Research Article

Crystallization Behavior and Microstructural Analysis of Strontium Rich ($\text{Pb}_x\text{Sr}_{1-x}$) TiO_3 Glass Ceramics in Presence of La_2O_3

C. R. Gautam,¹ Devendra Kumar,² and Om Parkash²

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 11 April 2011; Accepted 21 June 2011

Academic Editor: Joseph Lai

Copyright © 2011 C. R. Gautam et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Crystallization and microstructural behavior of various strontium-rich glass ceramics in the system $65[(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3]-24[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-5[\text{BaO}]-5[\text{K}_2\text{O}]-1[\text{La}_2\text{O}_3]$ ($0.0 \leq x \leq 0.4$) with addition of 1% La_2O_3 have been investigated. The addition of La_2O_3 has been found to play an important role in crystallization of perovskite $(\text{Pb,Sr})\text{TiO}_3$ as a solid solution phase. Also, it causes a change in the surface morphology of the fined crystallites of the major phase. Differential thermal analysis (DTA) shows only one exothermic crystallization peak, which shifts towards higher temperature with increasing amount of strontium oxide. Glasses were subjected to various heat treatment schedules for the crystallization. Very good crystallization of strontium-rich glass compositions is observed. X-ray diffraction studies confirm that cubic perovskite lead strontium titanate crystallizes as major phase. Lattice parameter decreases with increasing strontium content similar to lead strontium titanate ceramics. Uniform and interconnected crystallites are dispersed in glassy matrix.

1. Introduction

Strontium titanate has a cubic structure above -163°C where it transforms to a paraelectric phase. There is no dielectric anomaly at -163°C , but a strong elastic anomaly is observed [1]. The dielectric constant follows Curie-Weiss law below room temperature. Strontium titanate is a prototype ceramic with perovskite structure and is of much technological importance. Applications of strontium titanate glass ceramics for a long time have been limited to cryogenic temperature sensors and include a capacitance thermometer, a dielectric bolometer, and capacitive energy storage dielectrics [2]. The materials studied by Stookey [3] were essentially different from the group of glass ceramic materials discovered by King and Stookey [4]. In the later type of materials a relatively unstable glass was devitrified by the addition of a nucleating agent. They found that by dissolving TiO_2 in such a glass a situation could be created in which, in a certain temperature range, the material was supersaturated in TiO_2 , giving rise to crystallization of rutile. In some cases, TiO_2

did not crystallize as such, but combined with one of the modifying ions of the base glass to precipitate as a titanate, for example, crystallization of SrTiO_3 with perovskite structure. The crystallization and microstructural behavior of glass ceramic with perovskite titanate phases, SrTiO_3 [5–14] have been investigated. Thakur et al. [15] investigated the crystallization, microstructure and dielectric behavior of SrTiO_3 glass ceramic. SrTiO_3 could be crystallized as the major phase by addition of an appropriate concentration of K_2O and selected heat treatment schedules. In these glass ceramics addition of La_2O_3 enhances the crystallization of strontium titanate phase and increases the dielectric constant enormously. Recently Sahu et al. [16] explored the substitution of strontium for lead in lead titanate precipitated in borosilicate glass with suitable choice of composition and heat treatment schedule. The investigation on the phase development and microstructural characteristics of the glass ceramic in the system $[\text{SrOTiO}_2]-[2\text{SiO}_2\text{B}_2\text{O}_3]-[\text{K}_2\text{O}-\text{BaO}]$ showed that the solid solution of SrTiO_3 with

PbTiO₃ phases can be crystallized in borosilicate glasses [17].

The present paper reports our results of investigations carried out to crystallize perovskite lead strontium titanate/perovskite strontium titanate solid solution phase in a borosilicate glassy matrix in presence of La₂O₃. The donor doped La₂O₃ was chosen as an additive because it strongly affects the crystallization behavior and dielectric properties of the perovskite glass ceramic systems 65[(Pb_xSr_{1-x})TiO₃]-24[2SiO₂·B₂O₃]-5[BaO]-5[K₂O]-1[La₂O₃].

2. Experimental Procedure

The nomenclature, preparation, and characterization methods of glass and glass ceramic samples are described elaborately in part I of this paper entitled “Crystallization Behavior and Microstructural Analysis of Lead-Rich (Pb_xSr_{1-x})TiO₃ Glass Ceramics Containing 1 mole % La₂O₃”. A brief description is presented here. Sr-rich glass compositions in the system 65[(Pb_xSr_{1-x})OTiO₂]-24[2SiO₂·B₂O₃]-5[K₂O]-5[BaO]-1[La₂O₃] with varying lead-to-strontium ratios ($0.0 \leq x \leq 0.40$) have been prepared by melt quench method by melting the glass in the temperature range 1210–1330°C and annealing at 400°C for three hours in another furnace. All the glasses were characterized by DTA to determine glass transition and the crystallization temperatures (Table 1). On the basis of DTA results, various glass ceramic samples were prepared by heat treating the glasses in the temperature range 820–890°C. The different heat treatment schedules and nomenclature of glass ceramic samples are listed in Table 2. The nomenclature of various glasses and glass ceramic samples in the system is reported earlier [18]. The nomenclature of glass ceramic samples includes the code of their parent glass composition followed by heat treatment temperature then by 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 K α radiation. X-ray diffraction patterns were compared with standard d-values from JCPDS files for different constituting phases. The glass ceramic samples were ground and polished successively using SiC powders and diamond paste (1 μ m). The polished glass ceramic samples were etched for 1 minute with etchant (30% HNO₃ + 20% HF). Gold coatings were applied to the etched surface of various glass ceramic samples by the sputtering method in order to study the morphology of the different crystalline phases present by scanning electron microscopy (SEM).

3. Results

3.1. Differential Thermal Analysis (DTA). DTA patterns of various glass samples 4PL5B, 3PL5B, 2PL5B, 1PL5B, and STL5B are given in Figures 1 and 2.

All glasses show only a single exothermic peak in their DTA patterns. A shift in the base line is observed in the DTA plot, which depends on the composition of the glass. This shift in the base line shows a change in the specific heat of the glass, which is attributed to the glass transition temperature,

TABLE 1: Glass transition temperature, DTA peaks of various glass samples in system [(Pb_xSr_{1-x})·TiO₃]-[2SiO₂·B₂O₃]-[BaO·K₂O]-[La₂O₃].

Compositions (x)	Glass code	T _g (°C)	DTA Peaks T _c (°C)
0.4	4PL5B	600	820
0.3	3PL5B	635	871
0.2	2PL5B	635	865
0.1	1PL5B	660	878
0.0	STL5B	660	890

T_g. Glass transition and exothermic crystallization peak temperatures T_c for different glass samples are listed in Table 1. The crystallization peaks are differing with respect to their broadness and symmetry. The peak temperature increasing with increases the strontium content.

3.2. X-Ray Diffraction Analyses and Crystallization Behavior. On the basis of DTA results, various glass ceramic samples were prepared by heat treating the glasses in the temperature range 820–890°C for 3- and 6- hour heat treatment schedule. The different heat treatment schedules and nomenclature of glass ceramic samples are listed in Table 2. X-ray diffraction (XRD) patterns for various glass ceramic samples crystallized at different temperatures for 3 hours are shown in Figures 3 and 4, respectively. These glass ceramic samples show the formation of perovskite phase in major amount along with rutile (R) and/or strontium borate (SB) as minor phase. Minor rutile (R) phase is present in glass ceramic sample with $0.1 \leq x \leq 0.4$. SB phase appears only in the lead-free STL5B890T glass ceramic sample. Figure 5 shows XRD patterns for the glass ceramic samples 4PL5B820S 3PL5B871S and 2PL5B865. Perovskite lead strontium titanate crystallizes as the major phase. It is also observed that the secondary phase of rutile (trace amount) is also present in these glass ceramic samples. Figure 6 shows the XRD pattern for the glass ceramic samples 2PL5B878S and STL5B890S, respectively. These are strontium-rich compositions and major phase of perovskite strontium titanate with traces of rutile (TiO₂) and strontium borate (Sr₂B₂O₅) as secondary crystalline phases.

Excellent crystallization is observed in 4PL5B820S and STL5B890S glass ceramic samples. Both glass samples crystallize for six-hour heat treatment schedule. The excellent crystallization is attributed to the sufficient nucleation and growth for six-hour heat treatment schedule. It is too difficult to crystallize major phase of perovskite strontium titanate in glassy matrix. La₂O₃ plays an important role in crystallization of the glass samples and therefore acts as a nucleating agent. Heat treatment schedules, glass ceramic codes, and crystalline phases of different strontium rich glass ceramic samples are shown in Table 2.

The lattice parameters are much closer to standard lattice parameters [19]. The observed crystal structure is cubic, similar to SrTiO₃, over the entire composition range ($0.0 \leq x \leq 0.4$). Density of the glass and glass ceramic samples was determined by using Archimedes principle [20]. Density

FIGURE 1: DTA patterns of glasses (a) 4PL5B, $x = 0.4$, (b) 3PL5B, $x = 0.3$, and (c) 2PL5B, $x = 0.2$.

FIGURE 2: DTA pattern of glasses (a) 1PL5B, $x = 0.1$, and (b) STL5B, $x = 0$.

of the glass ceramic samples was determined using distilled water as the liquid medium.

The following weights were taken and used in the density calculations:

W_1 is the weight of empty specific gravity bottle (gram); W_2 is the weight of specific gravity bottle with sample (gram); W_3 is the weight of specific gravity bottle with

sample and distilled water (gram); W_4 is the weight of specific gravity bottle with distilled water (gram).

$$\text{Density} = \frac{W_2 - W_1}{W_4 - W_1 - (W_3 - W_2)}. \quad (1)$$

3.3. *Surface Morphological Analysis.* Figures 7(a), 7(b), and 7(c) illustrate the scanning electron micrographs for glass

FIGURE 3: X-ray diffraction patterns of glass ceramic samples (a) 4PL5B820S (b) 3PL5B871T and (c) 2PL5B865T.

FIGURE 4: X-ray diffraction patterns of different glass ceramic samples (a) 1PL5B878T and (b) STL5B890T.

FIGURE 5: X-ray diffraction patterns of glass ceramic samples (a) 4PL5B820S, (b) 3PL5B871S, and (c) 2PL5B870S.

TABLE 2: Heat treatment schedules, glass ceramic codes, and crystalline phases of different strontium rich glass ceramic samples in the system $[(\text{Pb}_x\text{Sr}_{1-x})\text{O} \cdot \text{TiO}_2] - [2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - [\text{K}_2\text{O}] - [\text{BaO}] - \text{La}_2\text{O}_3$.

Glass code	Glass ceramic code	Heat treatment schedules			Crystalline phases
		Heating rate ($^{\circ}\text{C}/\text{min}$)	Holding temp ($^{\circ}\text{C}$)	Holding time (hrs)	
4PL5B	4PL5B820T	5	840	3	P + R
	4PL5B820S	5	840	6	P
3PL5B	3PL5B871T	5	871	3	P + R
	3PL5B871S	5	871	6	P + R*
2PL5B	2PL5B870T	5	870	3	P + R + SB*
	2PL5B870S	5	870	6	P + R* + SB*
1PL5B	1PL5B878T	5	878	3	P + R
	1PL5B878S	5	878	6	P + R*
STL5B	STL5B890T	5	890	3	P + R* + SB*
	STL5B890S	5	890	6	P + R*

P: perovskite titanate, PT: PbTi_3O_7 , R: rutile (TiO_2), SB: strontium Borate. ($\text{Sr}_2\text{B}_2\text{O}_5$), *: trace amount.

FIGURE 6: X-ray diffraction patterns of glass ceramic samples (a) 1PL5B878S and (b) STL5B890S.

FIGURE 7: Scanning electron micrographs of glass ceramic samples (a) 4PL5B840T, (b) 3PL5B871T, and (c) 1PL5B878T.

ceramic samples (4PL5B840T, 3PL5B871T, and 1PL5B878T) obtained by crystallizing the glass samples 4PL5B, 3PL5B, and 1PL5B for 3 hours, respectively. Glass ceramic sample 4PL5B840T shows random growth of the crystallites of perovskite titanate as major phase, which are interconnected with one another. The secondary phase formation of the

rutile is also which is represented by the dark needle-like shapes in the micrographs. This secondary phase is also confirmed by XRD analysis.

Scanning electron micrographs of the glass ceramic sample 3PL5B871T are shown in Figure 7(b). The micrograph of this glass ceramic sample shows that the crystallites

FIGURE 8: Scanning electron micrographs of glass ceramic samples (a) 4PL5B840S, (b) 3PL5B871S, (c) 2PL5B870S, (d) 1PL5B878S, and (e) STL5B890S.

are fully developed in the glassy matrix. These crystallites are interconnected and randomly oriented in the glassy phase. The scanning electron microstructure of glass ceramic sample 1PL5B878T crystallized at 878°C for 3 hours is shown in Figure 7(c). This glass ceramic sample shows the square shape crystallites of the perovskite titanate phase, which are randomly distributed, in the residual glassy network. It is also observed that the large amount of residual glass remaining after crystallization is due to smaller soaking time. Figure 8 shows the scanning electron micrographs of the different glass ceramic samples 4PL5B840S, 3PL5B871S, 2PL5B870S, 1PL5B878S, and STL5B890S, respectively. All these glass ceramic samples are obtained by the crystallization of their respective glasses for 6-hour soaking time. The crystallization of 4PL5B840S is similar to the crystallization

of glass ceramic sample 3PL5B871S. It is also observed that the morphology of the crystallites of 4PL5B840S and 3PL5B871S was found to be the same. Only a small change is marked in secondary phase of rutile. Figure 8(c) shows the scanning electron micrograph for the glass ceramic sample 2PL5B870S, which is obtained by crystallization at 870°C for 6 hours corresponding to the exothermic peak in the DTA plot. Crystallite sizes of the order of a micron are formed which are uniformly distributed in the glassy matrix. Some of crystallites are aligned towards the right side and the rest are aligned towards the left side. Figure 8(e) depicts the scanning electron micrograph of the glass ceramic sample STL5B890S crystallized at 890°C for 6 hours. Well-interconnected crystallites of SrTiO_3 are randomly distributed in the glassy network. Needle-like fine

TABLE 3: Density of glass and glass ceramic, crystal structure, lattice parameters, and axial ratio of major crystalline phase in different strontium-rich glass ceramic samples in the system $[(\text{Pb}_x\text{Sr}_{1-x})\text{O} \cdot \text{TiO}_2] - [\text{2SiO}_2 \cdot \text{B}_2\text{O}_3] - [\text{K}_2\text{O}] - [\text{BaO}] - \text{La}_2\text{O}_3$.

Glass code	Density (gm/cc)	Glass ceramic	Density (gm/cc)	Crystal structure	Lattice parameters, a (Å)	(PbSr)TiO ₃ ceramic*, a (Å)
4PL5B	3.827	4PL5B820T	3.856	Cubic	3.915 ± 0.006	3.927
		4PL5B820S	4.109	Cubic	3.913 ± 0.002	
3PL5B	3.635	3PL5B871T	4.208	Cubic	3.911 ± 0.000	3.943
		3PL5B871S	3.256	Cubic	3.902 ± 0.003	
2PL5B	3.507	2PL5B870T	3.961	Cubic	3.899 ± 0.001	3.880
		2PL5B870S	3.671	Cubic	3.904 ± 0.005	
1PL5B	3.384	1PL5B878T	3.857	Cubic	3.904 ± 0.001	3.880
		1PL5B878S	3.426	Cubic	3.895 ± 0.002	
STL5B	3.212	STL5B890T	3.261	Cubic	3.897 ± 0.000	3.904
		STL5B890S	3.386	Cubic	3.901 ± 0.000	

* Reference [19].

The glass codes, density of glass and glass ceramics, crystal structure and lattice parameters are shown in Table 3.

crystallites present in trace amount are of rutile phase, which is confirmed by XRD studies. The crystallization temperature for this glass was found to be the maximum among all the glass compositions because of the absence of lead in this composition. The excellent crystallization was observed for this glass ceramic sample.

4. Discussion

The XRD data of the major perovskite phase in different glass ceramic samples for the Sr-rich glass ceramic compositions $x \leq 0.4$ were indexed on the basis of a cubic unit cell similar to SrTiO_3 . Values of lattice parameters “c” and “a” for perovskite phase in strontium-rich glass ceramic samples was determined from software “CEL” and are given in Table 3. Density of the glass and glass ceramic samples were determined using Archimedes principle [20, 21]. It is observed that the density of glasses systematically decreases with increasing the concentration of SrO (Table 3). Density of various glass samples lies between 3.212 and 3.287 gm/cc. It found to be larger for the glass sample 4PL5B while it is less for glass sample STL5B. Sahu [22] has reported that the strontium-rich glass ceramic samples without doping of La_2O_3 show that the phase separation is smaller and rate of crystallization is higher during heat treatment. Hence, high cooling rate is required during the quenching of the melt to get bulk transparent glasses. This might be one of the reasons for the difficulty of glass forming of these compositions. In the intermediate compositions, that is, when the $\text{Pb}^{2+}/\text{Sr}^{2+}$ ratio is 1 or nearly one, glass-in-glass phase separation takes place during the early stage of crystallization treatment. This also makes the glass formation easy with a relatively low cooling rate. But after doping the La_2O_3 in the strontium-rich glass ceramic samples the morphology of the crystallites is very dense and directionally distributed in the glassy matrix. The doping of La_2O_3 enhances the crystallization and retards the minor phase in these glass ceramic samples. Therefore, a very high value of dielectric constant and low loss are observed in these glass ceramic samples [18].

5. Conclusions

Very good transparent and bulky glasses were prepared in the strontium rich compositions. DTA patterns of strontium-rich glass samples show only a single exothermic peak. The addition of lanthanum oxide promotes the crystallization of major phase and retards the crystallization of minor phases. Therefore, very good crystallization is observed in these glass ceramic samples. X-ray diffraction patterns of strontium-rich glass ceramic compositions show presence of strontium titanate or perovskite lead strontium titanate as major phase with some secondary phase of rutile and strontium borate. Directional morphology of the perovskite fine crystallite growth was seen in the micrographs for these glass ceramic samples. XRD data of the major perovskite phase in strontium-rich glass ceramic samples show that the structure of crystalline phase is cubic, similar to SrTiO_3 , for $x \leq 0.4$.

Acknowledgments

The authors are deeply grateful to Defence Research Organization (India) for the financial support. Professor D. Pandey SMST, IT BHU., Varanasi, India, is also thanked for providing the XRD facilities.

References

- [1] H. E. Weaver, “Dielectric properties of single crystals of SrTiO_3 at low temperatures,” *Journal of Physics and Chemistry of Solids*, vol. 11, pp. 245–274, 1959.
- [2] W. N. Lawless, “Three application areas for strontium titanate glass-ceramics,” *Ferroelectrics*, vol. 3, pp. 287–293, 1972.
- [3] S. D. Stookey, “Method of making ceramics and product thereof,” United States Patent 2920971, 829, *British Patent*, 447, 1960.
- [4] C. B. King and S. D. Stookey, “United States Patent,” 2960801, 1960.
- [5] W. N. Lawless, “Cryogenic Engg. Cont. Boulder,” *Advances in Cryogenic Engineering*, Boulder, Colo, USA, 1970.

- [6] W. N. Lawless, "Capacitance thermometry characteristics of titanate glass-ceramics at low temperature," *Advances in Cryogenic Engineering*, vol. 16, pp. 261–267, 1971.
- [7] W. N. Lawless, "A low temperature glass-ceramic capacitance thermometer," *Review of Scientific Instruments*, vol. 42, pp. 561–566, 1972.
- [8] W. N. Lawless, *Private communication*, 1981.
- [9] S. L. Swartz, A. S. Bhalla, L. E. Cross, and W. N. Lawless, "Strontium titanate (SrTiO_3) glass ceramics part I. Crystallization and microstructure," *Journal of Materials Science*, vol. 23, pp. 3997–4003, 1988.
- [10] S. L. Swartz, A. S. Bhalla, L. E. Cross, and W. N. Lawless, " SrTiO_3 glass ceramics part II. Dielectric properties," *Journal of Materials Science*, vol. 23, no. 11, pp. 4004–4012, 1988.
- [11] R. K. Mandal, C. Durga Prasad, Om Parkash, and D. Kumar, "Dielectric behaviour of glasses and glass ceramics in the system $\text{BaO-PbO-TiO}_2\text{-B}_2\text{O}_3\text{-SiO}_2$," *Bulletin of Materials Science*, vol. 9, no. 4, pp. 255–262, 1987.
- [12] O. P. Thakur, D. Kumar, Om Parkash, and L. Pandey, "Dielectric and microstructural behaviour of strontium titanate borosilicate glass ceramic system," *Bulletin of Materials Science*, vol. 18, no. 5, pp. 577–585, 1995.
- [13] O. P. Thakur, D. Kumar, and Om Parkash, "Crystallization microstructure development and dielectric behavior of glass ceramics in the system $[(\text{SrO.TiO}_2)\text{-}(2\text{SiO}_2\text{.B}_2\text{O}_3)\text{-La}_2\text{O}_3]$," *Journal of Materials Science*, vol. 37, no. 12, pp. 2597–2606, 2002.
- [14] S. L. Swartz, E. Breval, and A. S. Bhalla, "Effect of nucleation on the crystallization and dielectric properties of strontium titanate glass-ceramics," *The American Ceramic Society Bulletin*, vol. 67, no. 4, pp. 763–770, 1988.
- [15] O. P. Thakur, D. Kumar, Om Parkash, and L. Pandey, "Effect of K_2O addition on crystallization and microstructural behavior of strontium titanate borosilicate glass ceramic system," *Materials Letters*, vol. 23, pp. 253–260, 1995.
- [16] A. K. Sahu, D. Kumar, and O. Parkash, "Crystallisation of lead strontium titanate perovskite phase in $[(\text{Pb}_{1-x}\text{Sr}_x)\text{O.TiO}_2]\text{-}[2\text{SiO}_2\text{.B}_2\text{O}_3]\text{-}[\text{K}_2\text{O}]$ glass ceramics," *The British Ceramic Transactions*, vol. 102, no. 4, pp. 139–147, 2003.
- [17] A. K. Sahu, D. Kumar, O. Parkash, and C. Prakash, "Effect of $\text{K}_2\text{O/BaO}$ ratio on crystallization, microstructure and dielectric properties of strontium titanate borosilicate glass ceramics," *Ceramics International*, vol. 30, no. 3, pp. 477–483, 2004.
- [18] D. Kumar, C. R. Gautam, and O. Parkash, "Preparation and dielectric characterization of ferroelectric $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ glass ceramics doped with La_2O_3 ," *Applied Physics Letters*, vol. 89, no. 11, pp. 112908–112911, 2006.
- [19] S. Subrahmanyam and E. Goo, "Nucleation of the ferroelectric phase in the $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ system," *Acta Materialia*, vol. 46, no. 3, pp. 817–822, 1998.
- [20] V. A. Hiremath, S. K. Date, and S. M. Kulkarni, "A new combustion route to $\gamma\text{-Fe}_2\text{O}_3$ synthesis," *Bulletin of Materials Science*, vol. 24, no. 6, pp. 617–621, 2001.
- [21] C. R. Gautam, D. Kumar, and Om Parkash, "Dielectric and impedance spectroscopic studies of $(\text{Sr}_{1-x}\text{Pb}_x)\text{TiO}_3$ glass ceramics with addition of Nb_2O_5 ," *Bulletin of Material Science*. In press.
- [22] A. K. Sahu, *Preparation microsture and dielectric properties of lead strontium titanate borosilicate glass ceramic system*, Ph.D. thesis, Institute of Technology, Banaras Hindu University, India, 2002.