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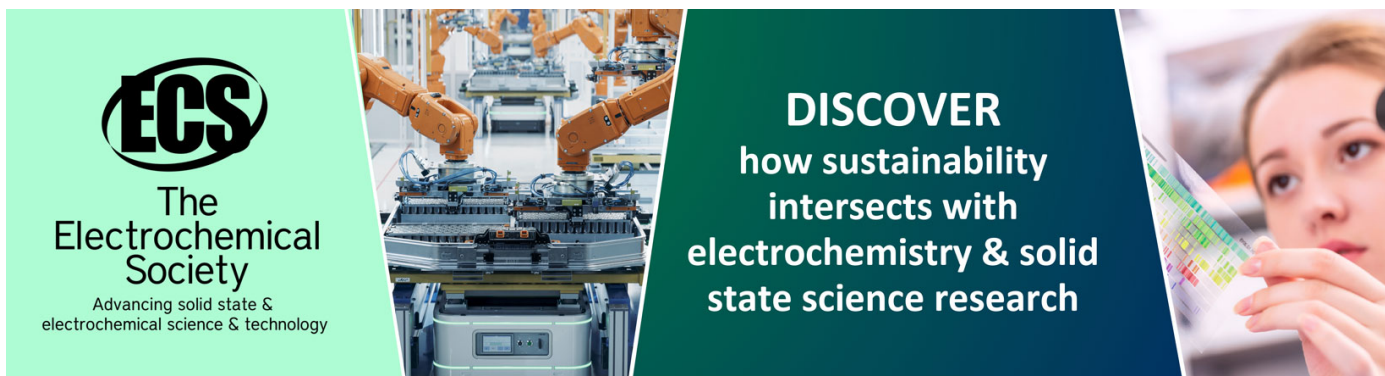
Phase composition and particle size distribution in $\text{Mg}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders

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Phase composition and particle size distribution in $\text{Mg}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders

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Abstract. Magnesium titanate-based ceramic dielectrics (MgTiO_3) has been recognized as a favourite material for antenna fabrication in the microwave frequency communications industry as well as for other electronic applications, such as chip capacitors, high-frequency capacitors, temperature compensating capacitors and dielectric resonators. Various compositions of MgTiO_3 -based ceramic dielectrics have been fabricated using different starting materials and preparation methods. The dielectric performance has also been reported. This paper is devoted to report the initial work on a series of new composition of $\text{Mg}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ powders for $x = 0 - 0.04$ prepared from liquid mixing method using metals powders as the starting materials. The phase composition and the particle size distributions in the systems were analysed and discussed in this paper.

1. Introduction

Ilmenite magnesium titanate has excellent dielectric properties and find extensive applications in mobile and satellite communication systems operated in microwave frequency region, such as for antenna, radar and global positioning system, as well as for chip capacitors, high-frequency capacitors, temperature compensating capacitors and dielectric resonators. Various compositions of MgTiO_3 -based ceramic dielectrics have been fabricated using different starting materials and various preparation methods. Some of them are as follows: MgTiO_3 that was synthesized from $\text{Ti}(\text{OH})_4$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using coprecipitation method [1]; 0.95MgTiO_3 – 0.05CaTiO_3 from $\text{Mg}(\text{OH})_2$, TiO_2 and CaCO_3 using the reaction sintering method [2]; MgTiO_3 prepared from $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, TiO_2 , CaCO_3 , Nb_2O_5 and ZnO using solid-state reaction method [3]; MgTiO_3 prepared from magnesium stearat, tetrabutyl titanate and stearic acid using stearic acid gel method [4]; $(1-x)(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ – $x\text{Ca}_{0.8}\text{Sm}_{0.4/3}\text{TiO}_3$ prepared from solid-state reaction method using $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ and $\text{Ca}_{0.8}\text{Sm}_{0.4/3}\text{TiO}_3$ precursors. Both precursors were developed from MgO , CoO , CaCO_3 , Sm_2O_3 and TiO_2 [5]; MgTiO_3 – $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ from MgO , TiO_2 , CaCO_3 , SnCO_3 and TiO_2 using solid-state reaction method [6]; MgTiO_3 powders were prepared from $\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ and TiO_2 using solid-state reaction method [7]; $(1-x)\text{La}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ – $x(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3$ prepared from CaCO_3 , SrCO_3 , La_2O_3 , MgO and TiO_2 using mixed oxides method [8]; B_2O_3 -doped MgTiO_3 prepared from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ and H_3BO_3 using sol-gel method [9]; Mg-excess MgTiO_3 prepared from solid-state reaction route [10]; and recently, the author [11-12] synthesized $\text{Mg}_{1-x}\text{Zn}_x\text{TiO}_3$ for $x = 0 - 0.5$ from Mg, Zn and Ti metal powders and HCl using a facile liquid mixing method. Dielectric performance of the above compositions has also been reported. In general, those compositions exhibited moderate level of dielectric constant values ($\epsilon_r \approx 17 - 20$) at various frequencies in the



microwave region, high quality factor, *e.g.* $Qf \approx 33,760$ GHz at 10 GHz [9] and a near-zero temperature coefficient at the resonance frequency (*e.g.* $\tau_f \approx -48$ ppm/°C) [9]. Another study that deals with dilatometric shrinkage and contribution of space charge and dipolar polarization mechanisms to the dielectric constant of the MgTiO₃-based ceramic systems were also reported by the author in [13] and [14], respectively.

In this paper, we adopted the facile synthesis method to prepare a new composition of MgTiO₃ powder by adding a series fraction of Sn metal powder into the systems. The initial results on the phase composition derived from the Rietveld analysis on the XRD data and the particle size distributions in the systems are presented in this paper.

2. Experiment

The series of Mg(Ti_{1-x}Sn_x)O₃ dried powders for $x = 0 - 0.04$ (MTS0 – MTS04) were prepared by dissolving the stoichiometric mol ratio of Mg, Ti and Sn metal powders (Merck) in HCl using the liquid mixing method following the steps given in [11, 12]. Calcination of the dried powders were carried out at 800 °C for 2 hours (h) using a Naberthem furnace at the rate of 10 °C/min. X-ray diffraction (XRD) spectra on the calcined powders were recorded at room temperature from $2\theta = 15$ to 70° using an X'Pert Diffractometer (Philips) with CuK_α radiation and the step size is 0.02°/min. The Rietveld method implemented in *Rietica* program was adopted to analyse the phase composition of the systems. Distribution of the particle sizes in the samples was measured using a particle size analyzer (PSA) Zetasizer Nano Series Software Version 7.01 (Malvern Instrument®). The PSA specimens were prepared by dispersing 0.5 g of the calcined powders in distilled water using an ultrasonic bath aided by 1-2 small drops of a dispersant liquid.

3. Results and Discussion

3.1 Phase Composition

Figure 1 shows XRD patterns of MTS0 – MTS04 powders calcined at 800 °C for 2 h and that were recorded from the X'Pert Diffractometer (Philips) with CuK_α radiation and the step size of 0.02 °/min.

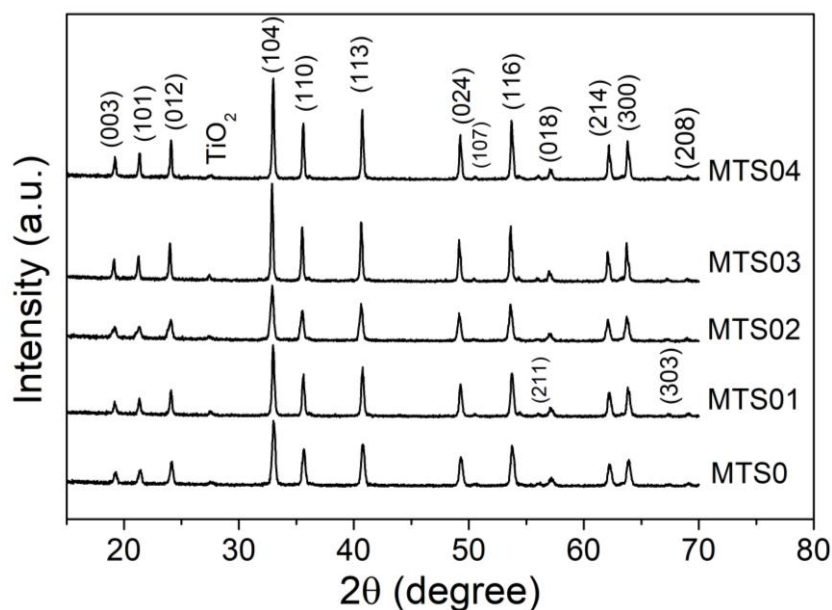


Figure 1. XRD patterns of MTS0 – MTS04 powders calcined at 800 °C for 2 h using the X'Pert Diffractometer (Philips) with CuK_α radiation. The peaks with $(hkl) = \text{MgTiO}_3$ (PDF No. 06-0494) and $a = \text{TiO}_2$ rutile (PDF No. 21-1276).

As seen, all spectra have similar diffraction peak patterns, which are composed of the peaks of the expected phase (MgTiO_3 , PDF No. 06-0494) and are accompanied by a peak of very low intensity belonging to the TiO_2 rutile (PDF No. 21-1276) at $2\theta = 27.5^\circ$ (labelled 'a'). On top of the MgTiO_3 diffraction peaks are labelled with the Miller (hkl) indices. The absence of diffraction peaks containing Sn on the spectra indicates that the fraction of doped Sn ions has occupied some of the sites of the Ti ions in the $\text{Mg}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ systems. The partial Ti^{4+} sites occupation by Sn^{4+} may be caused by the two ions have similar ionic radius, *i.e.* 0.069 nm for Sn^{4+} and 0.061 nm for Ti^{4+} so that gives rise to the formation of $\text{Mg}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ solid solutions. The fact that the size of the Sn^{4+} radius is slightly bigger than that of the Ti^{4+} radius may also lead to changes in the size of the unit cell volume of the Sn-doped MgTiO_3 systems (MTS01 – MTS04), which becomes slightly larger when compared to the volume size of the Sn-free MgTiO_3 system (MTS0). This claim, however, needs further clarification.

Detailed inspection to the highest peaks in the spectra in Figure 1, *i.e.* the (104) peaks at $2\theta = 32.9^\circ$ finds that, in general, the intensity of the intended peaks increases along the increase of the fraction of Sn doped in the systems (see Figure 2). The exception, however, is found on the MTS02 system. As shown in Figure 2, the (104) peak height in MTS02 is the lowest among the others. This fact, one of them, relates to the density of the scattering atoms in the sample, or in particular, relates to the density of the scattering atoms found in the (104) crystal planes of the system, *i.e.* orientation of the peak with the highest intensity. The denser the scattering atoms are found in the crystal planes with particular orientation, the more x-ray diffraction events will be recorded by the detector; this means that the intensity of the diffraction peak in that orientation becomes higher. Vice versa.

In addition, the 2θ -position of the (104) peaks in Figure 2 also shifted gradually towards the lower 2θ -value, except for the MTS04 peak. This peak-shift occurrence may also serve as an indication on the formation of solid solutions in the MTS0 – MTS04 systems. A quantitative analysis on the XRD spectra in Figure 1 is therefore mandatory to clarify the above findings. In this work, the intended analysis was performed using the Rietveld method implemented in the *Rietica* program; and the results are presented in the following paragraphs.

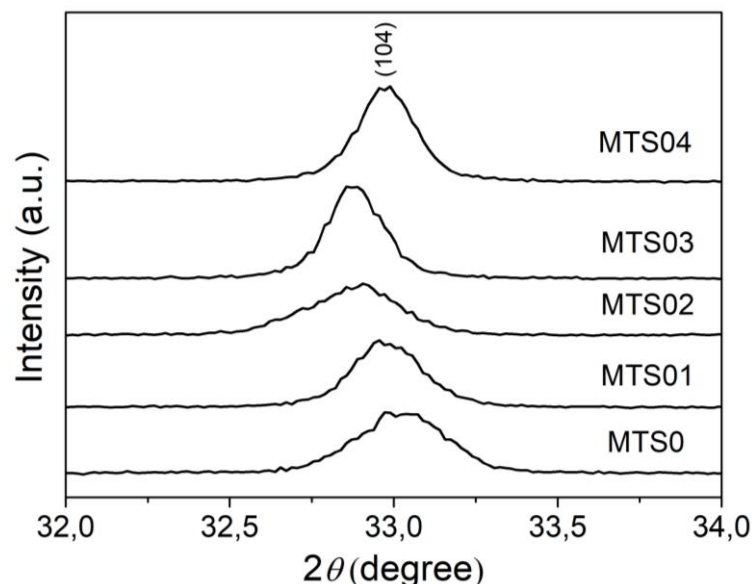


Figure 2. The (104) diffraction peaks of MTS0 – MTS04 calcined powders in Fig. 1 at $2\theta = 32.9^\circ$.

Figures 3 and 4 show the Rietveld refinement on the MTS0 and MTS04 XRD spectra on behalf of the refinement results on the rest spectra in Figure 1. In Figures 3-4, the '++' symbol reveals the experimental spectrum, the red line is the calculated spectrum, while the green line is the difference between these two spectra. The vertical-small-blue-bars underneath the spectrum represent the Bragg peaks of the identified phases in the systems; in this case, the MgTiO_3 and TiO_2 phases.

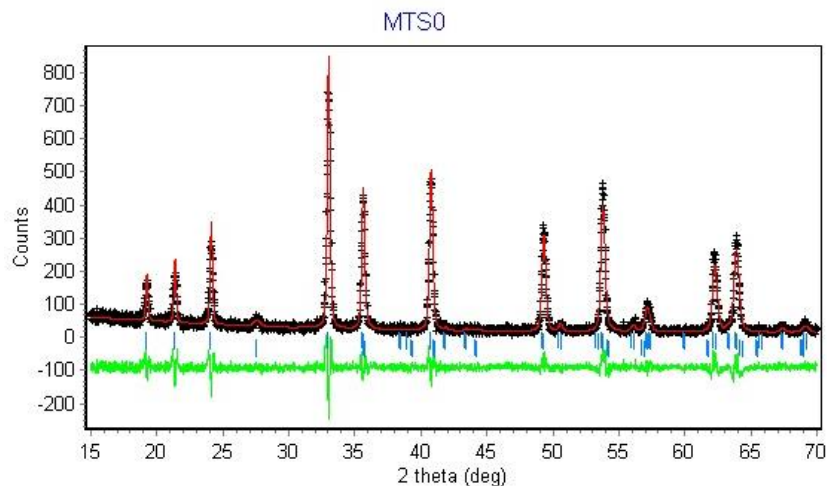


Figure 3. The Rietveld refinement on the MTS0 spectrum in Figure 1. Figures of Merit (FoM): $\text{GoF} = 1.88$, $R_{\text{wp}} = 18.71\%$, $R_p = 14.40\%$ and $R_{\text{exp}} = 13.62\%$.

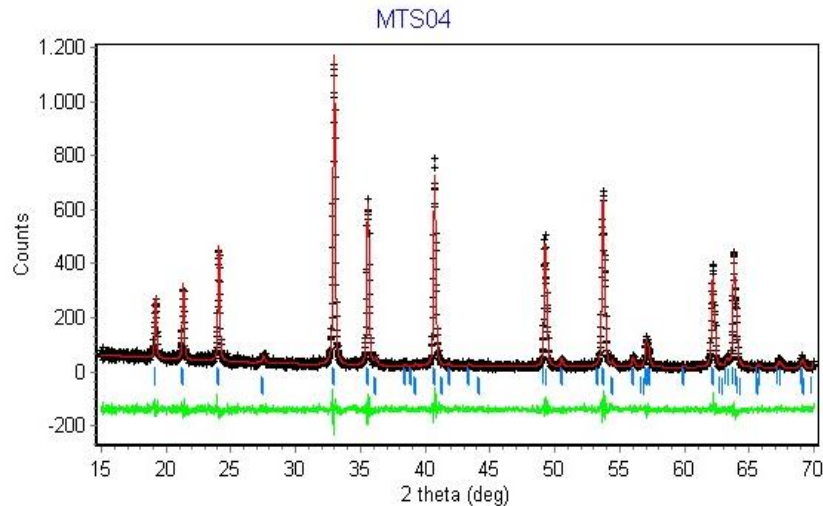


Figure 4. The similar refinement on the MTS04 spectrum. $\text{GoF} = 1.38$, $R_{\text{wp}} = 15.94\%$, $R_p = 11.47\%$ and $R_{\text{exp}} = 13.56\%$.

As seen in Figures 3-4, all the experimental peaks correspond to the Bragg peaks, showing that all the experimental peaks are well identified. The difference between the experimental and the calculated peaks are also minimum to indicate that the refinement was successful. This success is supported by the GoF values which are < 2.00 and also the R_{wp} , R_p and R_{exp} which are all much less than 20.00% . The refinement outputs, therefore, can be used for further analysis. Table 1 recapitulates the intended output in Figure 3-4 in terms of molar fraction, the unit cell volume and the density of the identified phases in MTS0 – MTS04 samples.

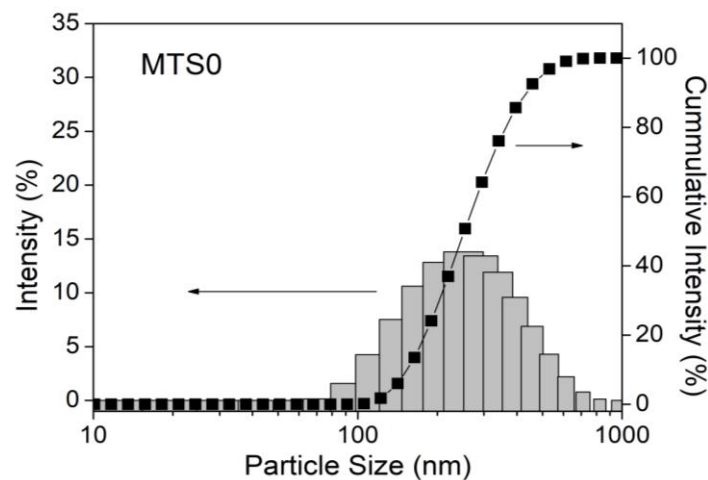
Table 1. The Rietveld refinement-based molar fraction, unit cell volume and the density of MTS0 – MTS04 samples.

Sample	Molar fraction (%)		Unit cell volume (nm ³)		Density (g.cm ⁻³)	
	MgTiO ₃	TiO ₂	MgTiO ₃	TiO ₂	MgTiO ₃	TiO ₂
MTS0	95.40 ± 1.89	4.60 ± 0.94	307.27 ± 1.19	61.98 ± 0.03	3.88	5.87
MTS01	97.03 ± 2.52	2.97 ± 0.46	307.15 ± 1.13	62.54 ± 0.02	3.90	5.95
MTS02	97.14 ± 3.34	2.86 ± 0.51	307.48 ± 1.20	62.46 ± 0.02	3.88	5.79
MTS03	97.23 ± 1.81	2.77 ± 0.38	307.57 ± 1.22	62.49 ± 0.03	3.89	5.94
MTS04	98.54 ± 1.81	1.46 ± 0.23	308.00 ± 1.15	63.41 ± 0.02	3.89	5.94

As listed in Table 1, the presence of MgTiO₃ phase, in terms of molar fraction, in the systems is very dominant, *i.e.* 95.40 – 98.50 %. The rest fraction belongs to TiO₂ rutile phase. In general, the unit cell volume of the main phase increases gradually along the increase of the Sn fraction in the systems. This result might become the answer of the above claim. Further, the density of MgTiO₃ phase both in the Sn-doped and in the Sn-free samples are all similar, 3.88 – 3.90 g.cm⁻³. However, among the Sn-doped samples, the density of MTS02 is slightly lower. This result, again, supports the analysis given above.

3.2 Particle Size Distribution

Figures 5-9 depict the distribution of particle sizes in the MTS0 – MTS04 systems measured from the PSA Zetasizer Nano Series Software Version 7.01.

**Figure 5.** Particle size distribution in MTS0 sample measured using PSA Zetasizer Nano Series Software Version 7.01.

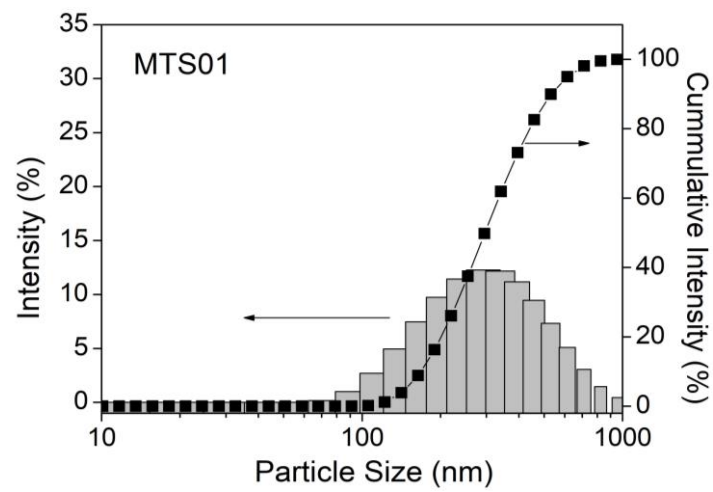


Figure 6. Particle size distribution in MTS01 sample.

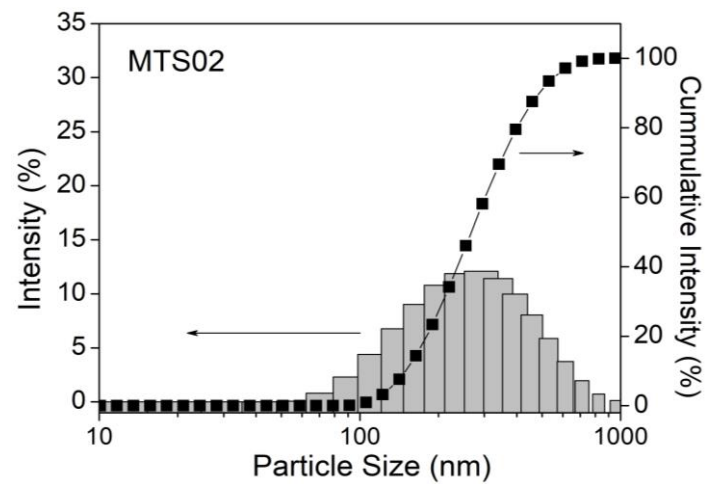


Figure 7. Particle size distribution in MTS02 sample.

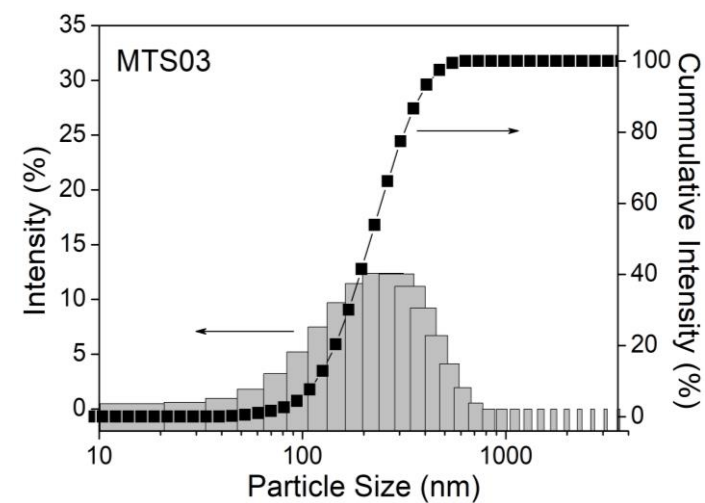


Figure 8. Particle size distribution in MTS03 sample.

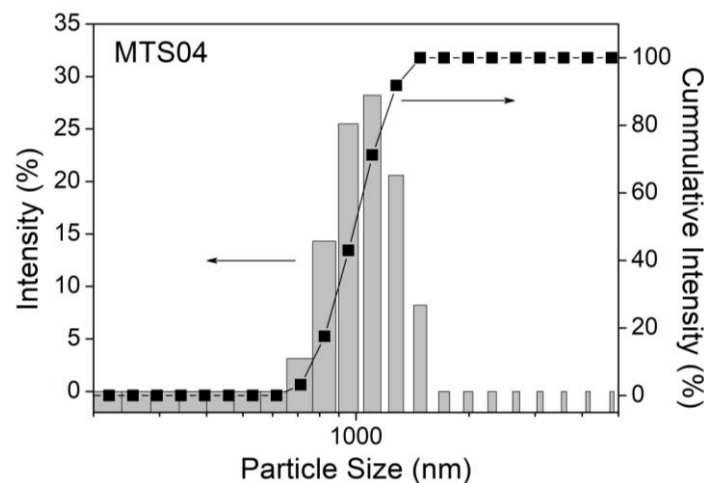


Figure 9. Particle size distribution in MTS04 sample.

It is noted in Figures 5-9 that the distribution of the particle size in MTS0 – MTS04 systems are (122 – 710) nm, (68 – 825) nm, (79 – 955) nm, (50 – 712) nm and (710 – 1483) nm, respectively. The average size is 256 nm in MTS0, 287 nm in MTS01, 263 nm in MTS02, 230 nm in MTS03 and 726 nm in MTS04, each with deviation of less than 2 %. Using the fact that the distribution curves in Figures 5 – 9 are all single modes and the deviation of the average size is diminutive, it can be concluded that the particles in MTS0 – MTS04 systems are all homogeneously distributed.

4. Conclusion

Based on the XRD study carried out in this work, the developed compositions of $\text{Mg}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ calcined at 800 °C for 2 h are all nearly MgTiO_3 single phase with the molar fraction of 95.40 – 98.50 %. The developed compositions are solid solutions. The PSA analysis tells that the particles in the samples are homogeneously distributed.

Acknowledgment

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