Grain Size-Dependent Phase Transformations Studies on (1-x)Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-xPbTiO$_3$ Ceramics

6.1 Introduction

Modifications in the crystal structure, ploarization, dielectric and phase transition behaviour of ferroelectric ceramics by decreasing grain size is well known in the literature [Duiker and Beale (1990], Frey and Payne, (1996), Hornebecq et al. (2004), Zhao et al. (2004), Curecheriu et al. (2012), Ghosh et al. (2014), Benabdallah et al. (2015)], Tan et al. (2015)], Muthuramalingam et al. (2016)], Khatua et al. (2017)], Koruza et al. (2017)]. Study of grain size effects in polycrystalline ferroelectric ceramic has drawn considerable interest of the researchers as it provides another degree of freedom to tune the ferroelectric properties and phase transition behaviour. Grain size dependent changes in the ferroelectric properties and structure of the materials have been investigated theoretically and experimentally for a long time [Uchinoet al. (1989); Yashima et al. (2005); Zhang et al. (2001); Chattopadhyay et al. (1995)]. The tetrgonality of the $BaTiO_3$ and $PbTiO_3$ is known to decrease with decreasing grain size [Yashima et al. (2005), Chattopadhyay et al. (1995)]. Tetragonality (c/a) of $PbTiO_3$ shows strong dependence on the grain size below 100 nm and below 7 nm cubic symmetry is stabilized with complete loss of ferroelectricity. Similarly, with decreasing grain size, the tetragonality and the ferroelectricity decrease in $BaTiO_3$ nanocrystals. The ferroelectric phase of $BaTiO_3$ vanishes at critical grain size of 48 nm [Yashima et al. (2005)]. In case of $Na_{0.5}Bi_{0.5}TiO_3$, it has been reported that monoclinic lattice distortion vanishes for the grain size ~2.5 μm and below [Khatua et al. (2017)]. For highly tetragonal (1-x)$BiFeO_3$-x$PbTiO_3$ ceramic with x=0.275 and 0.29, it has been reported that the pure tetragonal phase transforms to a coexisting tetragonal and rhombohedral structures as the average crystallite size is reduced from 10 μm to1 μm [Kothai et al. (2014)]. Further, in the MPB compositions of (1-x)$Bi(Mg_{1/2}Ti_{1/2})O_3$-x$PbTiO_3$ ceramics, it is reported that phase fraction of the coexisting monoclinic and

tetragonal phases varies as a function of grain size. Monoclinic phase fraction is observed to increase by decreasing grain size [Upadhyay and Singh (2017)]. Increased surface energy in the smaller crystallite size samples is expected to create an equivalent compressive stress that leads to the varied phase coexistence in the MPB systems with changing crystallite size.

Thus investigation of grain size effects for $(1-x)Bi(Mg_{3/4}W_{1/4})O_3-xPbTiO_3$ ceramics can provide valuable information about the crystallographic phase stabilities in this system as a function of grain size. In this chapter, we present the results of structural analysis on samples of various grain sizes for $(1-x)Bi(Mg_{3/4}W_{1/4})O_3-xPbTiO_3$ with x = 0.60, 0.61, 0.64 and 0.67. The calcined powders have been heat treated at different temperatures to get the samples of various grain sizes. In addition, the composition with x=0.64 have been high energy ball milled for different time duration to get the reduced grain size samples. The crystal structure and crystallographic phase stabilities of $(1-x)Bi(Mg_{3/4}W_{1/4})O_3-xPbTiO_3$ are found to be altered by changing the grain size.

6.2 Experimental Details

The $(1-x)Bi(Mg_{3/4}W_{1/4})O_3-xPbTiO_3$ solid solutions with x = 0.60, 0.61, 0.64 and 0.67 have been synthesized by solid-state ceramic method as described in Chapter 2. The calcined powders of the compositions with x=0.60, 0.61, 0.64 and 0.67 were heat treated at different temperatures to get the samples of varying grain size. In addition, the calcined powder (850°C) of 0.36BMW-0.64T ceramic was further Ball milled at 300 rpm for different time durations such as 5, 10, 15, 20, 25, 30, 35 and 52 hrs by using high energy ball mill (PM 400MA, RETSCH, Gmbh, Germany) to get the nanocrystalline samples of different crystallite sizes. Ethanol was used as the mixing medium during ball milling. The high energy ball milled mixture was collected from the

grinding jar and subsequently dried at 90 °C for 12 hrs on a hot plate. The phase purity of the sample was analyzed by powder X-ray diffractometer (Regaku Miniflex 600) with CuKα radiation. The grain size and surface morphology of samples were examined by scanning electron microscope (SEM), Zeiss, Evo Research 18.

6.3 Results and Discussion

The Rietveld analysis of the structure of the calcined powders of $(1-x)Bi(Mg_{3/4}W_{1/4})O_3$-$xPbTiO_3$ ceramics with x = 0.60, 0.61, 0.64 and 0.67 reveals that the crystal structure exhibits coexistence of ordered cubic (*Fm-3m* space group) and ordered tetragonal (*I4/m* space group) phases similar to the bulk (sintered) samples. In the following sections, we discuss the structural evolution of various compositions as a function of grain size.

6.3.1 Grain Size Dependent Structural Changes in $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ Prepared by High Energy Ball Milling

The room temperature XRD patterns of $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ ceramic high energy ball milled for different time durations 5, 10, 15, 20, 25, 30, 35 and 52 hrs are shown in **Fig. 6.1**. With increasing milling time the XRD patterns of the samples show increased peak broadening due to decreasing grain size. As seen from **Fig. 6.1**, the calcined powder before ball milling (bottom pattern) has the clear coexistence of ordered (*Fm-3m* space group) and ordered tetragonal (*I4/m* space group) phases. The intensity of the superlattice (111) peak at ~19.2º due to B-site cationic ordering is significantly strong. With increasing ball milling time, the nature of the diffraction profiles changes which suggests that the crystal structure and phase stabilities of the two coexisting phases is being altered by decreased grain size due to high energy ball milling. The XRD patterns of the samples milled for 5 and 10 hrs shows broadened peaks and the intensity of the XRD peaks due to cubic phase are

slightly decreased. The intensity of the superlattice peak (111) at 19.2º is also decreased for the 5 hrs and 10 hrs milled powders. When milling time increases to 15 hrs, the superlattice (111) peak due to B-site cationic ordering disappears. It confirms that both ordered cubic and ordered tetragonal phases transform into disordered crystallographic phase. The XRD peaks corresponding to the coexisting cubic structure also diminishes for this sample. The Rietveld structural analysis of the XRD pattern of the sample milled for 15 hrs confirms that the ordered cubic and ordered tetragonal phase in the calcined powder transform into disordered tetragonal phase after ball milling due to reduced grain size. The Rietveld structural analysis of the XRD patterns of the other samples milled for higher time durations (>15 hrs) reveals the disordered tetragonal structure in the *P4mm* space group. The grain size of the $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ calcined powder decreases from 2 μm to < 50 nm after the 52 hrs ball milling.

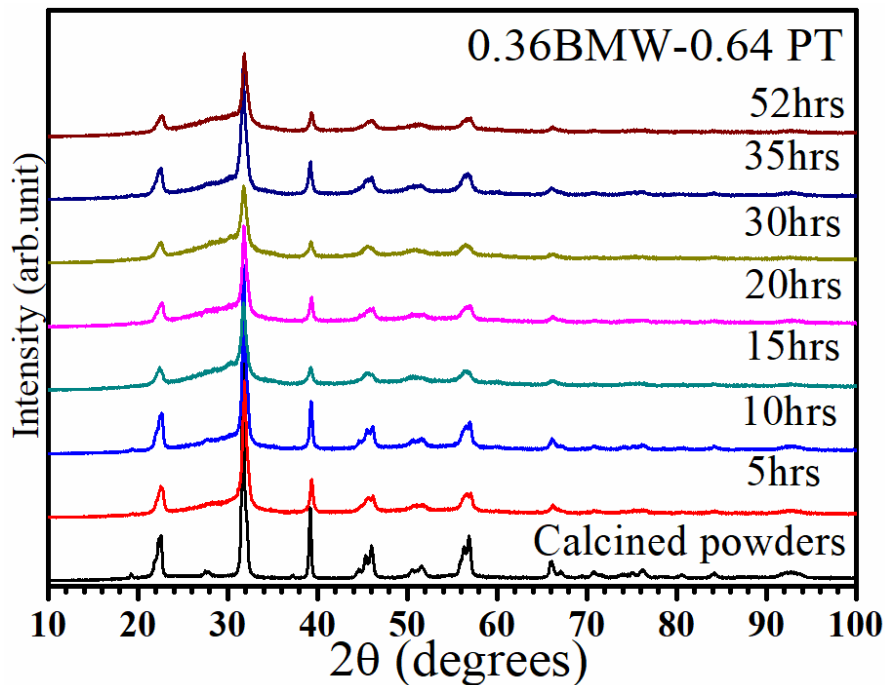**Figure 6.1** Room temperature XRD patterns of $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ ceramic high energy ball milled for 5, 10, 15, 20, 25, 30, 35 and 52 hrs (bottom to top).

There is broad background intensity around 30° in the XRD patterns of the samples milled for higher time durations. This suggests that part of the sample is getting amorphized due to high energy ball milling. Rietveld fit for the XRD pattern of the samples obtained after 52 hrs high energy ball milling considering disordered tetragonal phase in *P4mm* space group is shown in **Fig. 6.2**(a). The fit is quite good. Rietveld fit considering coexistence of ordered cubic (*Fm-3m* space group) and ordered tetragonal (*I4/m* space group) phases for the calcined powder of $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ ceramic is shown in **Fig.6.2**(b).
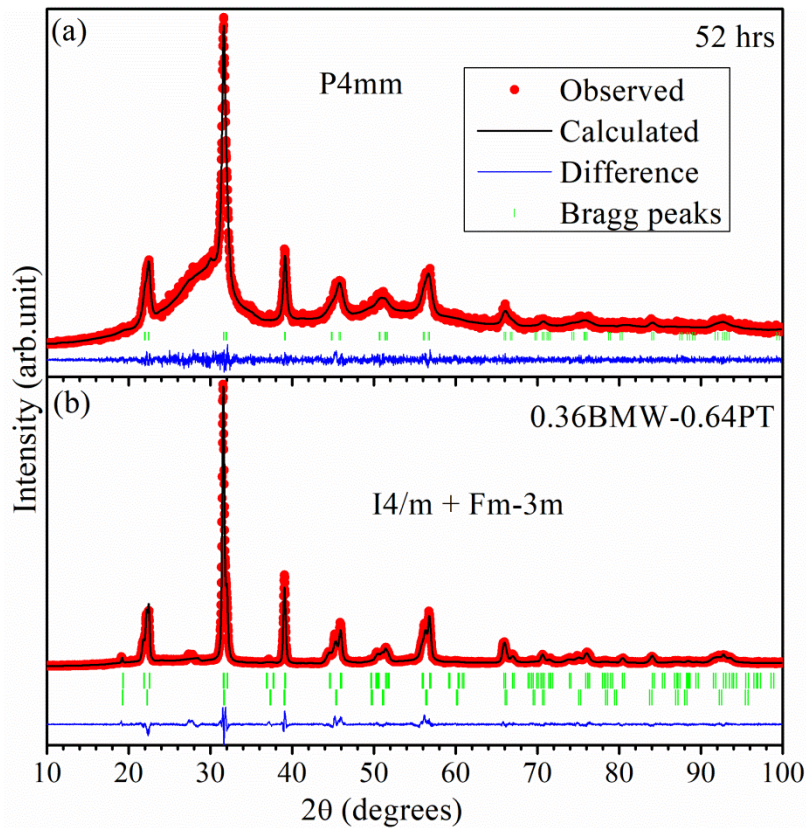
Figure 6.2 (a,b) Experimentally observed (dots), Rietveld calculated (overlapping continuous line) and difference (bottom curve) profiles for $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ ceramic obtained after Rietveld analysis of the structure using (a) tetragonal (*P4mm*) and (b) coexisting cubic (*Fm-3m*) and tetragonal (*I4/m*) structures. The vertical tick marks above the difference plot show the peak positions.

The lattice parameters for the phases in the un-milled calcined powder are $a_c = 7.99757(3)$ Å for cubic phase, $a_t = 5.585449(4)$ Å and $c_t = 8.13047(1)$ Å for tetragonal structure. The cubic phase fraction 43.92% and tetragonal phase fraction 56.08% as determined from the Rietveld structure refinement. The lattice parameter of the sample obtained after the 52 hours high energy ball milling with disordered tetragonal structure is $a_t = 3.96239(1)$ Å and $c_t = 4.04425(2)$ Å.

Fig. 6.2(c) shows SEM image of $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ ceramic sample high energy ball milled for 52 hrs. Because of the small grain size, grains are not well resolved and high degree of agglomeration is seen in the microstructure. The average grain size is determined to be of the order of 50 nm. Some very small sized grains are also observed in the microstructure.
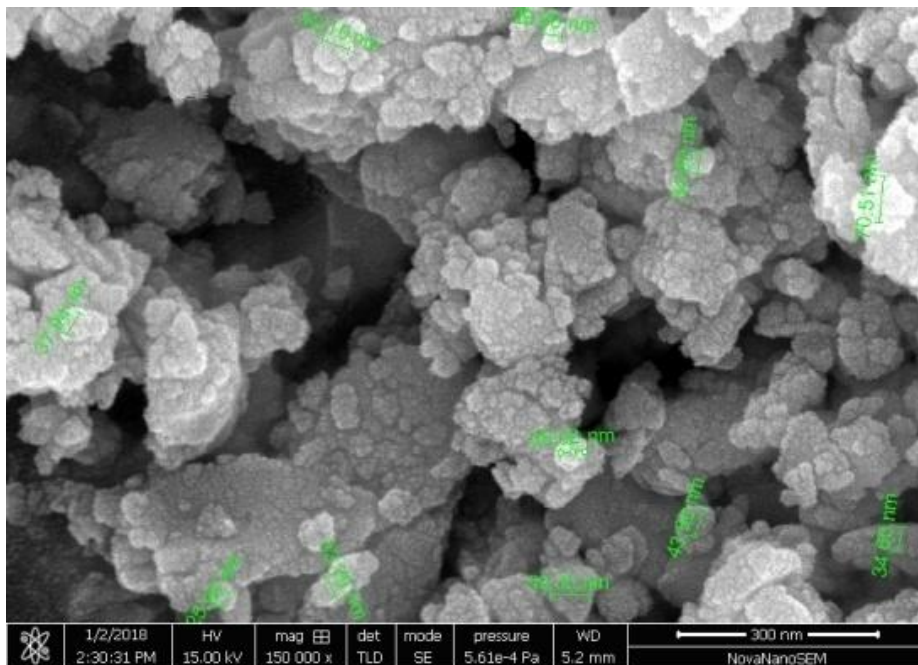

Figure 6.2 (c) SEM image of $0.36Bi(Mg_{3/4}W_{1/4})O_3$-$0.64PbTiO_3$ ceramic sample ball prepared by high energy ball milling for 52 hrs.

6.3.2 Grain Size Dependent Structural Changes in $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ Ceramic

Room temperature XRD patterns of $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ ceramics prepared by heat treatment at various calcination temperatures viz. 850°C, 900°C, 950°C and 1000°C for 3 hrs is shown in **Fig. 6.3**. As can be seen from **Fig. 6.3** the XRD pattern at 850°C temperature reveals coexistence of ordered cubic and tetragonal phases, as the (200) pseudocubic profile is a triplet and (111) superlattice reflection around 19° is present. With increasing heat treatment temperature the phase coexistence is altered as evidenced from the decreased splitting of the diffraction profiles and diminished intensity of the (111) superlattice reflection due to B-site cationic ordering. All the diffraction profiles shown in **Fig. 6.3** become less broadened for samples prepared at higher temperatures due to increased grain size. The crystal structure of the sample heat treated at 1000°C temperature becomes nearly pure ordered cubic phase with space group *Fm-3m*. The compositions on the BMW side of the MPB have tendency to crystallize into cubic structure. Because of this, for $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ sample calcined at 850°C, the coexisting tetragonal phase is metastable and its phase fractions reduces at higher heat treatment temperature with increased phase fraction of the stable cubic phase.
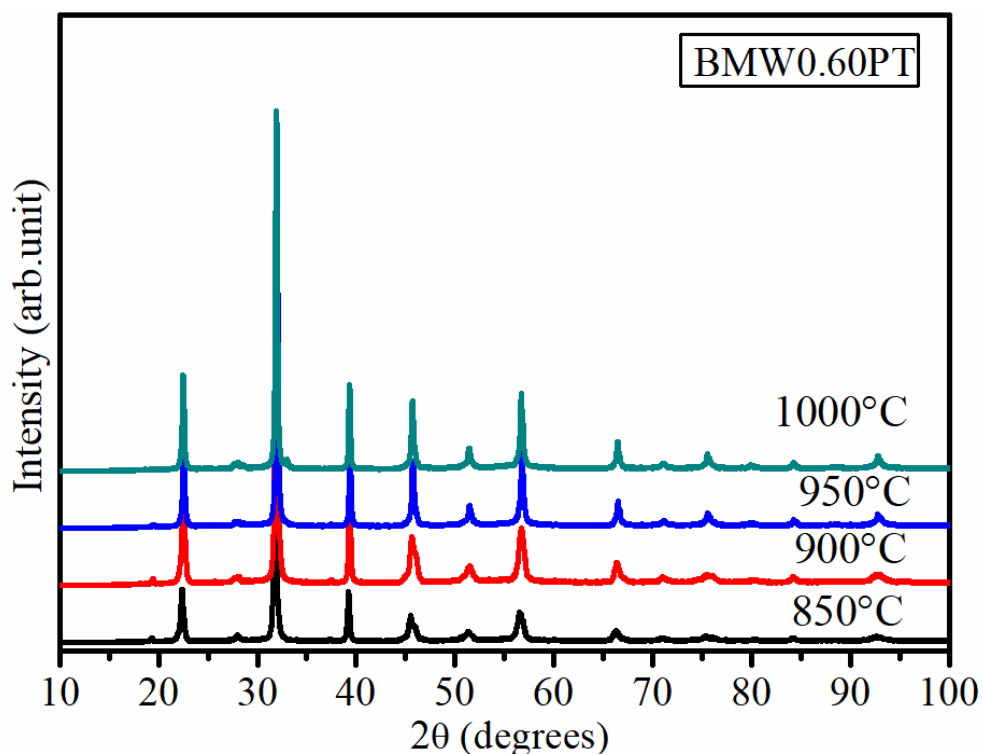
Figure 6.3 Room temperature XRD patterns of $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ samples prepared at 850°C, 900°C, 950°C and 1000°C.

To illustrate it further, we show in **Fig. 6.4** the selected pseudocubic (110), (111) and (200) XRD peak profiles for $(1-x)Bi(Mg_{3/4}W_{1/4})O_3$-$xPbTiO_3$ with x = 0.60 prepared at various heat treatment temperatures. The (200) pseudocubic XRD peak is a triplet having middle peak due to cubic phase and side peaks due to tetragonal phase. The crystal structure for sample calcined at 850 °C is predominantly cubic with minor tetragonal phase as could be seen from the characteristic splitting of XRD profiles shown in **Fig. 6.4**. With increasing calcination temperature from 850 °C to 1000 °C the middle peak in (200) pseudocubic XRD profile becomes stronger while intensity of the side peaks due to tetragonal phase becomes weaker. This suggests that the phase fraction of the cubic structure increases and phase fraction of tetragonal structure decreases with increasing calcination temperature. This reveals that cubic phase is

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stable in the samples prepared at higher temperature and tetragonal phase is a meta-stable phase for the $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$. The sample prepared at 1000 °C is completely cubic as evidence from the singlet XRD peaks shown in **Fig. 6.4**.

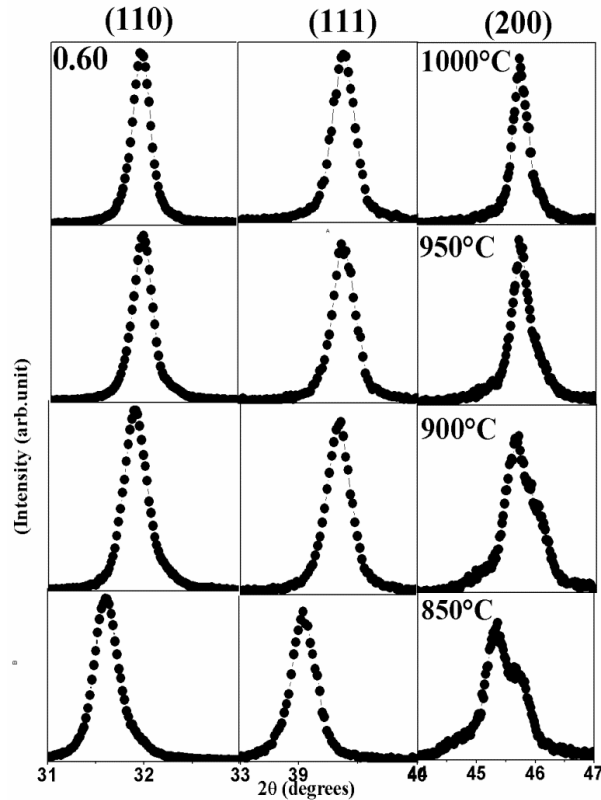**Figure 6.4** Evolution of XRD profiles for $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ ceramic samples calcined at different temperatures 850, 900, 950 and 1000 °C for 3 hrs.

The Rietveld structure refinement has been carried out for the composition x = 0.60 to confirm the crystal structures. The Rietveld structure refinement confirms ordered cubic phase (*Fm-3m* space group) for samples prepared at 1000 °C temperature as evidenced from the very good fit for the XRD data shown in **Fig. 6.5**(a). The structure of the samples prepared at 850°C temperature is confirmed to be coexisting ordered cubic (*Fm-3m* space group) and ordered tetragonal (*I4/m* space group) phases. The corresponding Rietveld fit of the XRD data is shown in **Fig. 6.5**(b). The lattice

parameter of the two phases for the samples prepared at 850 °C temperature is a_c = 7.99515(9) Å for cubic structure and a_t = 5.62707(9) Å and c_t = 8.06130(2) Å for tetragonal structure. The cubic phase fraction obtained after the refinement is 26.14% and tetragonal phase fraction is 73.86% for the $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ sample prepared at 850 °C. The lattice parameter of the sample prepared at 1000 °C heat treatment temperature is a_c = 7.97414(3) Å with B-site ordered cubic structure.
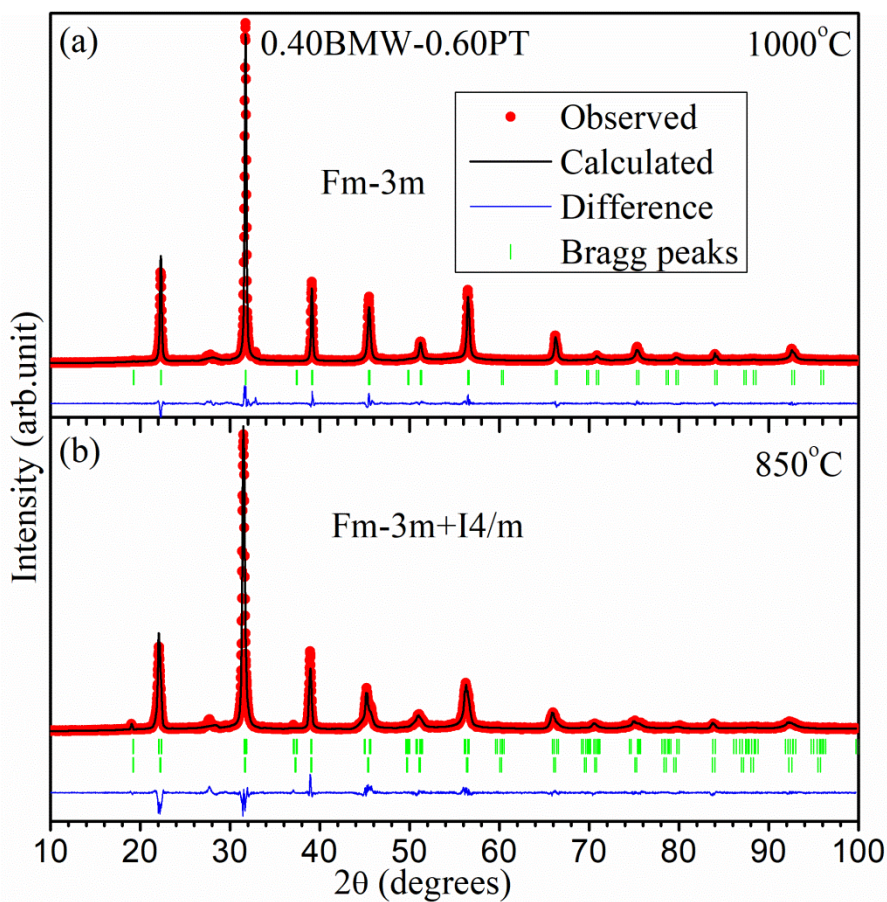
Figure 6.5 Experimentally observed (dots), Rietveld calculated (overlapping continuous line) and their difference (continuous bottom line) XRD profiles for $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ ceramic obtained after Rietveld analysis of the structure using (a) cubic (*Fm-3m*) (sample prepared at 850 °C) and (b) coexisting cubic and tetragonal (*Fm-3m + I4/m*) structures (sample prepared at 1000 °C). The vertical tick marks above the difference plot show the peak positions.

6.3.3 Grain Size Dependent Structural Changes in 0.39Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.61PbTiO$_3$ Ceramic

Room temperature XRD patterns of 0.39Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.61PbTiO$_3$ ceramic prepared at 850 °C, 900 °C, 950 °C and 1000 °C temperatures are shown in **Fig. 6.6**. The diffraction profiles become less broadened for samples prepared at higher temperatures due to increased grain size. As can be seen from the XRD pattern of the sample prepared at 850 °C temperature, the crystal structure is coexisting ordered cubic and tetragonal phases similar to that observed for the 0.40Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.60PbTiO$_3$ composition. The phase coexistence is altered by changing the sample preparation temperature from 850 °C to 1000 °C as revealed from the modifications of the XRD profiles.
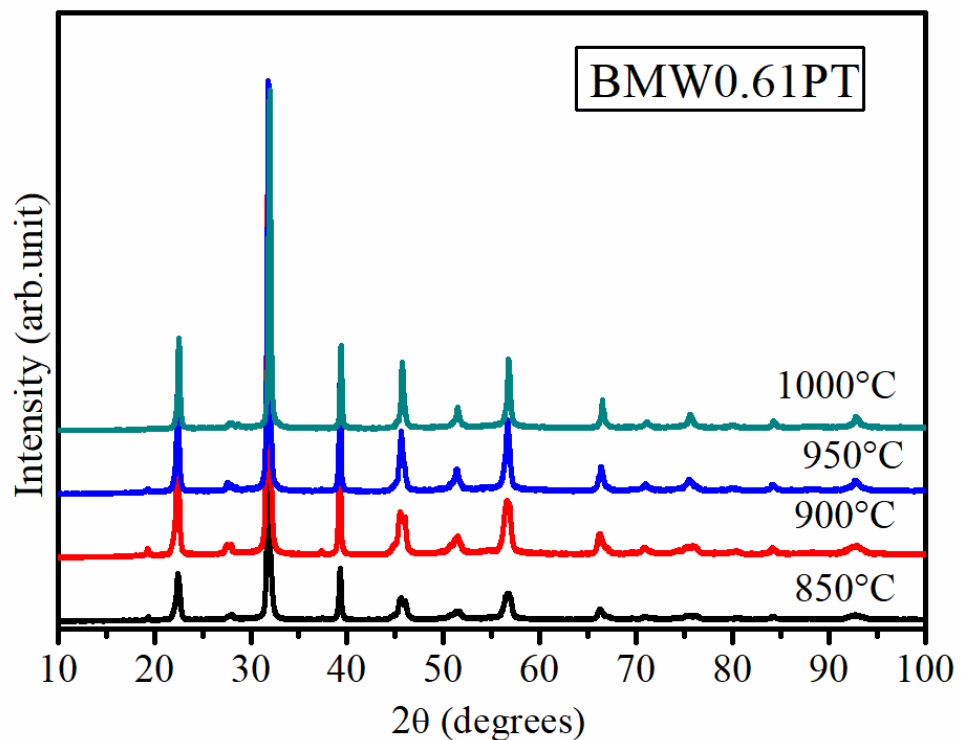

Figure 6.6 Room temperature XRD patterns of 0.39Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.61PbTiO$_3$ ceramic prepared at 850 °C, 900 °C, 950 °C and 1000 °C.

Similar to the $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$ composition, for $0.39Bi(Mg_{3/4}W_{1/4})O_3$-$0.61PbTiO_3$ composition also, the crystal structure transforms into pure cubic phase for the sample prepared at 1000 °C. In this composition also, the tetragonal phase is metastable phase so its phase fraction decreases at higher sample preparation temperature.

To analyze the structure in more detail, the selected pseudocubic (110), (111) and (200) XRD peak profiles of the $0.39Bi(Mg_{3/4}W_{1/4})O_3$-$0.61PbTiO_3$ ceramic prepared at various temperatures are shown in **Fig. 6.7**. The crystal structure of the sample calcined at 850 ^{o}C has coexistence of ordered cubic and ordered tetragonal phases as could be seen from the characteristic splitting of XRD profiles. The pseudocubic (200) peak profile gradually transforms into singlet with increasing calcination temperature from 850 °C to 1000 ^{o}C.
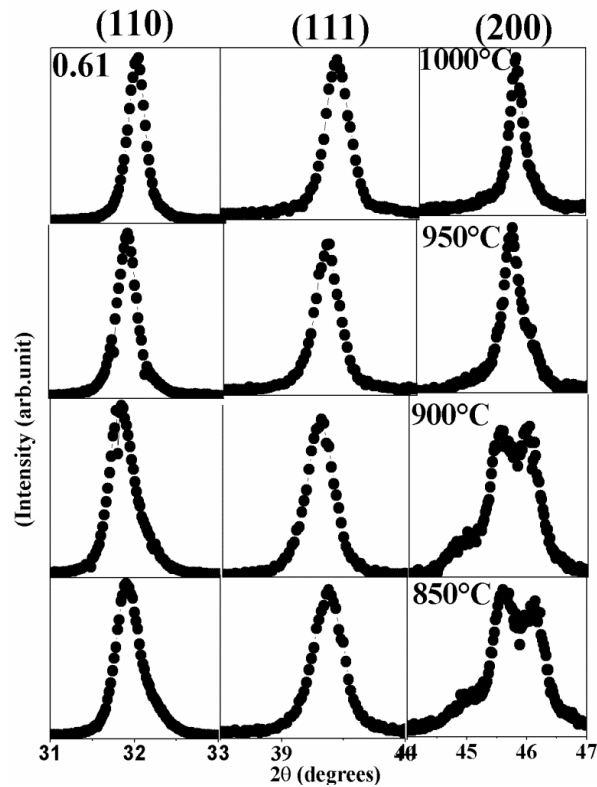

Figure 6.7 Evolution of XRD profiles for $0.39Bi(Mg_{3/4}W_{1/4})O_3$-$0.61PbTiO_3$ ceramic calcined at different temperatures 850, 900, 950 and 1000 °C for 3 hrs.

Thus, the phase fraction of cubic structure increases and phase fraction of the tetragonal structure decreases with increasing calcination temperature for $0.39Bi(Mg_{3/4}W_{1/4})O_3$-$0.61PbTiO_3$ also similar to that observed for the $0.40Bi(Mg_{3/4}W_{1/4})O_3$-$0.60PbTiO_3$. This reveals that cubic phase is stable at a higher temperature and tetragonal phase is a meta-stable phase. The samples prepared at 1000 °C completely transformed into ordered cubic structure.

The Rietveld structure refinement of $0.39Bi(Mg_{3/4}W_{1/4})O_3$-$0.61PbTiO_3$ ceramic reveals that the sample prepared at 850 ^{o}C has the coexistence of both ordered cubic (*Fm*-3*m* space group) and ordered tetragonal (*I*4/*m* space group) phases as shown by very good Rietveld fit in **Fig. 6.8**(b). The structure of the sample prepared at 1000 ^{o}C is confirmed to be ordered cubic with *Fm*-3*m* apace group and corresponding Rietveld fit is shown in **Fig. 6.8**(a). The lattice parameter of the coexisting structures for the sample prepared at 850 ^{o}C is a_c = 7.99439(1) Å (cubic) and a_t = 5.66115(6) Å and c_t = 7.91517(1) Å (tetragonal structure). The cubic phase fraction is 13.14% and tetragonal phase fraction is 86.86% as determined from the Rietveld structure refinement. The lattice parameter for the sample prepared at 1000 ^{o}C is a_c = 7.97308(3) Å.
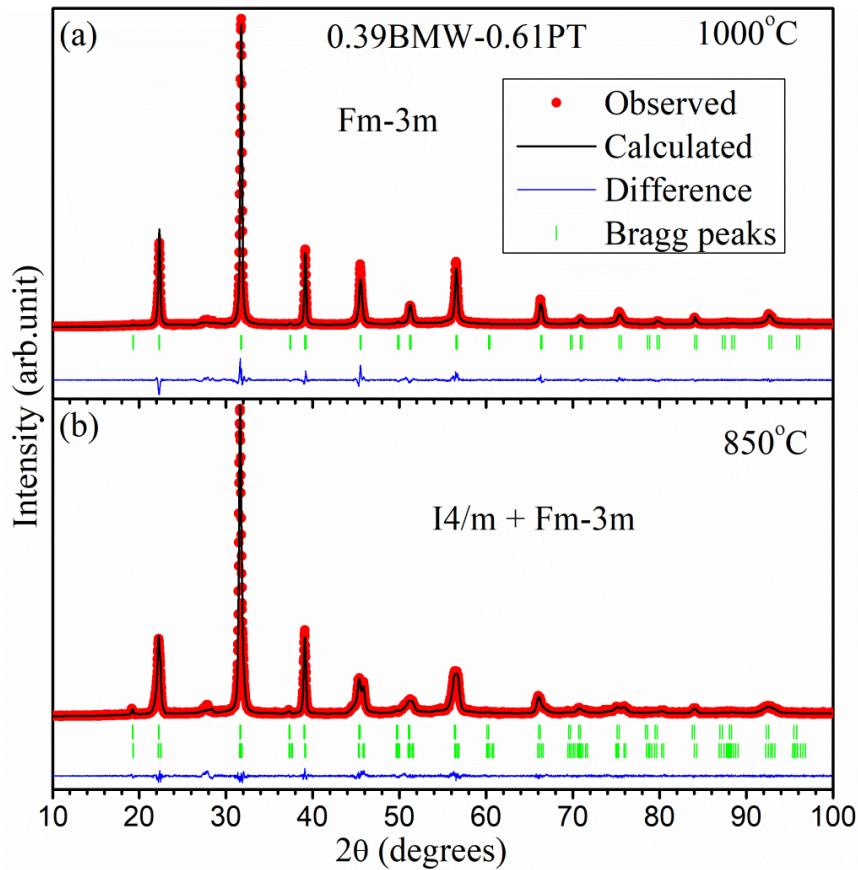
Figure 6.8 Experimentally observed (dots), Rietveld calculated (overlapping continuous line) and their difference (continuous bottom line) XRD profiles for 0.39Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.61PbTiO$_3$ ceramic obtained after Rietveld structural using (a) cubic (*Fm-3m*) (sample prepared at 1000 $^{\circ}$C) and (b) cubic and tetragonal (*Fm-3m* + *I4/m*) structures (sample prepared at 850 $^{\circ}$C). The vertical tick marks above the difference plot show the peak positions.

6.3.4 Grain Size Dependent Structural Changes in 0.33Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.67PbTiO$_3$ Ceramic

Room temperature XRD patterns of 0.33Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.67PbTiO$_3$ ceramic samples prepared at temperatures 850 °C, 900 °C, 950 °C and 1000 °C are shown in **Fig. 6.9**. Sharper diffraction profiles for the samples prepared at higher temperatures reveal increased grain size of the samples. As discussed in Chapter 3, the structure of the sintered sample for the 0.33Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-0.67PbTiO$_3$ composition is

predominantly ordered tetragonal in the *I*4/*m* space group. However, the diffraction profiles of the sample calcined at 850 °C temperature is quite different having larger proportion of the cubic phase. The proportion of the two coexisting phases changes with changing sample preparation temperature. In contrast to structure of the other compositions discussed in earlier sections, the structure of $0.33Bi(Mg_{3/4}W_{1/4})O_3$-$0.67PbTiO_3$ composition transforms into the ordered tetragonal phase for sample prepared at 1000 °C. In this composition, the cubic phase is metastable phase so its phase fraction is decreased at higher sample preparation temperatures while tetragonal phase is stablized.
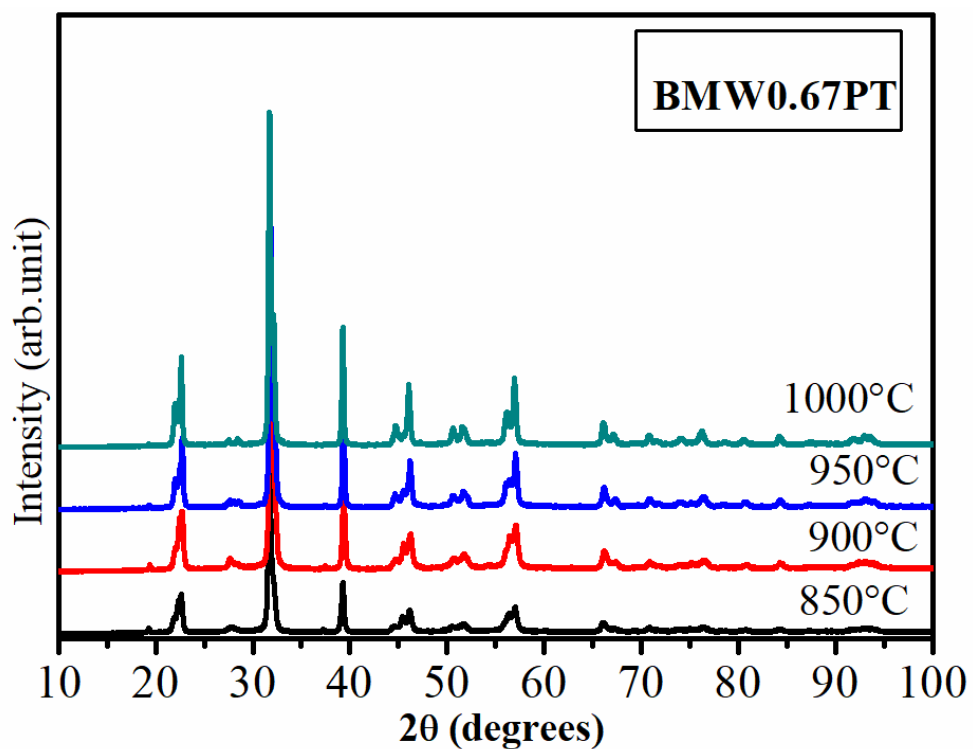

Figure 6.9 Room temperature XRD patterns of $0.33Bi(Mg_{3/4}W_{1/4})O_3$-$0.67PbTiO_3$ sintered at 850 °C, 900 °C, 950 °C and 1000 °C.

The triplet nature of the pseudocubic (200) peak profile shown in **Fig. 6.10** for the XRD pattern of $0.33Bi(Mg_{3/4}W_{1/4})O_3$-$0.67PbTiO_3$ prepared at 850 °C confirms

coexisting cubic and tetragonal structures. The sample prepared at 1000 °C has nearly pure tetragonal structure. Thus, the $0.33Bi(Mg_{3/4}W_{1/4})O_3-0.67PbTiO_3$ ceramic exhibits a structural phase transition from coexisting ordered cubic (*Fm*-3*m*) and ordered tetragonal (*I4/m*) structures to predominantly ordered tetragonal phase with increasing sample preparation temperature. Rietveld structure analysis also confirms these structural models and the corresponding Rietveld fits are shown in **Fig. 6.11**. The lattice parameter for coexisting structures in the $0.33Bi(Mg_{3/4}W_{1/4})O_3-0.67PbTiO_3$ sample prepared at 850 °C are a_c = 7.99439(1) Å (cubic) and a_t = 5.58317(6) Å and c_t = 8.09604(1) Å (tetragonal structure). The phase fraction of the cubic structure is 40.20% and tetragonal structure is 59.80% as obtained from the Rietveld structure refinement. The lattice parameter of sample prepared at 1000 °C heat treatment temperature is a_t = 5.58903(2) Å and c_t = 8.11311(5) Å with ordered tetragonal structure.

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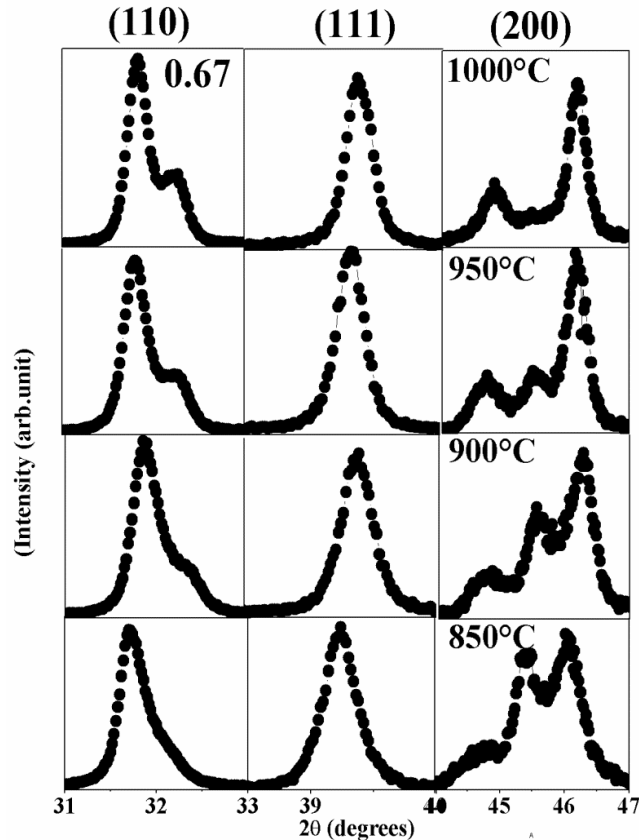**Figure 6.10** Evolution of the XRD profiles for $0.33Bi(Mg_{3/4}W_{1/4})O_3$-$0.67PbTiO_3$ ceramic prepared at 850, 900, 950 and 1000 °C temperatures for 3 hrs.
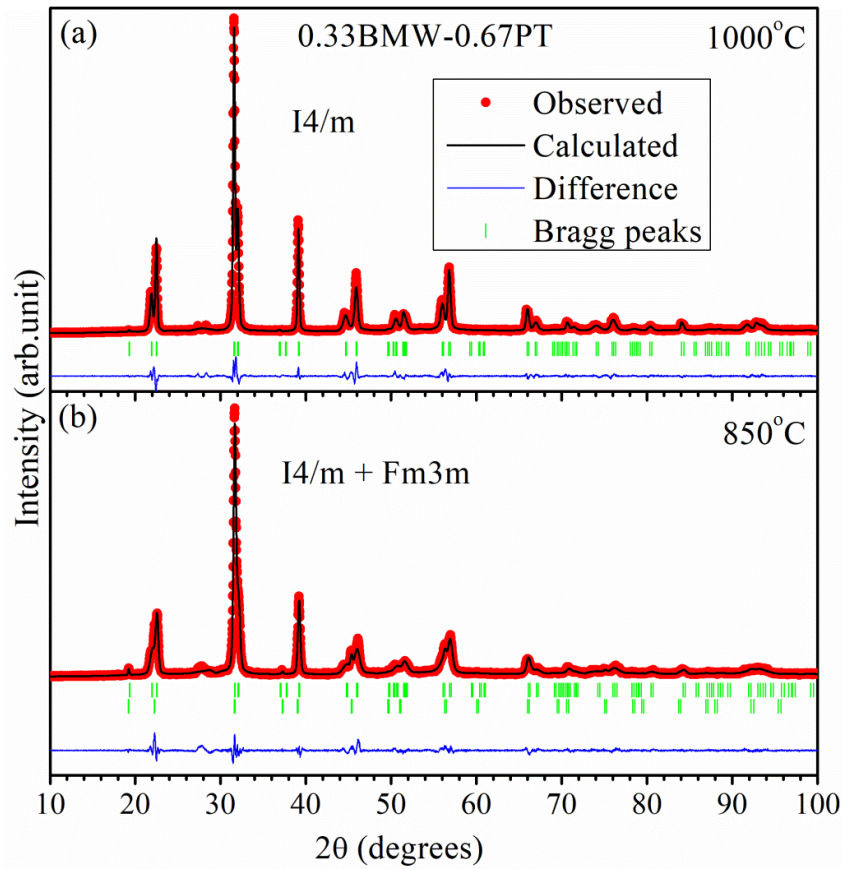

Figure 6.11 Experimentally observed (dots), Rietveld calculated (continuous line) and their difference (continuous bottom line) XRD profiles for $0.33Bi(Mg_{3/4}W_{1/4})O_3$-$0.67PbTiO_3$ ceramic obtained after Rietveld structural analysis using (a) tetragonal (*I4/m*) (sample prepared at 1000 °C) and (b) coexisting cubic and tetragonal (*Fm-3m* + *I4/m*) structures (sample prepared at 850 °C). The vertical tick marks above the difference plot show the peak positions.

6.4 Conclusions

Crystal structure and phase stability as a function of the grain size have been investigated for the $(1-x)Bi(Mg_{3/4}W_{1/4})O_3$-$xPbTiO_3$ ceramics with x = 0.60, 0.61, 0.64 and 0.67. All the studied compositions exhibit coexistence of ordered tetragonal (*I4/m*) and ordered cubic (*Fm-3m*) structures for the samples prepared at 850 °C with smaller grain size. The crystal structure of the nano-crystalline $0.36Bi(Mg_{3/4}W_{1/4})O_3$-

0.64PbTiO$_3$ sample, obtained after high energy ball milling, transforms into disordered tetragonal phase with *P4mm* space group. The structure of the (1-x)Bi(Mg$_{3/4}$W$_{1/4}$)O$_3$-xPbTiO$_3$ ceramics with x = 0.60 and 0.61 transform into ordered cubic phase with space group *Fm*-3*m* by increasing the sample preparation temperature to 1000 °C due to increased grain size. In contrast, the composition with x = 0.67, which also exhibits the coexistence of ordered cubic (*Fm*-3*m*) and tetragonal (*I4/m*) phases for the sample calcined at 850 °C, transform into ordered tetragonal (*I4/m*) phase by increasing the sample preparation temperature to 1000 °C.