy images revealed the production of nanoparticles, nanoflakes, sponge, and nanosheets (SEM).

Song *et al.* [52]. The researchers devised and built a rose Bengal-modified nanoporous structure. An organic sensitizer based on rose Bengal and a supporting host of rare-earth metal–organic-framework made up this composite structure (MOF). The x-ray diffraction (XRD) pattern, infrared (IR) spectra, thermal stability, and photophysical tests were used to identify it. 2, 4, 6-trinitrophenol enhanced its absorption. Its rose Bengal emission was raised proportionately. Its rare-earth emission, on the other hand, was well preserved, providing ratio metric indications. With a limit of detection (LOD) of 1.9 M, these two sensing modes showed a linear response and good selectivity. The use of rare-earth emission as an inner reference to develop ratio metric sensing is an advantage of our work. However, some issues must be addressed. The sensing region and sensitivity of ratio metric fluorescence sensing should be broadened in the future.

Motoc *et al.* [53]. Monazites are one of the most precious natural resources for rare-earth oxides (REOs), which are employed as dopants in ceramic materials with high added value for usage in severe environments. Because of their identical electronic configuration and physical-chemical properties, the separation procedure in individual REOs is complicated, resulting in high-priced products with a huge environmental footprint. Using diverse combinations of REOs as dopants for high-temperature ceramics, particularly ZrO_2-based thermal barrier coatings (TBCs) utilized in aeronautics and energy cogeneration, has sparked increased attention in recent years. TBC coatings based on ZrO_2 doped with synthetic REOs mixes imitating Ce-rich monazite concentrates are currently being developed. The results will be compared to those obtained using natural mixed REOs derived from monazite concentrates to determine whether they can be used as dopants and to illustrate their economic impact in aeronautics and energy generation.

The use of rare-earth emission as an inner reference to develop ratio metric sensing is an advantage of our work. However, some issues must be addressed. The sensing region and sensitivity of ratio metric fluorescence sensing should be broadened in the future.

3. SUMMARY

The stretching of fibrils (fibrillation) inter dispersed with microvoids characterizes the fracture initiation and propagation of clay–polyethylene nanocomposite. The crystal structure and interfacial interaction between the filler and the polymer matrix are responsible for the clay–reinforced polyethylene's lower toughness when compared with pure polyethylene.

PMMA's thermal stability was improved and was dependent on clay loading. PMMA/clay nanocomposites, on either hand, have good optical characteristics.

The thermal stability of PVC composites is slightly lower for nanoclay composites as compared to appropriate control formulations, as determined by a standard HCl evolution method, particularly for PVC.

The permittivity of the composite was unaffected by the small particle size of the ZnO nanoparticles. As a result, it appears that the interfaces between ZnO and LDPE do not contribute to the dielectric properties.

According to the findings of this study, including ZnO nanoparticles into the PP matrix can significantly improve the photodegradation resistance of PP to UV irradiation.

At low nanofiller loadings, epoxy nanocomposite systems with inorganic oxide fillers exhibit some favourable dielectric characteristics. The permittivity and tan delta values of nanocomposites are found to be lower than those of microcomposites and unfilled systems (for a limited number of filler loadings).

Incorporating a small amount of nanofiller into the base material results in a minor reduction in epoxy dc volume resistivity. Although the ac dielectric strength of nanocomposites is lower than that of unfilled epoxy systems, the type of filler appears to alter the results when compared to microcomposites.

4. CONCLUSION

In summary, the nebulized spray pyrolysis (NSP) method has been used to prepare successfully single-phase pyramidal-like and sphere-like grains on a glass substrate. All samples contain a tetragonal rutile structure of SnO_2 with no impurity phases, according to XRD analysis. The results reveal that sample SnO_2 doped with Ba improved crystallinity while also increasing carrier mobility. It also has a maximum transmittance of more than 90% and a 3.70 eV wide-bandgap. Because of these characteristics, the SnO_2:Ba thin film is a better option for use in transparent conductive electrodes in optoelectronic devices.

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