Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2011, Article ID 402376, 11 pages
doi:10.1155/2011/402376

Research Article

Crystallization Behavior and Microstructural Analysis of Lead-Rich (Pb_xSr_{1-x}) TiO_3 Glass Ceramics Containing 1 mole % La_2O_3

C. R. Gautam,[1,2] Devendra Kumar,[1,2] and Om Parkash[1,2]

[1] *Department of Physics, University of Lucknow, Lucknow 226007, India*
[2] *Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221005, India*

Correspondence should be addressed to C. R. Gautam, gautam_ceramic@yahoo.com

Received 1 March 2011; Accepted 15 June 2011

Academic Editor: Joseph Lai

Solid solution of perovskite $Pb,SrTiO_3$ in Pb-rich composition can be crystallized in borosilicate glassy matrix. The addition of rare earth and transition metal oxides is known to influence the crystallization behavior and surface morphology of perovskite crystallites in glassy matrix. In the present paper, the glasses in the lead-rich system $64[(Pb_xSr_{1-x})\cdot TiO_3]$-$25[2SiO_2\cdot B_2O_3]$-$5[K_2O]$-$5[BaO]$ $(1 \leq x \leq 0.5)$ with the addition of 1 mol % La_2O_3 were prepared to study its effect on their crystallization behavior. Differential thermal analysis (DTA) patterns show one or more exothermic crystallization sharp peaks, which shift towards higher temperature with increasing concentration of SrO. The glasses were subjected to various heat-treatment schedules for crystallization. X-ray diffraction analysis of these glass ceramic samples shows that major crystalline phase of the entire glass ceramic sample with $x \geq 0.5$ was found to have tetragonal structure similar to $PbTiO_3$ ceramic, and addition of La_2O_3 enhances the crystallization of the perovskite phase and retards the crystallization of minor phases.

1. Introduction

Glass ceramics are an important class of materials that have been commercially quite successful. The pore-free polycrystalline materials are produced by the controlled crystallization of glass and composed of randomly oriented crystals with some residual glass [1]. Crystallization is accomplished by subjecting the glasses to a carefully regulated heat treatment schedule, which results in the nucleation and growth of crystal phases within the glass samples [2]. Extensive studies have been reported on the crystallization and dielectric behavior of ferroelectric glass ceramics, specifically $PbTiO_3$ and $NaNbO_3$ [3]. These studies show that both the parent glass composition and heat treatment schedule determine the crystalline phase constitution, microstructure, and dielectric properties of respective glass ceramics. Bergeron and Russell investigated the growth of $PbTiO_3$ from PbO-B_2O_3-TiO_2 glasses and found that the crystallization proceeded mainly from the surface [4]. The crystallization and microstructural behavior of glass ceramic with perovskite titanate phases, such as $PbTiO_3$ [5–11] and $SrTiO_3$ [12–15], have been investigated. Limited work has been carried on the lead strontium titanate borosilicate glass-ceramic system, despite its wide applications. Thakur et al. [16] investigated the crystallization, microstructure, and dielectric behavior of $SrTiO_3$ glass ceramic with different oxide additions. They could crystallize $SrTiO_3$ as a major phase in borosilicate glass ceramic system with addition of proper concentration of alkali oxide K_2O and selected heat treatment schedules. It was also reported that the addition of La_2O_3 enhances the crystallization of strontium titanate [17]. Later on Sahu et al. [18, 19] explored the possibility of substitution of strontium for lead in the system $[(Pb_{1-x}Sr_x)O\cdot TiO_2]$-$[2SiO_2\cdot B_2O_3]$-$[K_2O]$-$[BaO]$ for crystallization of solid solution perovskite phase. The phase development, microstructural analysis, and dielectric behavior of the glass ceramics indicated that both the glass composition and heat-treatment schedules determine the crystalline phase constitution. Solid solution of $PbTiO_3$ and $SrTiO_3$ phases could be crystallized in borosilicate glasses [20–23].

Table 1: Glass transition temperature, density of glass, and DTA peaks of various glass samples in the system $[(Pb_xSr_{1-x})\ O{\cdot}TiO_2]$ - $[2SiO_2{\cdot}B_2O_3]$-$[BaO{\cdot}K_2O]$-$[La_2O_3]$.

Compositions (x)	Glass code	Density (gm/cc)	DTA Peaks (°C)			
			T_g	T_{c1}	T_{c2}	T_{c3}
1.0	PTL5B	5.655	510	—	620	700
0.9	9PL5B	4.485	540	597	635	695
0.8	8PL5B	4.357	570	—	—	726
0.7	7PL5B	4.125	575	—	686	739
0.6	6PL5B	3.965	575	—	—	730
0.5	5PL5B	3.912	600	—	—	806

Table 2: Heat treatment schedules, glass ceramic codes, and crystalline phases of different lead-rich glass ceramic samples in the system $[(Pb_xSr_{1-x})O{\cdot}TiO_2]$-$[2SiO_2{\cdot}B_2O_3]$-$[BaO{\cdot}K_2O]$-$[La_2O_3]$.

Glass code	Glass ceramic code	Heat treatment schedules			Crystalline phases
		Heating rate (°C/min)	Holding time (hrs)	Holding temp (°C)	
PTL5B	PTL5B700T	5	3	700	P + PT
	PTL5B700S	5	6	700	P + PT
9PL5B	9PL5B597T	5	3	597	P + PT
	9PL5B635T	5	3	635	P + PT
	9PL5B700T	5	3	700	P + PT*
	9PL5B700S	5	6	700	P + Pb
8PL5B	8PL5B726T	5	3	726	P + R
	8PL5B726S	5	6	726	P + R*
7PL5B	7PL5B686T	5	3	686	P + R* + PT
	7PL5B739T	5	3	739	P
	7PL5B739S	5	6	739	P + PT
6PL5B	6PL5B730T	5	3	730	P + R
	6PL5B730S	5	6	730	P + U*
5PL5B	5PL5B806T	5	3	806	P + R
	5PL5B806S	5	6	806	P + R*

P: Perovskite titanate, PT: $PbTi_3O_7$, R: Rutile (TiO_2), Pb: Pb_2O_4, *Trace amount.

A brief report on crystallization and dielectric behavior of lead strontium titanate borosilicate glass ceramics with addition of La_2O_3 was reported [21]. In the present paper, a detailed study has been made to understand the crystallization behavior and microstructural morphology in the lead-rich glass ceramic samples in the system $64[(Pb_xSr_{1-x})TiO_3]$-$25[2SiO_2B_2O_3]$-$5[K_2O]$-$5[BaO]$ with addition of 1% La_2O_3. The crystallization and surface morphology of strontium-rich compositions are given in the second paper "Crystallization behavior and surface morphology of strontium rich $(Pb_xSr_{1-x})\ TiO_3$ glass ceramics in presence of La_2O_3-II."

2. Experimental Procedure

Glasses in the system $64[(Pb_xSr_{1-x})TiO_3]$-$25[2SiO_2{\cdot}B_2O_3]$-$5[K_2O]$-$5[BaO]$-$1[La_2O_3]$ with varying lead to strontium ratio ($1 \leq x \leq 0.5$) have been prepared by melt-quench method. The highly pure chemicals powder of PbO, $SrCO_3$, TiO_2, SiO_2, H_3BO_3, $BaCO_3$, K_2CO_3, and La_2O_3 was mixed in a mortar using acetone as a grinding medium. The dry powders were melted in the temperature range 1120–1240°C in an electrically heated furnace. The melt was poured into an aluminium mould, pressed by a thick aluminium plate, and immediately annealed at temperature 400°C for three hours in another furnace. All the glasses were characterized by differential thermal analysis (DTA) to determine glass transition and the crystallization temperatures (Table 1). Differential thermal analysis was done on the powdered glass samples at a heating rate of 10°C/min. On the basis of DTA results, various glass ceramic samples were prepared by heat treating the glasses in the temperature range 600–806°C. The different heat-treatment schedules and nomenclature of glass ceramic samples are listed in the Table 2. The glasses were heat treated by heating them at a heating rate of 5°C/min to the desired temperature and holding them for 3 or 6 hours. The samples were then cooled to room temperature at a cooling rate of 10°C/min. Three-hour heat treatment was given to all glasses at their respective DTA peaks, whereas six-hour heat treatment was given to all glasses at their DTA corresponding to major crystalline perovskite phase. The nomenclature of glass ceramic samples includes the code of their parent glass composition followed by heat-treatment temperature and followed by a letter "T" and "S" for 3 and 6 hours heat treatment, respectively. X-ray diffraction patterns

were recorded using a Rigaku X-ray diffractometer using Cu Kα radiation. X-ray diffraction patterns were compared with standard d-values from JCPDS files for different constituting phases. Gold coatings were applied by the sputtering method to the etched surfaces of various glass ceramic samples intended for scanning electron microscopy (SEM) in order to study the morphology of different crystalline phases.

3. Results

3.1. Differential Thermal Analysis (DTA). DTA curves for these glasses with different (Pb) lead to strontium (Sr) ratio ($x = 1.0$ to 0.5) are shown in Figures 1 and 2. DTA patterns of different glasses show one or more exothermic peaks. These exothermic peaks represent the temperature at which the rate of crystallization of different phases is maximum. All glasses show a shift in the base line at a temperature, depending on the composition, in the temperature range of 510–600°C. This shift in the base line shows a change in the specific heat of the glass, which is attributed to the glass transition temperature, T_g. Glass transition temperatures of different glass samples are given in Table 1. The glass transition temperature has been found to increase with the increasing concentration of SrO. This may be due to increase in the viscosity of the melt.

DTA pattern of the glass PTL5B with no strontium shows two exothermic peaks at 620 and 700°C (Figure 1(a)). The peak at 700°C represents the crystallization of the major perovskite lead titanate, (P), $PbTiO_3$ phase in the glass ceramic. The peak at 620°C represents the crystallization of the minor $PbTi_3O_7$ (PT). This is confirmed by powder X-ray diffraction (XRD) studies. The peak corresponding to crystallization of major perovskite phase is present in DTA patterns of all the glasses. Two DTA peaks are also observed for the glass 7PL5B.

Three DTA peaks are observed for the glass 9PL5B. All other glasses show a single exothermic peak in their DTA patterns. The temperature of peaks T_{c1}, T_{c2}, and T_{c3} for different glasses in this system with PbO to SrO ratio and 1% La_2O_3 is given in Table 1.

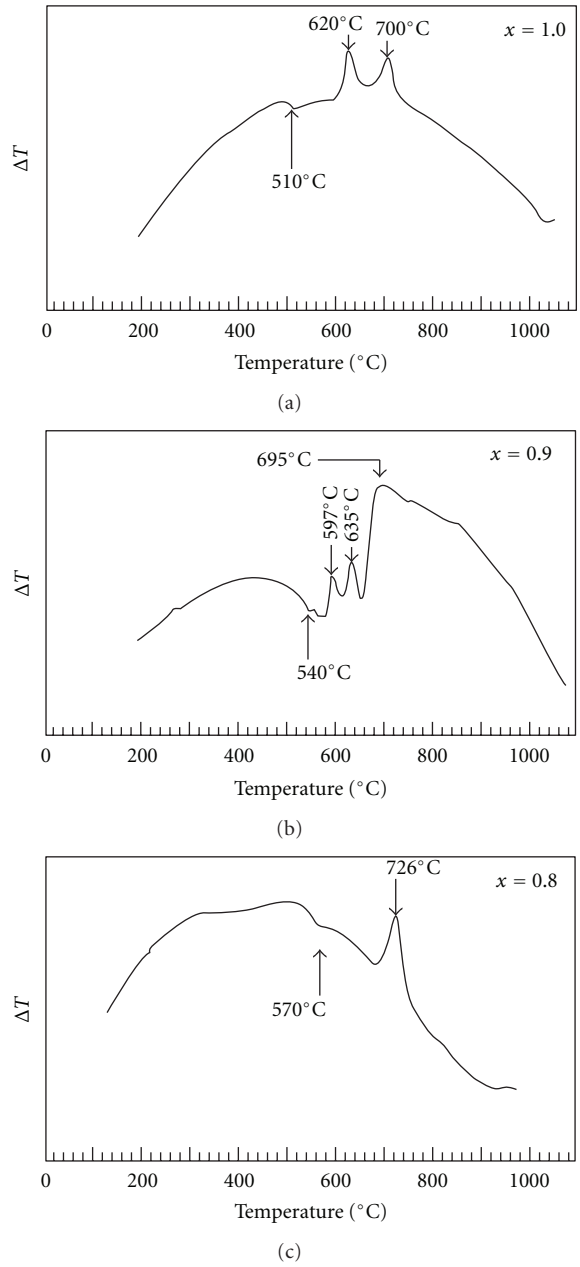

Figure 1: DTA pattern of glasses: (a) PTL5B, $x = 1.0$, (b) 9PL5B, $x = 0.9$, and (c) 8PL5B, $x = 0.8$.

3.2. X-Ray Diffraction Analysis and Crystallization Behavior. X-ray diffraction (XRD) patterns for various glass ceramic samples crystallized at different temperatures for 3 hours are shown in Figure 3. All the peaks in respective XRD patterns were matched with JCPDS of various compounds data for constituent oxides. X-ray diffraction pattern for the glass ceramic samples PTL5B700T ($x = 1.00$) is shown in Table 2.

In Figure 3(a), it is observed from the XRD pattern that $PbTiO_3$ (P) is the major crystalline phase and $PbTi_3O_7$ (PT) is the secondary phase in this glass ceramic sample. Figures 3(b) and 3(c) show the XRD patterns of glass ceramic samples 9PL5B695T and 8PL5B726T with heat treatment at different temperatures. XRD patterns of glass ceramic sample 9PL5B695T show the presence of tetragonal perovskite phase as major phase and $PbTi_3O_7$ as a minor phase. When the glass is heat treated at lower temperature, the amount of minor $PbTi_3O_7$ phase is more in comparison to the glass ceramic sample obtained by heat treating at 695°C. This is indicated by the relative intensity of XRD lines of P and PT phases. This shows that the DTA peaks at lower temperatures correspond to crystallization of minor phase, while the peak T_{c3} at 695°C corresponds to crystallization of perovskite phase.

The XRD data of the major phase of these glass ceramic samples were indexed on the basis of tetragonal unit cell similar to lead titanate. The lattice parameters (s) for the major crystalline phases in the glass ceramic system were obtained by using software CEL. The structure, lattice parameters (c, a), tetragonality, c/a, for the crystalline phase are given in Table 3. The glass ceramic samples obtained by

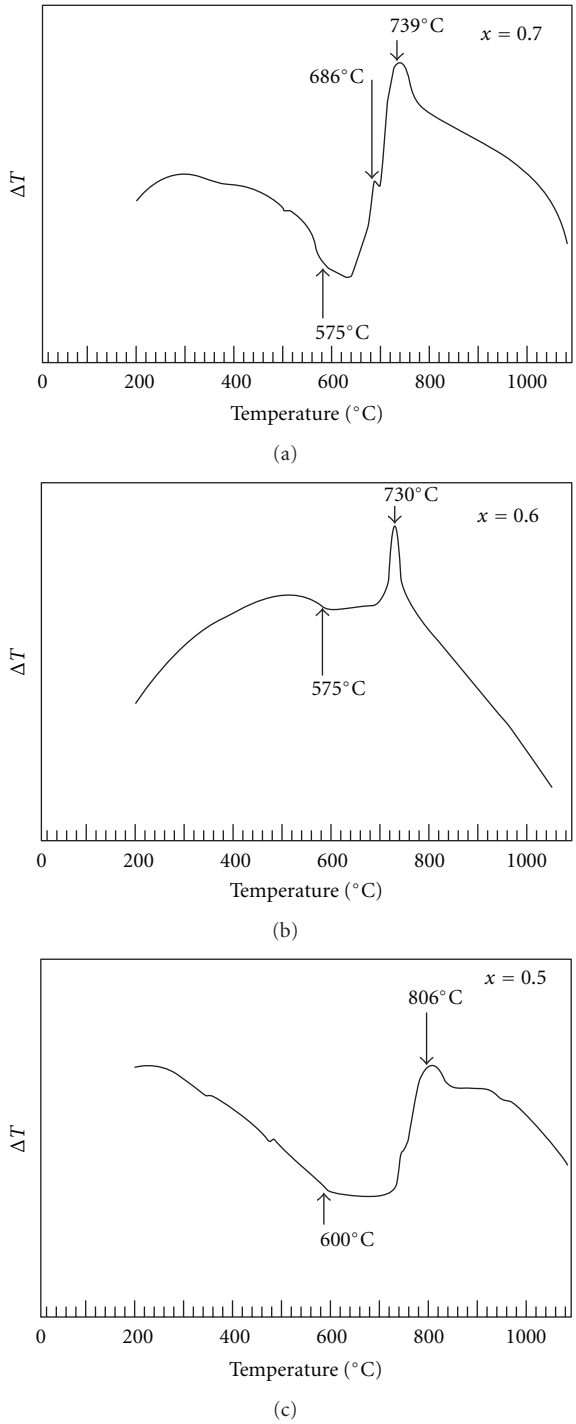

Figure 2: DTA pattern of glasses: (a) 7PL5B, $x = 0.7$, (b) 6PL5B, $x = 0.6$, and (c) 5PL5B, $x = 0.5$.

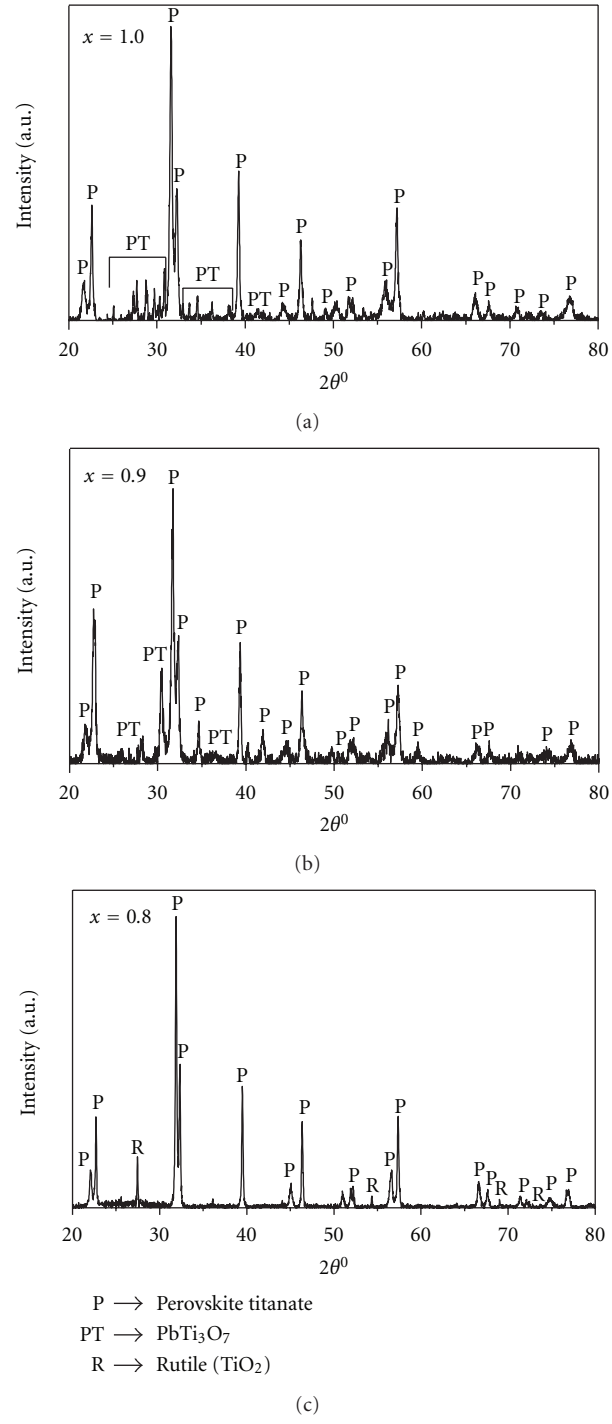

Figure 3: X-ray diffraction patterns of different glass ceramic samples: (a) PTL5B700T, (b) 9PL5B695T, and (c) 8PL5B726T.

heat-treating glasses with $x = 1.0$ and 0.9 were found to show similar crystallization behavior (Figure 3). They differ only in terms of minor phase and value of lattice parameters. XRD patterns for glass ceramic samples 9PL5B597T; 9PL5B635T; 9PL5B695T are shown in Figure 4. The XRD patterns for these glass ceramic samples show the formation of perovskite as a major phase. Large amount of PT and small amount of rutile (R) are also present. The amount of secondary phase of $PbTi_3O_7$ for $x = 0.9$ obtained by heat treatment at higher temperature is found to be less in comparison to the composition with $x = 1.0$. The glass with $x = 0.7$ was heat treated for 3 and 6 hours at 686°C and 739°C to study the effect of the crystallization temperature and soaking time on the microstructure and dielectric behavior of the resulting glass ceramic samples. Perovskite titanate was found to be major phase with secondary $PbTi_3O_7$ and trace amount of

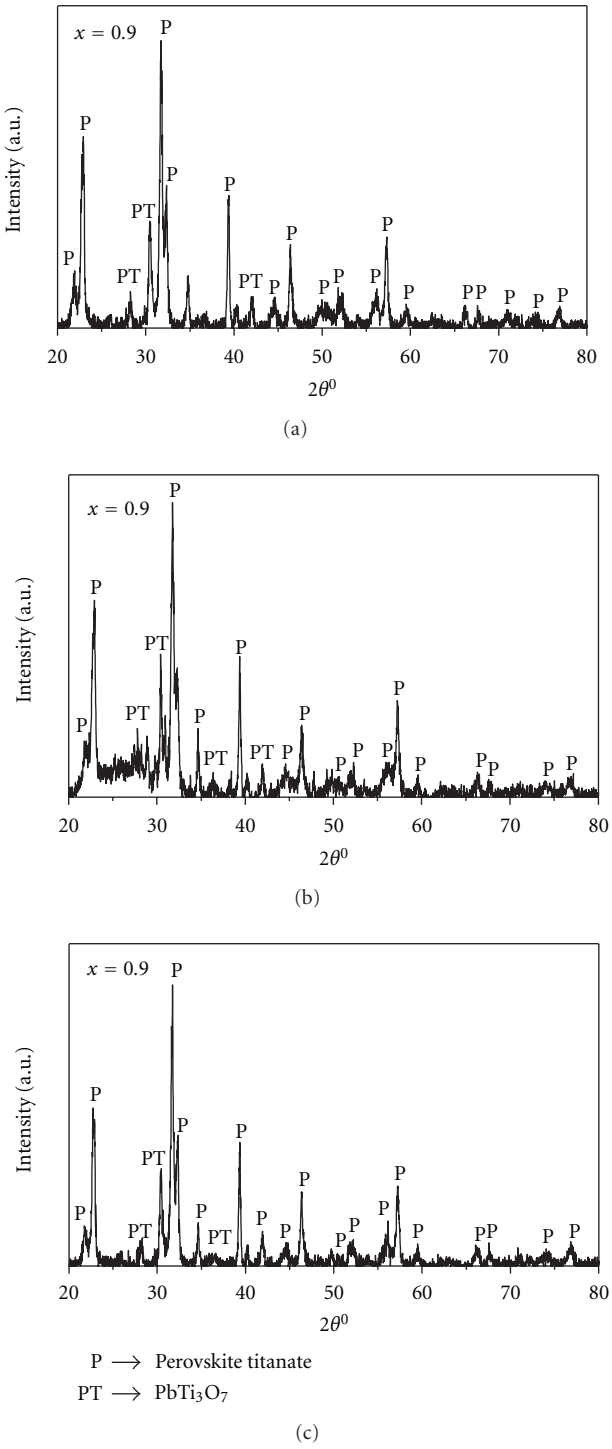

Figure 4: X-ray diffraction patterns of different glass ceramic samples: (a) 9PL5B597T, (b) 9PL5B635T, and (c) 9PL5B695T.

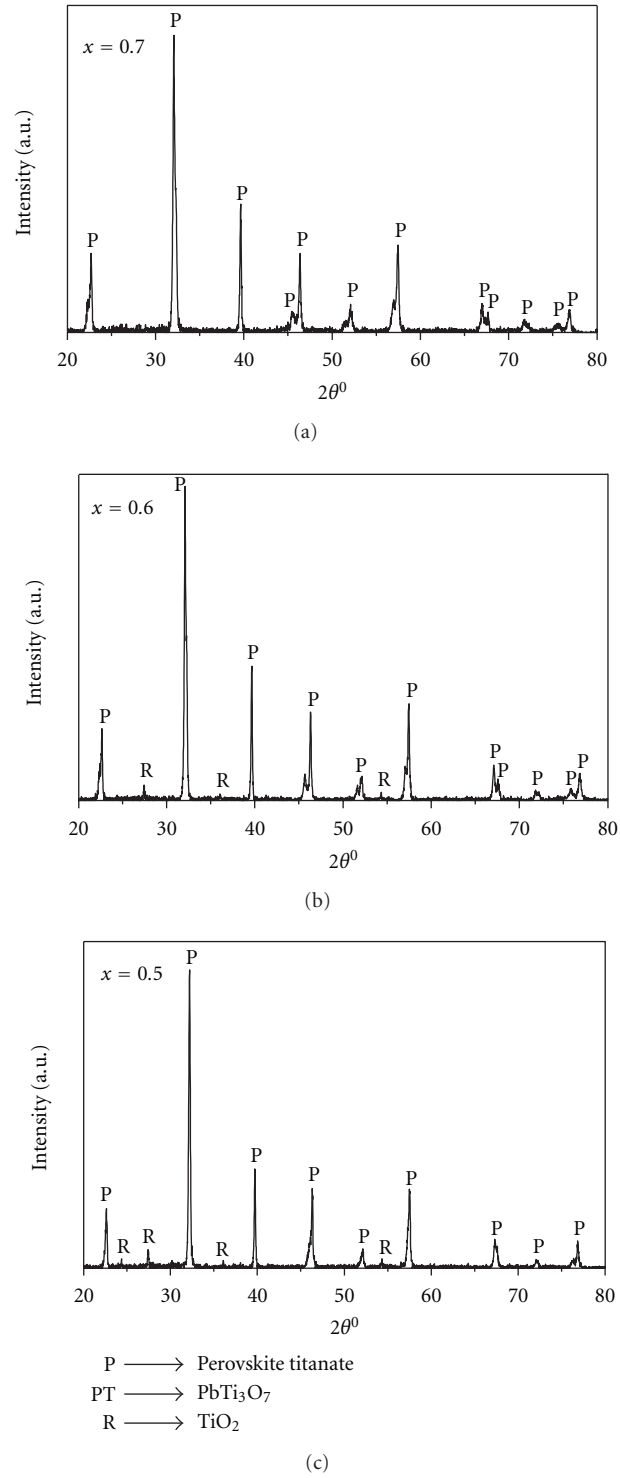

Figure 5: X-ray diffraction patterns of different glass ceramic samples: (a) 7PL5B739T, (b) 6PL5B730T, and (c) 5PL5B806T.

rutile phase. But for glass ceramic obtained by heat-treating at 739°C for 3 hours, the presence of secondary phases of $PbTi_3O_7$ and rutile (TiO_2) was not observed. Figure 5 shows the XRD patterns for the glass ceramic samples 6PL5B730T and 5PL5B806T. Perovskite titanate (P) was found as a major phase and rutile (R) as a minor phase. They contain the same phases but only differ in the tetragonality.

XRD patterns for glass ceramic samples PTL5B700S, 9PL5B700S, and 8PL5B726S crystallized at 700°C and 726°C for 6 hours, respectively, are shown in Figure 6. Glass ceramic sample PTL5B700S has the phase constitution similar to PTL5B700T that is obtained by heat treating the glass for 3 hours.

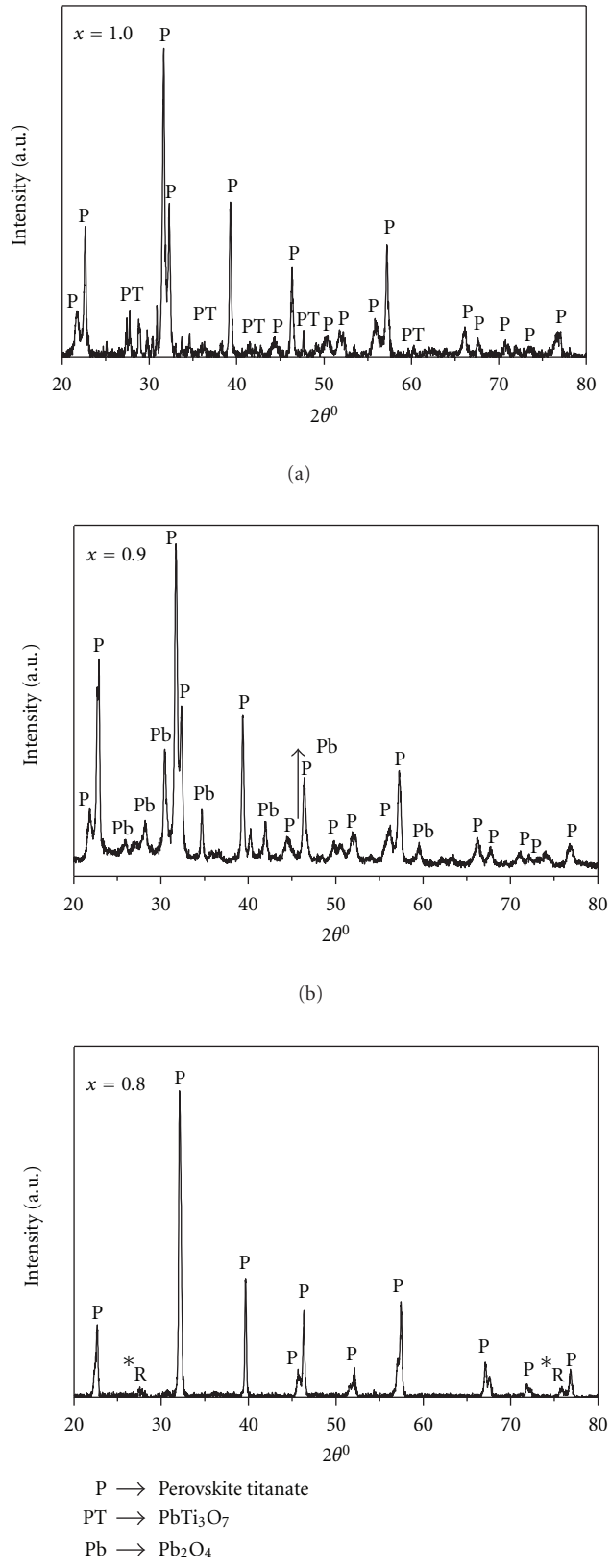

Figure 6: X-ray diffraction patterns of different glass ceramic samples: (a) PTL5B700S, (b) 9PL5B700S, and (c) 8PL5B726S. ∗: Trace amount of Rutile (TiO_2) phase.

For the glass ceramic sample 9PL5B700S, a change is observed in the crystalline phase in comparison to 9PL5B700T. This change is in the form of secondary phases, $PbTi_3O_7$ (PT) and Pb_2O_4 (Pb). For sample heat treated at 700°C for 3 hours, the secondary phase is $PbTi_3O_7$ whereas for 6 hrs of heat treatment, the secondary phase is Pb_2O_4. Figure 6(c) depicts the XRD pattern of glass ceramic sample 8PL5B726S. This shows the presence of perovskite titanate as the major phase. A little amount of TiO_2 (rutile) phase is also present. This glass ceramic sample shows better amount of perovskite phase in comparison to 3-hour heat treatment schedules. Figure 7(a) shows the XRD pattern for the glass ceramic sample 7PL5B739S. This sample contains $PbTi_3O_7$ as minor phase along with perovskite as major phase.

Figures 7(b) and 7(c) show XRD patterns for the glass ceramic samples 6PL5B730S and 5PL5B806S. Perovskite lead strontium titanate is crystallized as the major phase. It is also observed that the secondary phase of rutile (trace amount) is also present in these glass ceramic samples except for the glass ceramic sample 6PL5B730S. In 6PL5B700S glass ceramic sample, an unidentified phase is observed in small amount in place of rutile phase.

Comparison of XRD data of these glass ceramic samples with standard data from JCPDS files for different possible phases of constituent oxides indicates that although the major phase is lead titanate or lead strontium titanate, solid solution perovskite and many minor phases form in significant proportion. The parent glasses for lead rich glass ceramic samples also show many exothermic peaks in their respective DTA plots. Since these glass ceramic samples are rich in lead, minor phases $PbTi_3O_7$ and Pb borate form. As the strontium content increases in the glass ceramic sample, the exothermic peaks corresponding to the crystallization of minor phases are suppressed. It results in the crystallization of lead strontium titanate perovskite phase predominantly. XRD patterns of these glass ceramic samples indicate the presence of the other minor phases only in trace amount. In strontium-rich compositions, rutile is mostly present in trace amount. Glass ceramic samples for all glasses were also prepared with 6 hours holding time at their respective crystallization temperatures for the major phase. XRD patterns of these glass ceramic samples with the XRD patterns of the respective glass ceramic samples, which were crystallized for 3 hours, were compared. It is found that XRD peaks of the major phase are well developed and sharp for samples obtained by heating for 6 hours. The peak intensity of minor phase/s decreases. In a few cases, there is a change in the nature of the minor phase. In case of glass ceramic samples 9PL5B695T, the minor phase is $PbTi_3O_7$ (PT), whereas in glass ceramic samples, the minor phase present is PbB_2O_4. The crystallization rate of PbB_2O_4 may be slower than that of $PbTi_3O_7$ and hence PbB_2O_4 minor appears on longer heat treatment.

3.3. Surface Morphology. The surface morphology of all glass ceramic samples shows fine crystallites of perovskite major phase of lead titanate and lead strontium titanate. Qualitative inspection of all these micrographs revealed that the relative

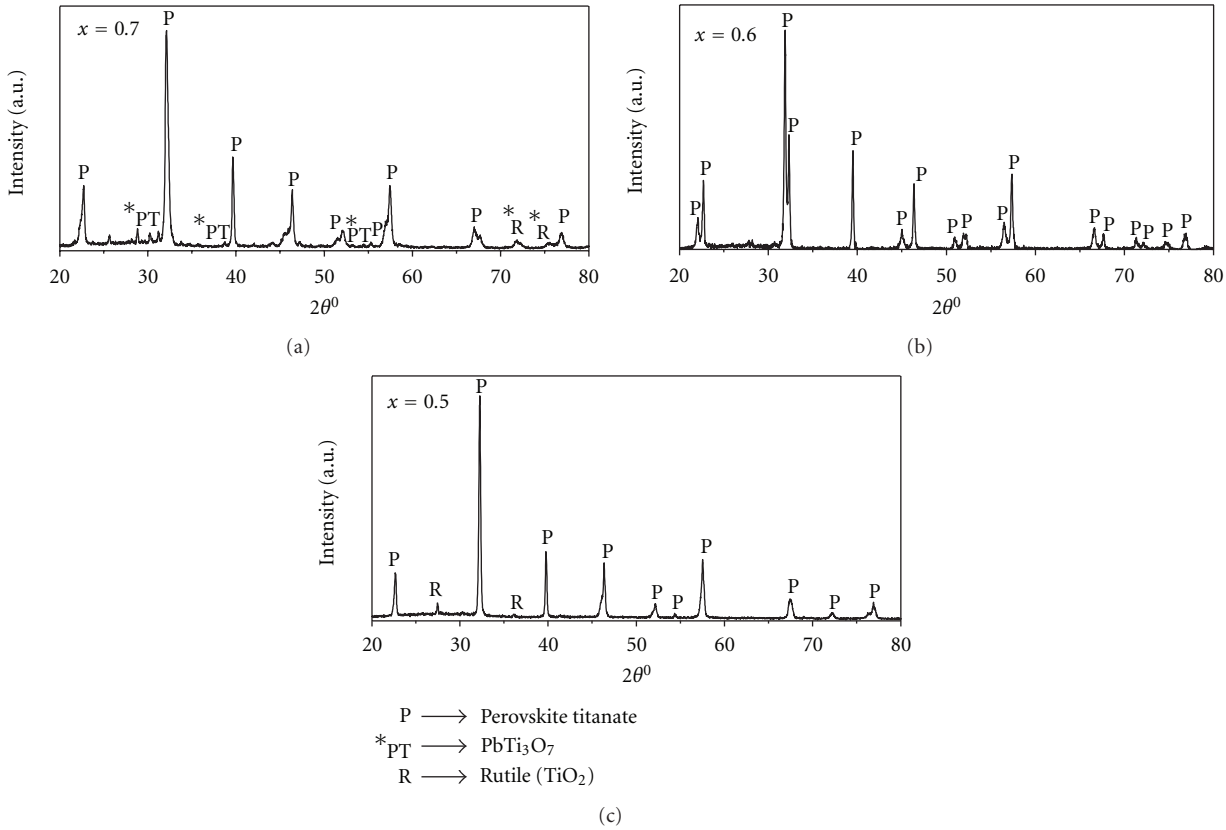

Figure 7: X-ray diffraction patterns of different glass ceramic samples: (a) 7PL5B739S, (b) 6PL5B730S, and (c) 5PL5B806S.

Table 3: Crystal structure, lattice parameters, and axial ratio of major crystalline phase in different lead-rich glass ceramic samples.

Glass ceramics	Crystal structure	Lattice parameters		Axial ratio (c/a)	$(Pb,Sr)TiO_3$ ceramic*		
		c (Å)	a (Å)		c (Å)	a (Å)	c/a
PTL5B700T	Tetragonal	4.117 ± 0.005	3.916 ± 0.005	1.051	4.138	3.892	1.063
PTL5B700S	Tetragonal	4.125 ± 0.005	3.906 ± 0.005	1.056			
9PL5B700T	Tetragonal	4.080 ± 0.002	3.910 ± 0.002	1.043	4.004	3.837	1.043
9PL5B700S	Tetragonal	4.079 ± 0.005	3.909 ± 0.005	1.043			
8PL5B726T	Tetragonal	4.019 ± 0.001	3.916 ± 0.001	1.026	3.983	3.864	1.030
8PL5B726S	Tetragonal	4.163 ± 0.007	3.910 ± 0.007	1.064			
7PL5B739T	Tetragonal	3.974 ± 0.001	3.921± 0.001	1.013	3.984	3.903	1.020
7P5B739S	Tetragonal	3.977 ± 0.002	3.922 ± 0.002	1.014			
6PL5B730T	Tetragonal	3.967 ± 0.001	3.916 ± 0.001	1.013	3.947	3.882	1.016
6PL5B730S	Tetragonal	4.024 ± 0.001	3.915 ± 0.001	1.027			
5PL5B806T	Tetragonal	3.932 ± 0.002	3.927 ± 0.002	1.001	3.960	3.896	1.016
5PL5B806S	Tetragonal	3.938 ± 0.001	3.918 ± 0.001	1.005			

* Reference [20].

content of residual glass phase was little or not significant. The coexistence of coarse and ne perovskite particles has also been observed and reported in similar lead titanate glass ceramics [18, 24]. Scanning electron micrographs of the various glass ceramic samples heat treated for 3 and 6 hours are shown in Figures 8 and 9. Figure 8 shows scanning electron micrographs of glass ceramic samples PTL5B700T, 9PL5B695T, 8PL5B726T, 7PL5B739T, and 5PL5B806T. The glass ceramic sample PTL5B700T is found to be composed of interconnected fine crystallites of lead titanate ($PbTiO_3$), which are dispersed in the glassy matrix (Figure 8(a)). XRD studies confirm that the fine crystallites are of $PbTiO_3$, which is the major crystalline phase. In general, the white region in the microstructure represents the major crystalline phase/secondary phase, while the black region depicts the residual glass in all scanning electron micrographs. For the

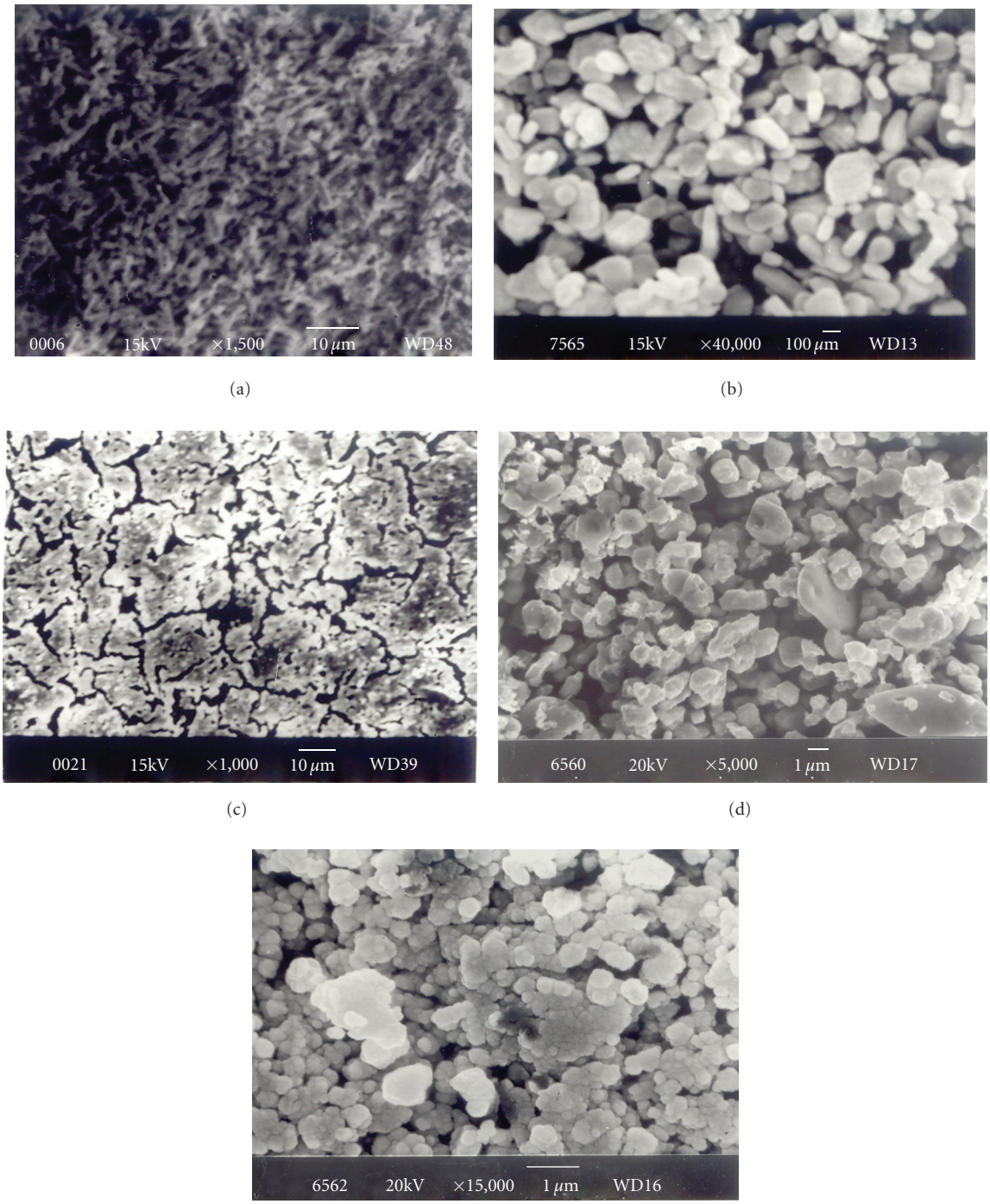

Figure 8: Scanning electron micrographs of glass ceramic samples: (a) PTL5B700T, (b) 9PL5B695T, (c) 8PL5B726T, (d) 7PL5B739T, and (e) 5PL5B806T.

glass ceramic sample PTL5B700S, there is a change in the morphology of the crystallites of the major phase, $PbTiO_3$, (Figure 9(a)). These crystallites are found to have round shape and are agglomerated. The size of the crystallites is higher in comparison to that for 3-hour of heat-treated glass ceramic sample. Figure 8(b) shows the scanning electron micrograph of the glass ceramic sample 9PL5B700T. The crystallites size is in the submicron range. The volume fraction of the residual glass is small. Some smaller whitish grains represent the secondary phase of $PbTi_3O_7$. Figures 8(c) and 9(b) are the scanning electron micrographs for the glass ceramic samples 8PL5B726T and 8PL5B726S, respectively. The glass ceramic sample 8PL5B726T shows dispersion of the major perovskite phase in the glassy matrix. As the

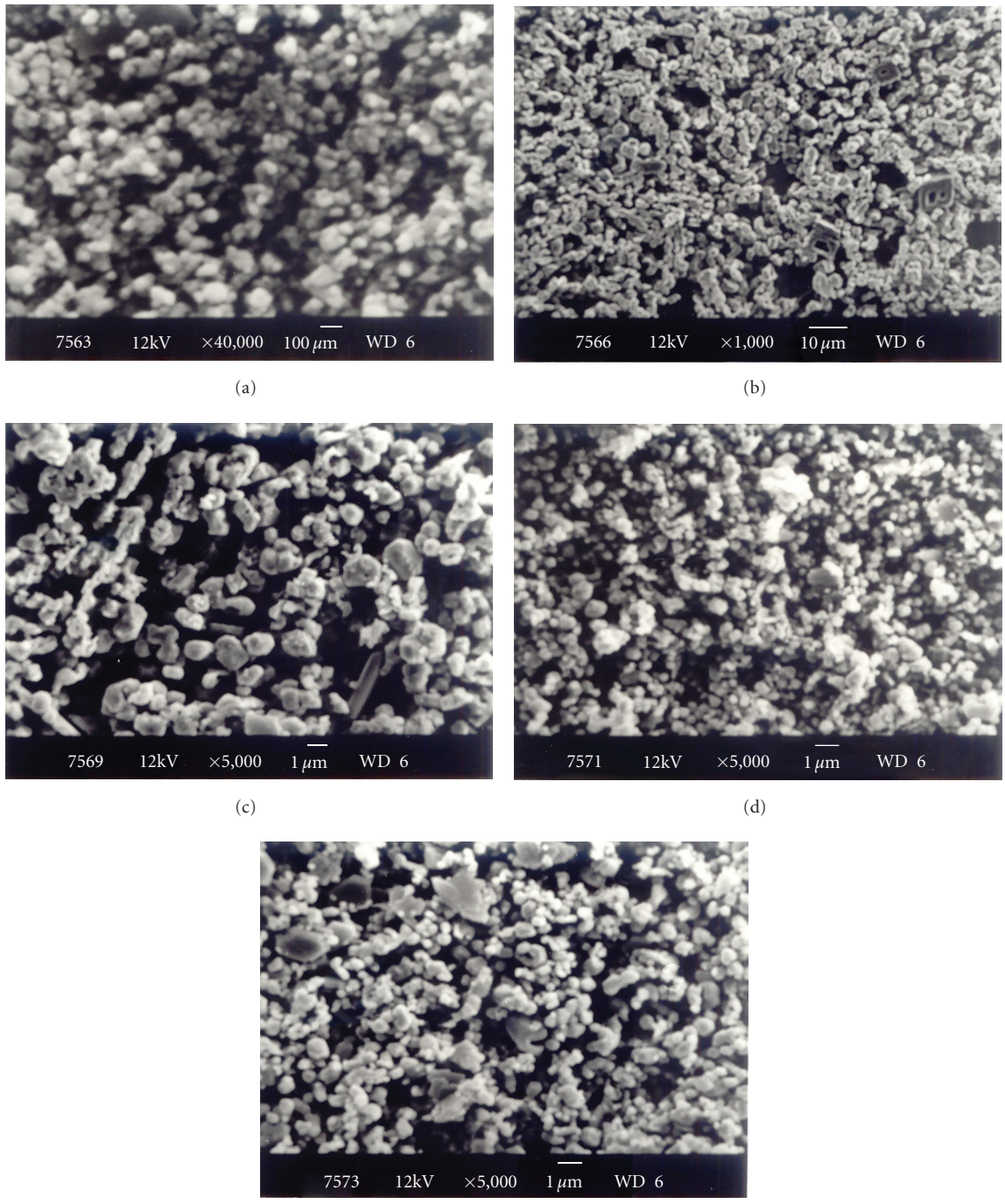

Figure 9: Scanning electron micrographs of glass ceramic samples: (a) PTL5B700S, (b) 8PL5B726S, (c) 7PL5B739S, (d) 6PL5B730S, and (e) 5PL5B806S.

crystallization time is increased from 3 to 6 hours, well-separated crystallites of major phase are formed as shown in Figure 9(b).

It is confirmed from the study of XRD and SEM that the 6-hour heat-treatment schedule is not suitable for the crystallization of glass sample 7PL5B ($x = 0.7$). The scanning electron micrograph of glass ceramic sample 6PL5B730S shown in Figure 9(d) shows crystallization of submicrometer grains of perovskite phase. The shiny white region represents the trace amount of the unidentified phase.

Figures 8(e) and 9(e) show the scanning electron micrographs of chemically etched surfaces of glass ceramic samples 5PL5B806T and 5PL5B806S, which are obtained by the crystallization of the glass 5PL5B at 806°C for 3 and 6 hours of heat treatment schedule. The large amounts of rutile (TiO_2) are crystallized on the upper side of the perovskite

titanate major phase, while for the 6-hour heat-treated glass ceramic sample 5PL5B806S, the trace amount of rutile is distributed inside the glassy matrix.

4. Discussion

There is a shift in different XRD peaks positions of major perovskite phase with changing lead to strontium ratio in the compositions of the base glasses. The position of XRD peaks for various glass ceramic samples shifts systematically with composition, x or Pb/Sr ratio. The lattice parameters "c" and "a" and the axial ratio (c/a) of the perovskite phase continuously decrease as the concentration of SrO increases in the glass. In general, XRD patterns of the glass ceramic samples rich in lead with $x = 1.0$ to 0.5 indicate the formation of tetragonal crystals similar to lead titanate. The shift in the XRD peak positions and hence the resulting changes in the lattice parameters from that of undoped $PbTiO_3$ ceramics could be due to two factors: (i) formation of $PbTiO_3$ solid solution with $SrTiO_3$ (ii) and strain due to crystal clamping. Since both of these effects may have been present, the crystal phase developed in these compositions cannot be identified unambiguously through room temperature XRD techniques. Some other characterization techniques have to be adopted to confirm the composition of crystallites.

5. Conclusions

Differential thermal analysis (DTA) patterns show more than one peak in the lead-rich glass compositions. These peaks are sharp. Doping of La_2O_3 affects the crystallization behavior and dielectric properties of the glass ceramic samples. The addition of La_2O_3 promotes the crystallization of major phase and retards the crystallization of minor phases. X-rays diffraction patterns of lead-rich glass ceramic samples show that the major phase of $PbTiO_3$ or perovskite $(Pb,Sr)TiO_3$ and a trace amount of pyrochlore phase of $PbTi_3O_7$. Crystalline phase of all the glass ceramic sample of glasses with $x \leq 0.5$ was found to have tetragonal structure. Surface morphology of the fined crystalline phase is observed uniform and well interconnected in residual glassy matrix.

Acknowledgments

The authors are highly grateful to Dr. Chandra Prakash and Dr. O. P. Thakur of the Electroceramic Division, Solid State Physics Laboratory, Delhi (India) for providing access to the gold coating facility for the glass ceramic samples. Financial support from Defence Research and Development Organization (India) is gratefully acknowledged.

References

[1] M. W. Barsoum, *Fundamental of Ceramics*, McGraw-Hill, Singapore, 1997.

[2] P. W. Mc Millan, *Glass Ceramics*, Academic Press, London, UK, 2nd edition, 1974.

[3] T. Kokubo and M. Tashiro, "Dielectric properties of fine-grained $PbTiO_3$ crystals precipitated in a glass," *Journal of Non-Crystalline Solids*, vol. 13, no. 2, pp. 328–340, 1974.

[4] C. G. Bergeron and C. K. Russell, "Nucleation and growth of lead titanate from a glass," *Journal of the American Ceramic Society*, vol. 48, no. 3, pp. 115–118, 1965.

[5] D. G. Grossman and J. O. Isard, "Lead Titanate glass-ceramics," *Journal of the American Ceramic Society*, vol. 52, pp. 230–241, 1969.

[6] D. G. Grossman and J. O. Isard, "Crystal clamping in $PbTiO_3$ glass-ceramics," *Journal of Materials Science*, vol. 4, no. 12, pp. 1059–1063, 1969.

[7] S. M. Lynch and J. E. Shelby, "Crystal clamping in lead titanate glass-ceramics," *Journal of the American Ceramic Society*, vol. 67, no. 6, pp. 424–427, 1984.

[8] W. Mianxue and Z. Peinan, "Piezoelectricity, pyroelectricity and ferroelectricity in glass ceramics based on $PbTiO_3$," *Journal of Non-Crystalline Solids*, vol. 84, no. 1–3, pp. 344–351, 1986.

[9] J. J. Shyu and Y. S. Yang, "Crystallization of a PbO-BaO-TiO_2-Al_2O_3-SiO_2 glass," *Journal of the American Ceramic Society*, vol. 78, no. 6, pp. 1463–1468, 1995.

[10] W. N. Lawless, "Thermometer equations for low-temperature glass-ceramic capacitance thermometers," *Cryogenics*, vol. 42, pp. 561–566, 1972.

[11] W. N. Lawless, "Three application areas for strontium titanate glass-ceramics," *Ferroelectrics*, vol. 3, pp. 287–293, 1971.

[12] W. N. Lawless, "Some low-temperature properties and applications of $SrTiO_3$ crystallized from glass," *Ferroelectrics*, vol. 7, pp. 379–381, 1974.

[13] S. L. Swartz, E. Breval, and A. S. Bhalla, "Effect of nucleation on the crystallization and dielectric properties of strontium titanate glass-ceramics ," *American Ceramic Society Bulletin*, vol. 67, no. 4, pp. 763–770, 1988.

[14] S. L. Swartz, E. Breval, C. A. Randall, and B. H. Fox, "Strontium Titanate ($SrTiO_3$) glass ceramics—part I: crystallization and Microstructure," *Journal of Materials Science*, vol. 23, no. 11, pp. 3997–4003, 1988.

[15] S. L. Swartz, A. S. Bhalla, L. E. Cross, and W. N. Lawless, "Strontium Titanate ($SrTiO_3$) glass ceramics—part II: dielectric properties," *Journal of Materials Science*, vol. 23, pp. 4004–4012, 1988.

[16] O. P. Thakur, D. Kumar, O. Parkash, and L. Pandey, "Effect of K_2O adiition on crystallization and microstructural behavior of strontium Titanate borosilicate glass ceramic system," *Journal of Materials Letters*, vol. 23, pp. 253–260, 1995.

[17] O. P. Thakur, *Crystallization, microstructure and dielectric behavior of strontium Titanate borosilicate glass ceramics with some additives*, Ph.D. thesis, Banaras Hindu University, Varanasi, India, 1998.

[18] A. K. Sahu, D. Kumar, and O. Parkash, "Crystallisation of lead strontium titanate perovskite phase in $[(Pb_{1-x}Sr_x)O \cdot TiO_2]$–$[2SiO_2 \cdot B_2O_3]$–$[K_2O]$ glass ceramics," *British Ceramic Transactions*, vol. 102, no. 4, pp. 139–147, 2003.

[19] A. K. Sahu, D. Kumar, and O. Parkash, "Lead-strontium titanate glass ceramics: I—crystallization and microstructure," *Journal of Materials Science*, vol. 41, no. 7, pp. 2075–2085, 2006.

[20] S. Subrahmanyam and E. Goo, "Nucleation of the ferroelectric phase in the $(Pb_xSr_{1-x})TiO_3$ system," *Acta Materialia*, vol. 46, no. 3, pp. 817–822, 1998.

[21] A. K. Sahu, D. Kumar, O. Parkash, O. P. Thakur, and C. Prakash, "Effect of K_2O/BaO ratio on crystallization, microstructure and dielectric properties of strontium titanate borosilicate glass ceramics," *Ceramics International*, vol. 30, no. 3, pp. 477–483, 2004.

[22] D. Kumar, C. R. Gautam, and O. Parkash, "Preparation and dielectric characterization of ferroelectric $(Pb_xSr_{1-x})TiO_3$ glass ceramics doped with La_2O_3," *Applied Physics Letters*, vol. 89, no. 11, pp. 112908–112910, 2006.

[23] W. Liu, C. H. Mao, G. X. Dong, and J. Du, "Effects of PbO and SrO contents on crystallization and dielectric properties of PbO–SrO–Na_2O–Nb_2O_5–SiO_2 glass-ceramics system," *Ceramics International*, vol. 35, no. 3, pp. 1261–1265, 2009.

[24] A. Bahramia, Z. Ali Nematia, P. Alizadehb, and M. Bolandia, "Crystallization and electrical properties of $[(Pb_{1-x}Sr_x)\cdot TiO_3]$-$[(2SiO_2\cdot B_2O_3)]$-$[K_2O]$glass–ceramics," *Journal of Materials Processing Technology*, vol. 206, pp. 126–131, 2008.