Preparation of Lead Free Piezoelectric Composite Based on Polyester Resin and (LKNN6-0.5%CeO_2) Ceramic Particles

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ABSTRACT

For the sake of guarding the environment from the vital problems that results from the toxic effects of lead components, lead free (LKNN6-0.5%CeO_2/polyester) piezoelectric composite are prepared in this work using cold press technique. Firstly, the lead free (LKNN6-0.5%CeO_2) piezoceramics are prepared using normal sintering technique. The dielectric and piezoelectric properties of the composites were examined as a function of the volume fraction of ceramic particles, all composites showed well dispersion of the piezoceramic particles in the polyester matrix as shown in SEM images. The piezoelectric and dielectric coefficients were found to be improved as the concentration of ceramic particles increases. Although the procedure is simple, the composite prepared in this study exhibited better piezoelectric and dielectric constants with (d_{33}=41 and ε_r=157) at (80%) volume fraction.

Keywords: Piezoelectric, Composite, Dielectric, LKNN-6 ceramics, volume fraction, Polyester, piezoceramics.

INTRODUCTION:

One of the foremost restrictions in utilizing the original piezoelectric material in the engineering applications is the high brittleness. Development of the composite piezoelectric products offers a solution to overcome this difficulty. The key-advantages of piezoelectric composite products are high flexibility as well as the ability to withstand the extensive deformation without causing damages. [1] Additionally, they are in compatible with the composite structures‟ the processing procedure. This will make piezoelectric composite an ideal material for applications such as an embedded sensor, power harvesting device, and a force actuator within the composite structures. [2] Piezoelectric composite particularly the (ceramic–polymer) piezocomposite attracts great attention due to the significance of biomedical and piezoelectric energy harvesting applications using piezoelectric composites is rapidly increasing. The (0–3) category connectivity is the simplest structure of piezoelectric (ceramic-polymer) composites. In such category, the ceramic particles are randomly dispersed in a polymer matrix, whose main benefit is the simplicity in the fabrication of products with numerous shapes. [3]

Pb-based piezoelectric materials are commonly employed due to their excellent electromechanical properties. Nowadays, lead free piezoelectric ceramics are intensively investigated for banding Pb-based ceramics since many states started to ban unsafe elements including (Pb) in electronic products. [4] Recently, alkali niobates lead free piezoceramics

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especially potassium sodium niobate, (K,Na)NbO_3 (abbreviated as KNN) are proposed as alternative piezoceramic materials, and that can be a competitive alternative to (PZT) for certain applications because of its high Curie temperature (Tc), good piezoelectric properties and better environmental compatibility. [2]

Mgbemere and coworkers. 2015 [5] studied the effect of (Ti) on the properties of (KNN) based lead free ceramics. The results showed that the increasing of (Ti) dopant leads to decreasing the sintering temperature for each (1 %) of the dopant added. Microstructural analysis revealed that the average grain size decreases with increasing (Ti) amount. The dielectric, piezoelectric constant values and ferroelectric properties of the KNN ceramics decreased with increasing (Ti) amount.

Vendrell and coworkers. 2015 [6] investigated the influence of the acceptor doping on the structural and functional properties of (ZrO_2) and (TiO_2) modified lead-free (KNN) piezoceramic prepared by solid-state sintering reaction. With doping, it was observed that an increment in the values of dielectric constant were recorded. In terms of piezoelectric properties, an increment was recorded with small concentrations dopants. ZrO_2 doped (KNN) ceramics showed good piezoelectric properties.

Mohammad and coworkers. 2015 [7] used conventional sintering as well as microwave sintering to prepare lead free LKNNT modified with different amounts of $SrTiO_3$. The results showed that the microwave sintering produce dense, more fine and uniform microstructure compared to conventional sintering. With (3%) $SrTiO_3$, ceramics showed relaxor behavior. Moreover microwave sintered reveled higher piezoelectric coefficient ceramic due to denser as well as closer composition to stoichiometry when compared with the conventional sintered ones.

Khorrami and coworkers. 2015 [8] synthesized lead free (KNN) nanopowders by a modified sol–gel method, using starch as stabilization and polymerization agent. The XRD patterns confirmed that the structure of the prepared powders, calcined at (600 °C), were orthorhombic and the particles of KNN compounds have cubic shape with the average size of 26, 58, and 34 nm, respectively from the results of TEM images.

Han and coworkers. 2015 [9] embedded lead free KNN nanoparticles in [P(VDF–TrFE)] polymer to fabricate piezoelectric composite nanofibers by electrospinning method. (KNN) Perovskite nanoparticles with (30–105) nm were separately prepared by using combustion synthesis technique. From the measurement of the Location-dependent piezoelectricity, the region of embedded (KNN) particles exhibited better piezoelectricity than the P(VDF–TrFE) matrix region.

Experimental part:

Preparation of LKNN-6 piezoelectric ceramics:

Pure grades of K_2CO_3, Na_2CO_3, Li_2CO_3, Nb_2O_5 and CeO_2 powders (>99.99%) were used as initial materials. In this study ($Li_{0.06}Na_{0.47}K_{0.47}$) NbO_3 (LNKN-6) lead free piezoelectric ceramics were prepared by a conventional mixed oxide method. After preparation (LNKN-6) lead free piezoelectric ceramic as a matrix material, (0.5%) of rare earth oxide (CeO_2) are used as a dopant to enhance the electrical properties of LKNN-6 ceramics.

The starting powders are accurately weighed according to the stoichiometric formula and then mixed and milled with balls for (24 hr) using ethanol as a medium to obtain homogenous powder mixture. At the end of the milling, the slurry was dried and kept in an oven at 220^{o}C. After mixing, the mixture was dried and calcined at (750^{o}C) for (4h) to ensure the formation of single niobate phase formation according to following thermal cycle (furnace oscillation was ±50C).

The inner furnace chamber was protected by purging Argon (%99.99 purity) gas to reduce oxygen content. After calcination the samples were powdered by hammering then milled for (24 hr.) in the same condition mentioned above and dried at 220 ºC for (4 hr.) respectively. Then (1%) of polyethylene glycol 6000 (PEG-6000) added to mixture and pressed in dies into disk of

(14) mm in diameter. Finally, the pressed pellet are sintered in a double crucible configuration of alumina with a heating rate of (5 ^oC/min) and the cooling rate of (10 ^oC/min) at different sintering temperatures, which yielded the relative density up to (96–97%) (Theoretical density is 4.51 g/cm3).

Preparation of LKNN6-polyester piezocomposite:

After preparing (LKNN-0.5%CeO_2) piezoceramics, the samples are kindly crushed to fine powder with a mortar and pestle. On the other hand, different volume fractions of these ceramic particles are prepared in order to incorporate them into polymer matrix making piezoelectric composite materials by using hand-lay-up process method. The principal advantages of the hand-lay-up processes are versatility, there is little limitation on the size and complexity of the molding and low capital cost, the only significant investment being that of tooling. The unsaturated polyester is the polymeric resin material that used in this work. One of their major advantages is the ability for cure at room temperature. In order to change the resin from its liquid state into solid (plastic), so a hardener material must be added to form the solid unsaturated polyester. The unsaturated polyester are mixed with (4%) of (MEKP) hardener, which is liquid and transparent material, in order to cure polyester resins. The resulting powders are incorporated into unsaturated polyester with different volume fractions of (20%, 40%, 60% and 80%) at ordinary room temperature.

A change in viscosity will be noticed from the first mixing of these materials and a good mix between them should be done to ensure a full reaction with complete solidification of the resin. The most important thing is to avoid adding the above materials at the same time, because it will produce a violent decomposition which will not produce the plastic material. So that both the (LKNN6-0.5CeO_2) piezoelectric ceramics powder, unsaturated polyester and its hardener are mixed via a magnetic stirrer in order to obtain a uniform distribution of ceramic particles in the matrix and until gel-like paste was achieved. The major problem in forming the unsaturated polyester reinforced with the LKNN6 ceramics particles is the precipitation of the particles in the base of the sample; so to avoid this problem the LKNN6 ceramics particles should be added before the gelation stage forming and prevent precipitation of the ceramic particles in the base of the sample. After mixing, the mixture is poured in a mold with (15mm) diameter and (10mm) thickness in order to cure the composite for (24hr) and then finally obtain well shaped hard disks piezoelectric composite materials.

Poling process for electrical measurements:

All the samples must be poled prior to dielectric and piezoelectric measurements. Before the poling, the samples are coated by applying silver paste on both surfaces and then poled under a DC field of (5) KV/mm in a silicon oil bath for (30) min at room temperature.

Measurements of electrical properties:

Two types of instruments are used in this project to determine the dielectric and piezoelectric properties. The dielectric properties are measured by using (LCR meter) provided from (Protek Electronics, LCR28200) while the piezoelectric properties are measured via a (Piezo-d_{33} meter), ZJ-6B Model provided from (China). Both Measurements are done at specific value of the frequency which is (1 kHz).

Density measurements:

After the sintering process, the density of each specimen for LKNN-6 and doped LKNN-6 was measured respectively. The volume of each specimen after sintering was measured by (VMM) instrument and the weight was measured by (0.0001) gr accuracy scale**.**

X-ray characterization

After preparing the sintered samples and prior to X-ray characterization, the samples are milled by hammer to achieve appropriate powder for XRD investigation. The (XRD) was carried out by GNR MPD 3000 instrument Cu lamp from 4 to 80 degree with ($K\alpha$) and (0.02) degree steps with (1s) step time.

SEM characterization:

TESCAN Vega II XMU SEM characterization used in this work which provides high resolution images by rastering a focused electron beam across the surface and detecting the secondary or backscattered electron signal at different magnification ranging from 5X to 200,000X. Both the microstructure and fracture surface are analyzed.

EDS chemical analysis:

EDS analysis was taken from each samples by bulk analysis that obtain semi quantitative measurements of elements (Except elements which atomic number smaller than 6). The exposure time for bulk analysis was (10) min.

Results and Discussion:

Fig.1 represents x-ray diffraction of the (LKNN6-0.5%CeO_2) piezoceramics. This pattern shows a pure perovskite structure at room temperature with a combination of orthorhombic and tetragonal structure. The intensity of (002) peak at lower angle and the intensity of (200) peak at higher angle and also from the intensity ratio of these distinct peaks (I_{002}/I_{200}), it was revealed that the (LKNN6-0.5%CeO_2) piezoceramics possess both of the orthorhombic and tetragonal phases.

Fig.2 represents the SEM image of (LKNN6-0.5%CeO_2) piezoceramics, (SEM) images detected two classes of grain size: some grains have a larger diameter, whereas others are smaller. Backscatter detector image shows the presence of cubic crystals for the sintered powder with dense microstructure. Fig.3 shows the results of the chemical analysis and the major elements of lead free (LKNN6-0.5%CeO_2) ceramic detected by (EDS) characterization. Fig.4, fig.5, fig.6 and fig.7 shows the influence of the different volume fractions of lead free (LKNN6-0.5CeO_2) piezoelectric ceramics particles on the density, piezoelectric coefficient, dielectric constant and dielectric loss of the polyester polymer matrix. Four volume fractions of modified (LKNN-6) ceramic particles (20, 40, 60 and 80%) are used in this study.

Fig.4 shows the effect of the volume fraction on the density of polyester matrix , it was found that the density of composite increased with increasing the volume fraction of ceramic particles where reached a high value about 3.75 at (80%) volume fraction. Also, from the attained results from both fig.5 and fig.6, it was seen when the ceramic particles volume fraction is increased and reached (80%), both piezoelectric coefficient and dielectric constant of piezoelectric composite reached the peak values of (41) pC/N and (157), individually.

This enhancement in the electrical properties is attributed to the uniform distribution of the ceramic particles in the polyester polymer matrix for different volume fraction as shown from SEM images in fig.8. In contrast, the effect of volume fraction on the dielectric loss of composite is shown in fig.7, it was revealed that, as the piezoceramic particles concentration increased, the dielectric loss of composites deceased and reached a lower value with (0.036) at (80%) volume fraction.

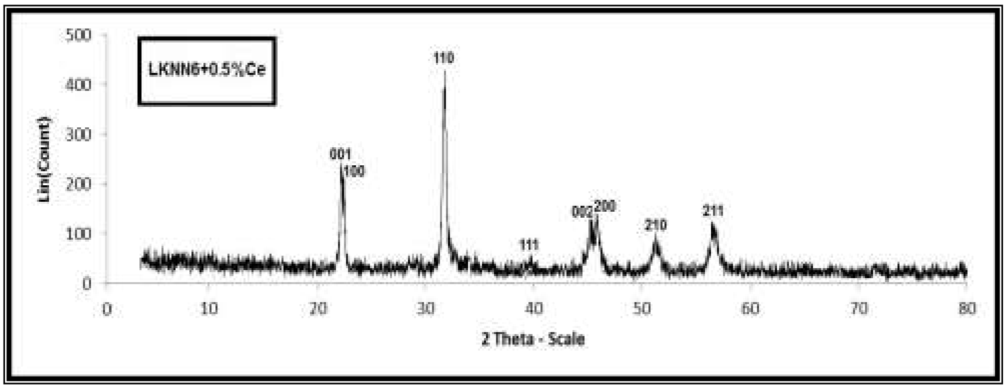


Figure (1): XRD Pattern of LKNN6-0.5%CeO_2 Ceramics.

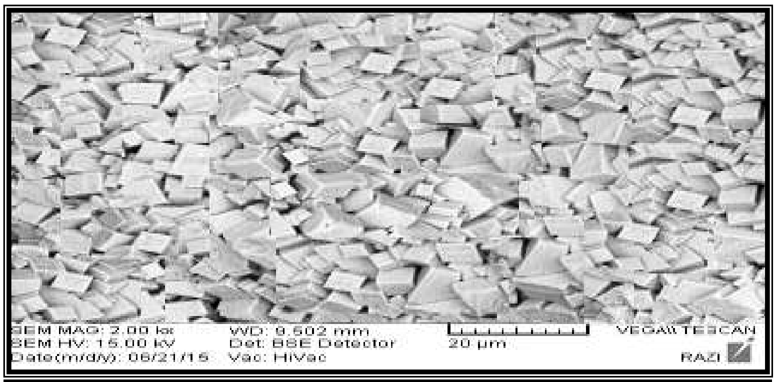
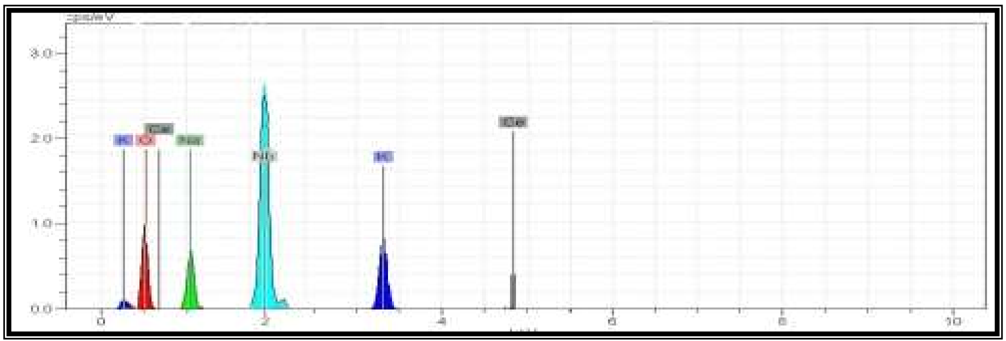


Figure (2): SEM Image of (LKNN6 – 0.5% Ce O_2).



(LKNN6 – 0.5% CeO_2)

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Oxygen	K series	29.21	27.43	51.19
Sodium	K series	7.11	7.42	11.89
Potassium	K series	12.09	13.87	13.47
Niobium	L series	51.02	50.77	23.33
Cerium	L series	0.54	0.51	0.12
	Total:	99.97 %		

Figure (3): EDS Results of (LKNN6 – 0.5% CeO_2)

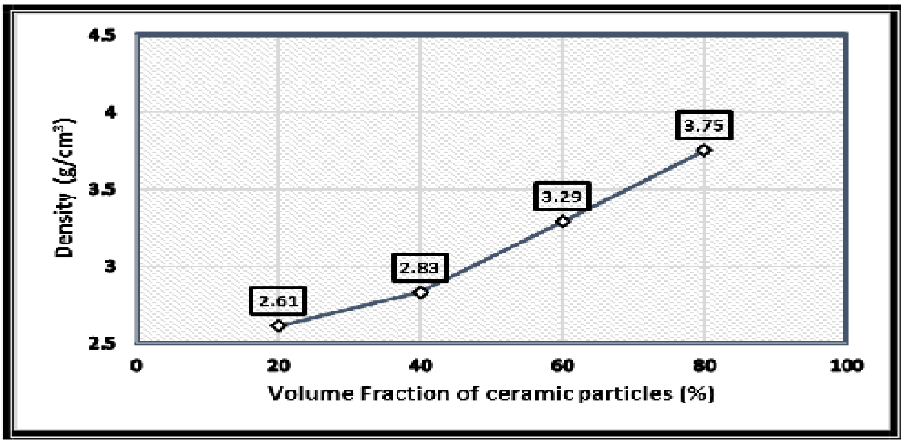


Figure (4): Changes in Density of (Polyester/$LKNN6-0.5CeO_2$) as a Function of Volume Fraction

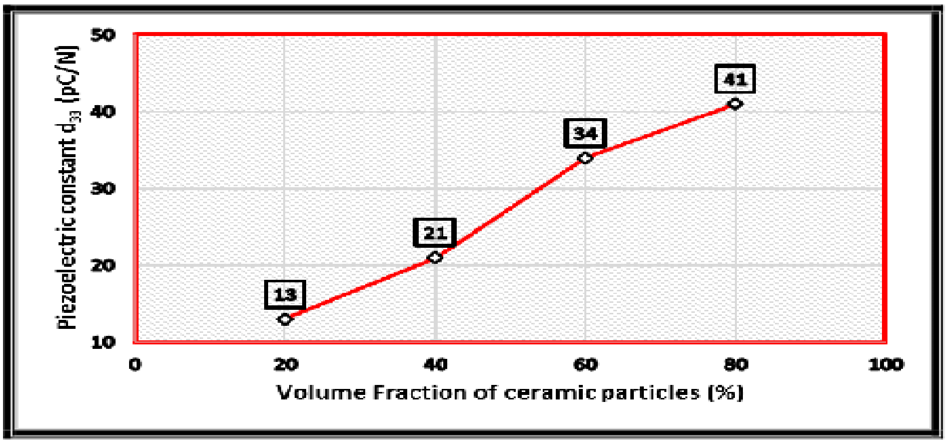


Figure (5): Changes in (d_{33}) of (Polyester/$LKNN6-0.5CeO_2$) as a Function of Volume Fraction.

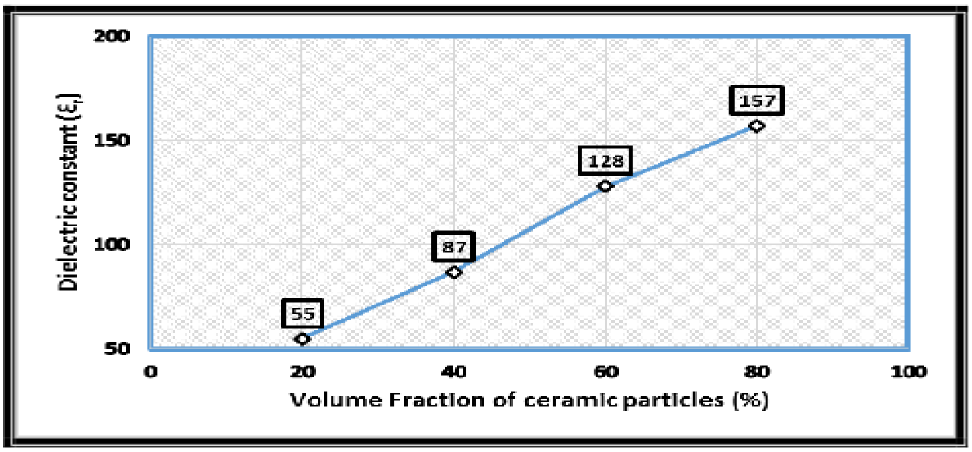


Figure (6): Changes in (Ɛr) of (Polyester/$LKNN6-0.5CeO_2$) as a Function of Volume Fraction.

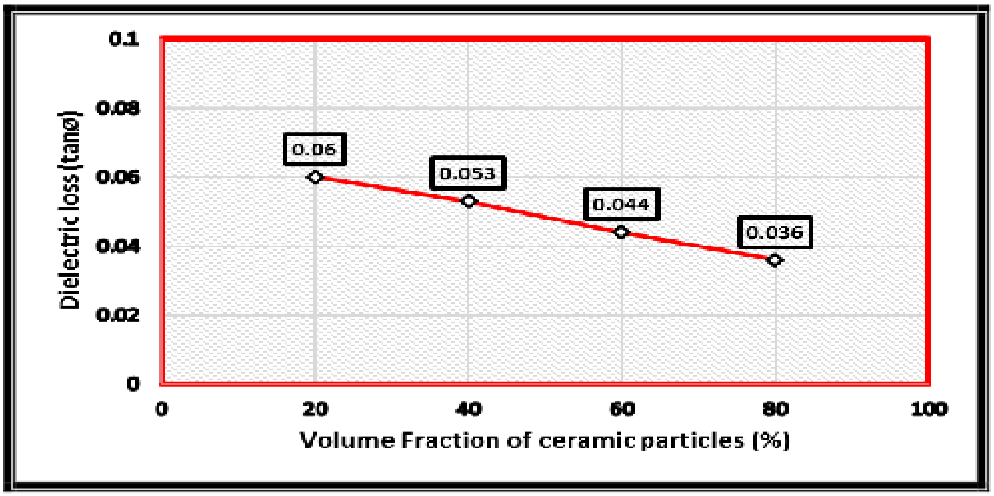
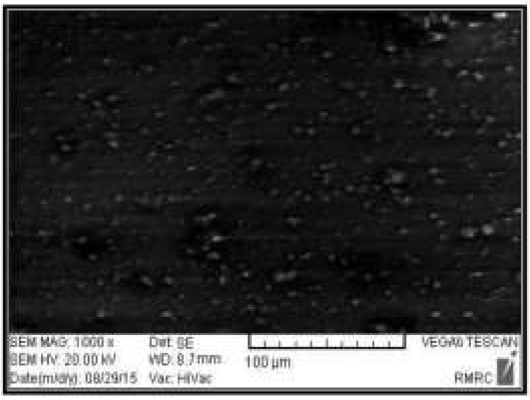
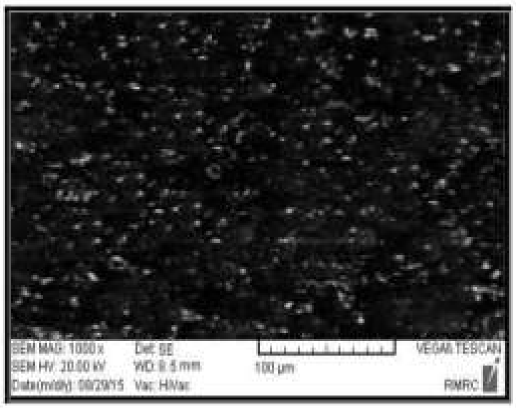


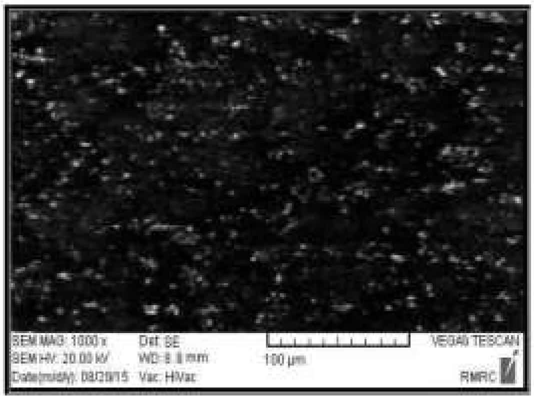
Figure (7): Changes in (tan Ø) of (Polyester/LKNN6-0.5CeO$_2$) as a Function of Volume Fraction.



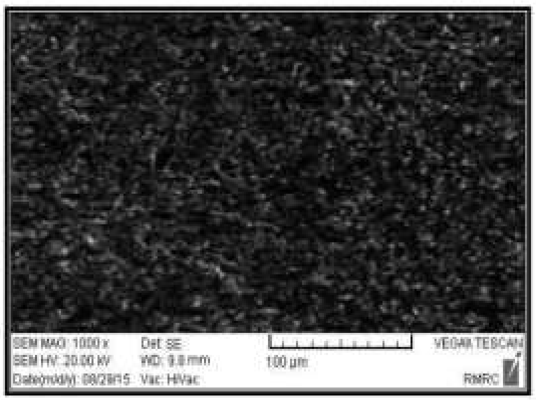
(20%)



(40%)



(60%)



(80%)

Figure (8): SEM Image of (Polyester/LKNN6-0.5CeO$_2$) at Different Volume Fraction.

CONCLUSIONS:

From the experimental results, it was concluding the following:

1- The prepared lead free (LKNN6-0.5%CeO_2) piezoceramics have pure perovskite structure at room temperature with a combination of orthorhombic and tetragonal structure.

2- The prepared piezoceramics have two classes of grain size: some grains have a larger diameter, whereas others are smaller. Backscatter detector image shows the presence of cubic crystals for the sintered powder with dense microstructure.

3- The density, piezoelectric coefficient, dielectric constant and the dielectric loss of (Polyester/LKNN6-0.5CeO2) is very dependent on the volume fractions of piezoceramics particles, all these parameters enhanced with increasing the volume fractions of particles and best properties are obtained at (80%) volume fraction.

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