

Effect of K₂O/BaO ratio on crystallization, microstructure and dielectric properties of strontium titanate borosilicate glass ceramics

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Abstract

Crystallization, microstructural and dielectric behaviour of glass ceramics in the system [SrO.TiO₂]-[2SiO₂.B₂O₃]-[(1-*y*)K₂O.*y*BaO] with varying *y*, have been investigated. K₂O to BaO ratio has been found to play an important role in glass forming and crystallization of strontium titanate phase. It has been observed that optimum amounts of K₂O and BaO are required for easy glass formation and crystallization of strontium titanate phase.

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1. Introduction

Crystallization, microstructure and dielectric properties of strontium titanate glass ceramics have been widely investigated because of their technological importance [1–13]. These materials have been used in many applications including cryogenic capacitive temperature sensors [1–5]. The crystallization of SrTiO₃ in aluminosilicate glassy matrix is complex. High temperature is required for melting of glass compositions and crystallization of glass [8,9]. Minor phases such as various forms of TiO₂ and SrAl₂Si₂O₈ were also reported to be present in glass ceramics in substantial amount along with SrTiO₃ [8,9]. When aluminosilicate glassy matrix is replaced by borosilicate matrix, the melting temperature of glasses decreases. However, strontium borate (Sr₂B₂O₅) phase crystallized as the major phase followed by TiO₂ (rutile) and Sr₃Ti₂O₇. SrTiO₃ did not crystallize [14,15]. Strontium titanate phase has been crystallized in the borosilicate glass ceramic system only with proper addition of modifier alkali oxide K₂O and suitable heat treatment schedule [12]. Crystallization of SrTiO₃ in these glass ceramics is indirect; first Sr₂B₂O₅ phase forms which on further heating reacts with TiO₂

rich glass and forms SrTiO₃. These glass ceramics also suffer from some disadvantages. High cooling rate during quenching of the melt is required to have completely amorphous and transparent glasses. Presence of K₂O increases their dielectric loss. So there is a need to improve the glass formability as well as improvement in other properties such as tendency for crystallization of SrTiO₃ and dielectric properties of resulting glass ceramic samples.

Alkali oxide K₂O has been used as an additive for the successful crystallization of SrTiO₃ phase in the borosilicate glassy matrix [11,12]. It is known that K₂O introduces a lot of non-bridging oxygen ions in the glass structure which reduces the viscosity of the melt and renders difficulty in preparing thick transparent glasses. In the present investigation K₂O has been replaced partially or fully by alkaline earth oxide BaO based on the results of earlier investigations [16] and the effect of K₂O/BaO ratio on glass formability, phase and microstructure development and dielectric properties of strontium titanate borosilicate glass ceramics has been studied.

2. Experimental procedure

Glasses in the system [SrO.TiO₂]-[2SiO₂.B₂O₃]-[(1-*y*)K₂O.*y*BaO] were prepared with *y*=0.3, 0.5, 0.7 and 1.0 keeping the amount of other constituents the same for all compositions. Well mixed, dried powders containing appropriate amount of reagent grade SrCO₃,

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TiO₂, SiO₂, H₃BO₃, K₂CO₃ and BaCO₃ were melted in pure alumina crucibles for an hour in the temperature range 1250–1300 °C under normal atmospheric conditions. The melt was quenched by pouring it into an aluminum mould and pressing with a thick aluminum plate. The glasses were then annealed at 450 °C for 3 h.

Differential thermal analysis (DTA) of powdered glass samples was done using a Netzsch Simultaneous Thermal Analyzer 409 from room temperature to 1000 °C employing a heating rate of 10 °C/min. From the DTA curve, glass transition temperature and crystallization temperatures for possible crystalline phases were determined. Each glass was subjected to similar single stage heat treatment schedules. The glasses were heat treated at two different temperatures i.e. 850 and 900 °C in air for 3 h to get glass ceramic samples.

Phases were identified using powder X-ray diffraction (XRD) analysis. Diffraction patterns were recorded employing a Rich-Seifert ID 3000 diffractometer using CuK_α radiation. The crystalline phases in each glass ceramic sample were identified by comparing its XRD patterns with standard powder diffraction patterns of various crystalline phases which might have formed from different constituent oxides of the glass. The glass ceramic samples were polished, etched with 30% HNO₃ + 20% HF solution for 60 s and then coated with a thin film of gold for scanning electron microscopy (SEM) observations (Model Jeol 840A). Density of glass and glass ceramic samples was determined using a liquid displacement method.

The dielectric behaviour of a few selected glass ceramic samples was studied by recording capacitance and dissipation factor as a function of temperature in the temperature range 27–250 °C at a few selected frequencies.

3. Results and discussion

Fig. 1 shows DTA traces for glasses containing various amounts of K₂O and/or BaO. The glass transition temperature and crystallization peak temperatures of different glasses are listed in Table 1. The glass transition temperature of these lies around 670–690 °C and hence not much variation in glass transition temperature was found with varying amounts of K₂O and BaO. Two distinct exothermic peaks (T_{C1} and T_{C2}) were observed for the glass 7K3B at 760 and 850 °C. Only one exothermic peak occurs for the glasses 5K5B, 3K7B and 10B at 900, 860 and 900 °C respectively. Although the nature of all exothermic peaks appear to be similar at first sight, a close examination reveals that they differ in respect of broadness and symmetry. The single exothermic peak seems to be a combination of two peaks. It seems that both T_{C1} and T_{C2} change with changing K₂O:BaO ratio in the glass. The temperature of the first

exothermic peak, T_{C1} increases with increasing BaO content, whereas the second exothermic peak temperature T_{C2} does not change with changing BaO content. It leads to overlapping of both the peaks in the glasses 2, 3 and 4. The first exothermic peak probably represented a phase separation process as reported in the literature [17]. This fact is supported by microstructural studies. The second exothermic peak was caused by crystallization of SrTiO₃ which was confirmed by XRD analysis.

Table 1

DTA peaks of different glass samples in the system [SrO.TiO₂]–[2SiO₂.B₂O₃]–[(1–y)K₂O.yBaO]

Glass no.	K ₂ O:BaO [(1–y):y]	Glass code	DTA peaks (°C)		
			T_g	T_{C1}	T_{C2}
1	7:3	7K3B	680	760	850
2	5:5	5K5B	690	–	900
3	3:7	3K7B	670	–	860
4	0:10	10B	680	–	900

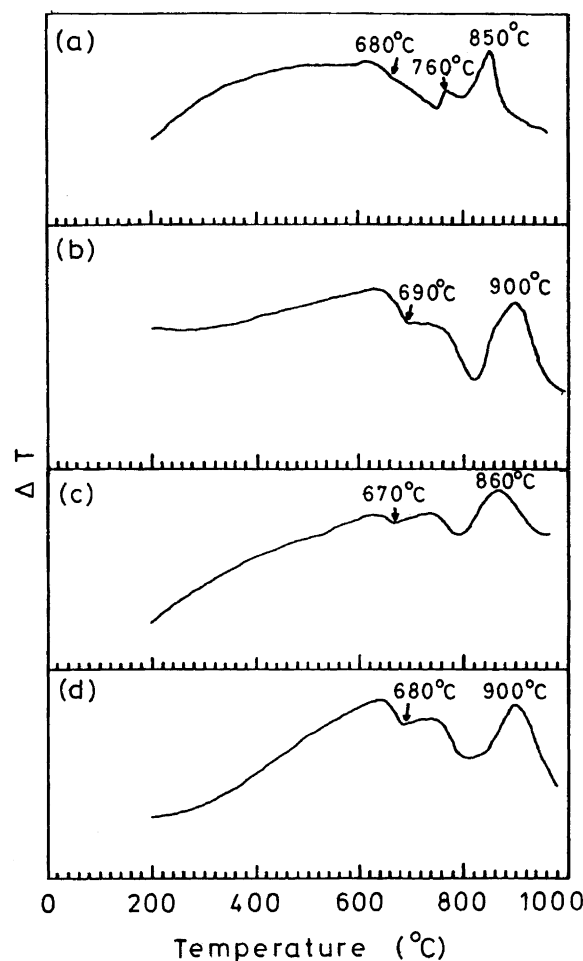


Fig. 1. DTA patterns of glasses, (a) 7K3B, (b) 5K5B, (c) 3K7B and (d) 10B.

Representative XRD patterns of glass ceramic samples obtained by heat-treating the glasses 7K3B and 5K5B at different temperatures are shown in Figs. 2 and 3. All the glass ceramic samples were found to have strontium titanate as the major phase (Table 2). Rutile is the minor phase observed in some of the glass ceramic samples (Table 2). A few unidentified lines of very low intensity are also observed in XRD patterns of most of

the glass ceramic samples. The glass 5K5B was also heat treated at 900 °C for 6 and 12 h. No change was observed in terms of phase constitution in the resulting glass ceramic samples 5K5B900S and 5K5B900T (Fig. 4). The lattice parameter of the SrTiO_3 phase developed in different glass ceramic samples is found to be in the range 3.898–3.902 Å and did not vary much with the crystallization temperature and holding time at

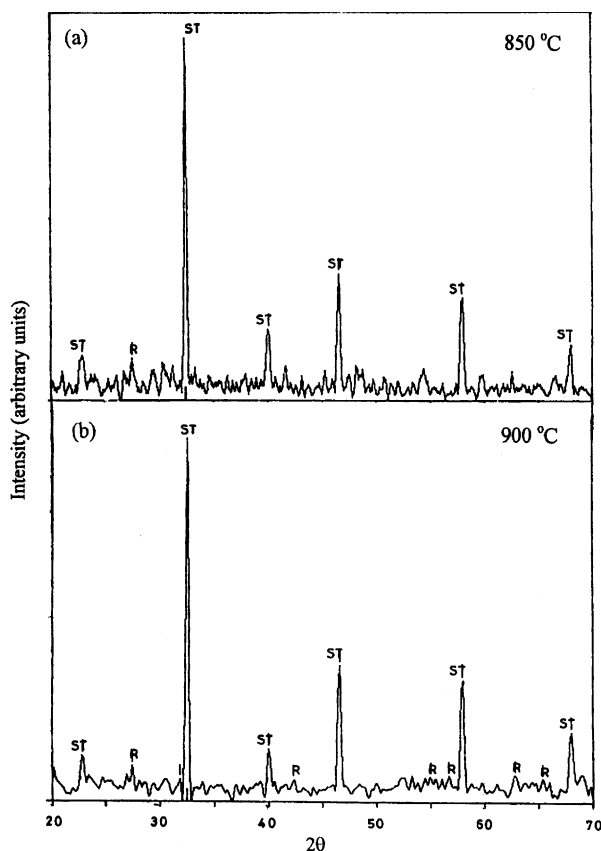


Fig. 2. XRD patterns of glass ceramic samples: (a) 7K3B850 and (b) 7K3B900.

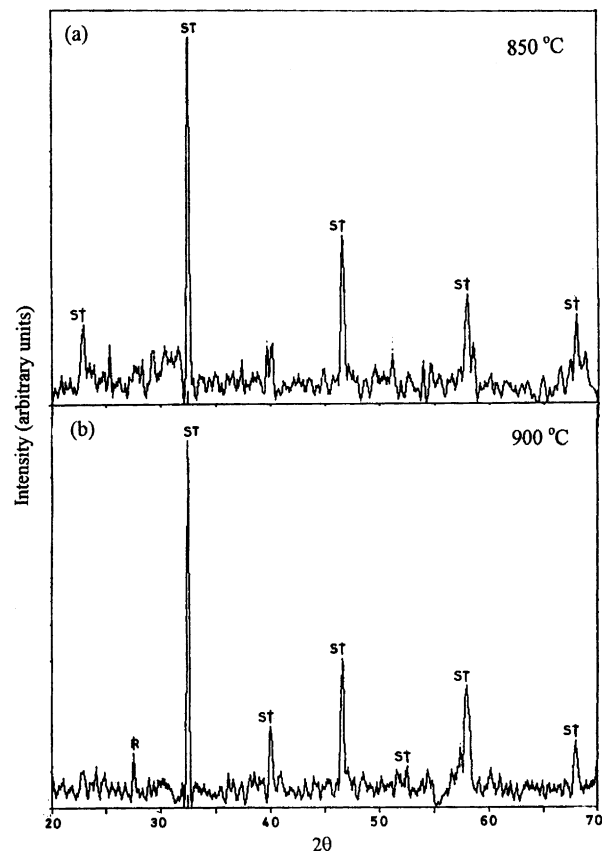


Fig. 3. XRD patterns of glass ceramic samples: (a) 5K5B850 and (b) 5K5B900.

Table 2

Heat treatment schedules, crystalline phases and lattice parameter of SrTiO_3 phase of different glass ceramic samples

Glass ceramic sample	Heat treatment schedules			Crystalline phase(s)	Lattice parameter, a (Å) of SrTiO_3 phase
	Heating rate (°C/min)	Holding temperature (°C)	Holding time (h)		
7K3B850	5	850	3	ST + R ^a + U ^a	3.901 ± 0.008
7K3B900	5	900	3	ST + R ^a + U ^a	3.902 ± 0.003
5K5B850	5	850	3	ST + U ^a	3.898 ± 0.005
5K5B900	5	900	3	ST + R ^a + U ^a	3.900 ± 0.001
5K5B900S	5	900	6	ST + R ^a + U ^a	3.903 ± 0.001
5K5B900T	5	900	12	ST + R ^a	3.887 ± 0.003
3K7B850	5	850	3	ST + U ^a	3.898 ± 0.001
3K7B900	5	900	3	ST + R ^a	3.901 ± 0.001
10B850	5	850	3	ST + U ^a	3.899 ± 0.001
10B850	5	900	3	ST + R ^a	3.903 ± 0.001

ST = SrTiO_3 , R = TiO_2 (rutile), U = unidentified phases(s).

^a Trace amount.

crystallization temperature. It was also not affected by K_2O to BaO ratio.

Figs. 5–8 show scanning electron micrographs of some representative glass ceramic samples. Almost similar microstructures are observed for different glass ceramic samples.

Micrometer or sub-micrometer grains of perovskite $SrTiO_3$ form during crystallization. In most of the cases

these grains show agglomeration and dense microstructure regions with some glassy region in-between. This type of microstructure is normally observed for those glasses, which show initial phase separation before crystallization [12]. Two regions show different tendency for crystallization during heat treatment. The region with higher tendency of crystallization occupies a greater volume with respect to the region, which do not crystallize and remain glassy.

When the glass 7K3B was heat treated at the temperature $850^\circ C$ for 3 h corresponding to the exothermic peak in the DTA plot, micron size ($1\text{--}2\text{ }\mu m$) crystallites formed which are randomly distributed in the glassy matrix (Fig. 5a). When the crystallization temperature was increased to $900^\circ C$ (a slightly higher temperature than the DTA peak), submicrometer size crystallites are found to be uniformly distributed in the glassy matrix (Fig. 5b). Scanning electron micrographs of the glass ceramic sample 5K5B850 (Fig. 6a) indicate that glass-in-glass phase separation might have taken place during the early stage of crystallization of the glass at $850^\circ C$ for 3 h. However, the crystallites are not fully developed in the glass region containing the oxides of perovskite titanate phase. Insufficient growth of crystallites may be due to the fact that the temperature of crystallization is $50^\circ C$ less than the exothermic peak observed in the DTA pattern ($900^\circ C$) of the glass. When the glass was heat treated at $900^\circ C$ for 3 h, fine crystallites of sub-micron size uniformly distributed in regions separated by narrow channels of residual glass were observed (Fig. 6b). In the 5K5B glass when K_2O and BaO are present in equal amount, crystallization treatment at its DTA peak temperature results in a microstructure consisting of fine crystallites uniformly distributed in the glassy matrix. This type of microstructure (5K5B900) is desired for reproducibility and reliability of performance of glass ceramic products. A scanning electron micrograph of glass ceramic sample 3K7B900 (Fig. 7) shows fine crystallites of $SrTiO_3$ phase uniformly

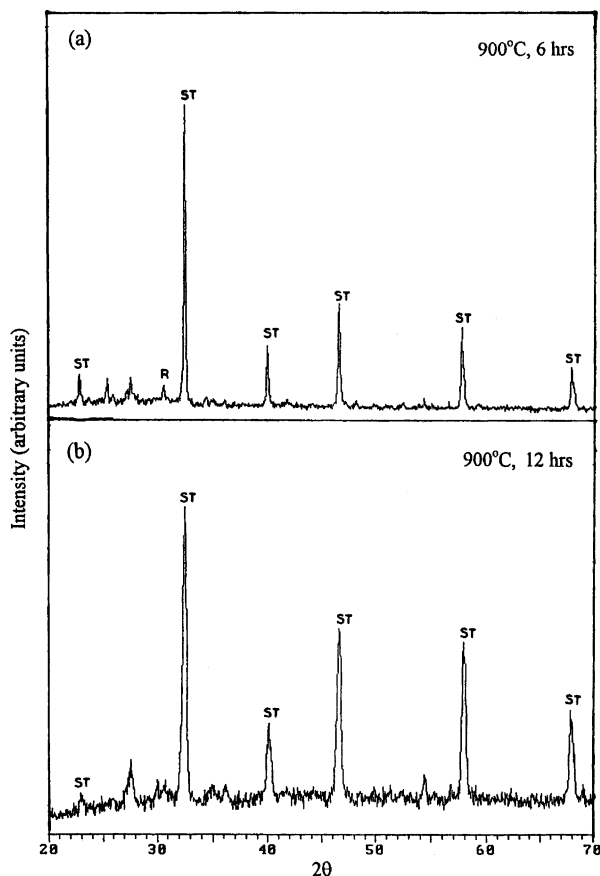


Fig. 4. XRD patterns of glass ceramic samples: (a) 5K5B900S and (b) 5K5B900T.

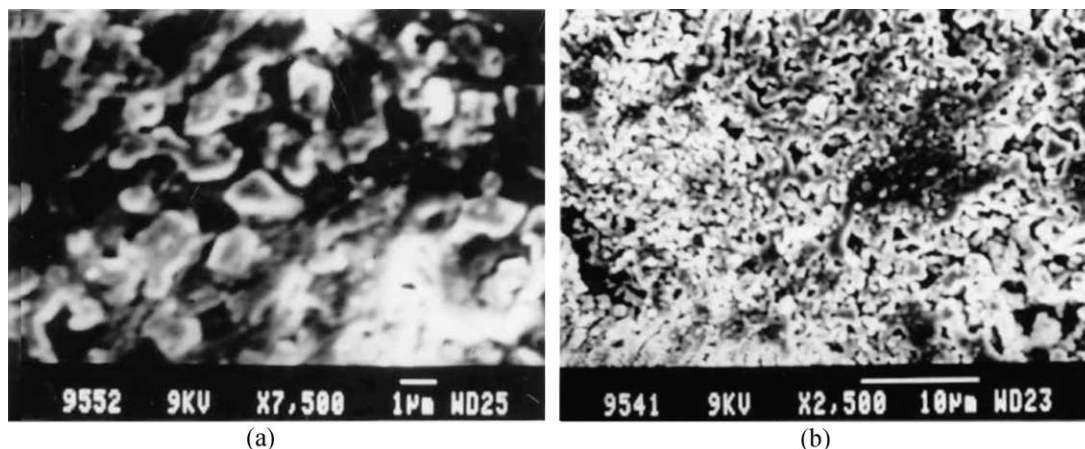


Fig. 5. Scanning electron micrographs of glass ceramic samples: (a) 7K3B850 and (b) 7K3B900.

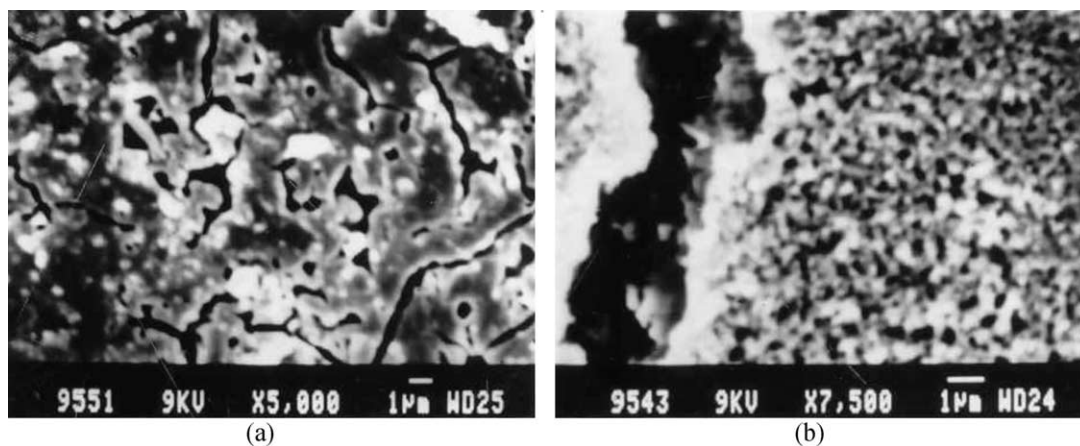


Fig. 6. Scanning electron micrographs of glass ceramic samples: (a) 5K5B850 and (b) 5K5B900.

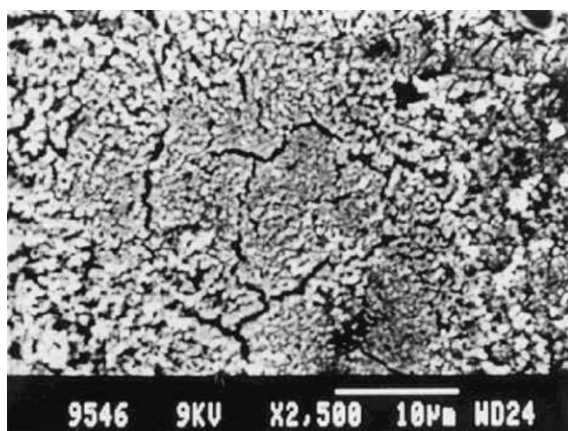


Fig. 7. Scanning electron micrograph of glass ceramic sample 3K7B900.

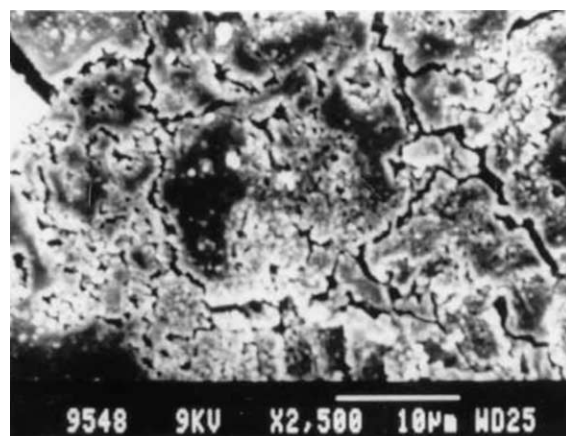


Fig. 8. Scanning electron micrograph of glass ceramic sample 10B900.

distributed throughout the glassy matrix. The microstructure of the glass ceramic 10B900 (Fig. 8) is similar to that of the glass ceramic 7K3B900.

The density of glass ceramic is an additive function of the densities of constituent crystal and glass phases present. Table 3 lists the density of glass and glass ceramic samples studied. The density of glass was found to increase with increasing concentration of BaO as expected with the exception of the SK5B sample. The initial decrease in density of glass may be due to change in structure of glass with initial BaO addition. The later increase in density may be due to heavier nature of Ba^{2+} ions in comparison to K^{+} ions. For glasses 7K3B and 5K5B the crystallization is accompanied by an increase in density (i.e. the density of glass ceramic sample is higher than that of glass) whereas the reverse trend is observed for the glass 10B. No such change in density was observed in glass to glass ceramic transformation for the glass 3K7B. The density of glass ceramics was not affected by crystallization temperature except for the glass ceramics obtained from the glass

Table 3
Bulk density (gm/cc) of glass and glass ceramic samples

Sample code	Glass	Glass ceramics	
		850 °C	900 °C
7K3B	3.43	3.61	3.58
5K5B	3.34	3.43	3.41
3K7B	3.62	3.61	3.63
10B	3.91	3.42	3.61

10B. There is a significant difference in densities of the glass 10 B and the resulting glass ceramics.

No change (3K7B) or a small change (SK5B) in density was observed in glass to glass ceramic transformation for the glasses 5K5B and 3K7B. It has been observed that the presence of BaO in the glass leads to easy glass formation whereas K_2O favours crystallization of the perovskite phase. So an optimum amount of BaO and K_2O should be present in the glass for easy glass formation and crystallization of the perovskite

phase without any hassle. So the glass 5K5B is preferred over 3K7B.

Variation of dielectric constant and dissipation factor with temperature at a few selected frequencies (1, 10, 100 kHz and 1 MHz) for glass ceramic samples heat treated at 900 °C have been studied. Fig. 9 depicts the dielectric behaviour of the glass ceramic sample 7K3B900. This behaviour is typical of all strontium titanate glass ceramics. The dielectric constant ϵ' and dissipation factor D for all the glass ceramic samples lies in the range 20–60 and <0.1 respectively in the tem-

perature range 27–250 °C. The dielectric constant decreases as the temperature is raised from room temperature (27 °C) to 250 °C. The dielectric loss is small and changes very little below a particular temperature and thereafter rises rapidly. The rise is steep at 1 kHz. This may be due to the movement of alkali and alkaline earth ions (present in the residual glass) at higher temperature. A similar trend in dielectric behaviour is observed for glass ceramic samples 5K5B900, 3K7B900 and 10B900 crystallized at 900 °C. To study the effect of holding time on dielectric behaviour, the glass 5K5B was also heat treated at 900 °C for 6 and 12 h and thus glass ceramics 5K5B900S and 5K5B900T are obtained. The variation of dielectric constant and dissipation factor was found to follow the same trend as that of the glass ceramic 5P5K900. The value of dielectric constant is found to increase a little (Table 4) otherwise the dielectric behaviour is not affected by these extended holding times at the crystallization temperature. The value of dielectric constant ϵ' , dissipation factor D at 1 MHz at room temperature and temperature coefficient of dielectric constant (T_{ce}) of all the glass ceramic samples in the temperature range 27–250 °C are given in Table 4. All these glass ceramic samples have similar crystalline phase constitution containing mainly SrTiO₃ and traces of TiO₂ (rutile) and thus have similar dielectric behaviour. The value of dielectric constant is not significantly affected by the K₂O to BaO ratio. All the glass ceramic samples were found to show negative temperature coefficient of dielectric constant. Negative value of T_{ce} is due to the crystallization of SrTiO₃ phase in major amount. The negative temperature coefficient of dielectric constant supplements the XRD results i.e. the presence of SrTiO₃ as the major phase. The value of T_{ce} depends on the compensation between negative temperature coefficient of SrTiO₃ and the positive temperature coefficient of glass. Its value depends on the relative amount of glassy and SrTiO₃ phase. T_{ce} value of all the glass ceramic samples also does not vary much with the initial composition of glass (Table 4) which indicates that the degree of crystallization in these glass ceramics is also not dependent on K₂O/BaO ratio.

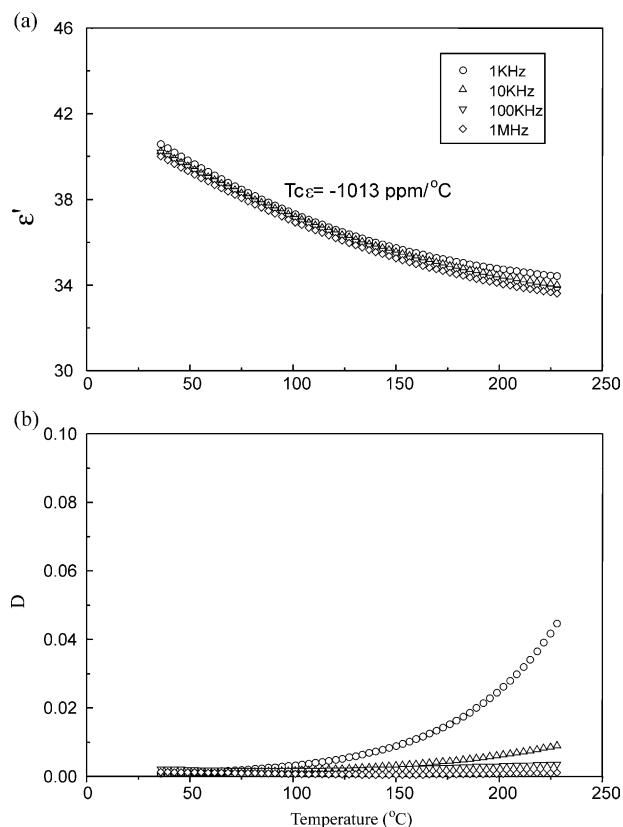


Fig. 9. Variation of (a) dielectric constant, ϵ' and (b) dissipation factor, D with temperature at different frequencies for the glass ceramic sample 7K3B900.

Table 4

Crystalline phases, dielectric constant ϵ' , dissipation factor D and temperature coefficient of dielectric constant (T_{ce}) of some representative glass ceramic samples

Glass ceramic sample no.	Crystalline phase(s)	ϵ' at 1 MHz at room temperature (27 °C)	D at 1 MHz at room temperature (27 °C)	T_{ce} at 1 MHz (ppm/°C) (RT–250 °C)
7K3B900	ST + R ^a + U ^a	40	0.0012	–1013
5K5B900	ST + R ^a + U ^a	27	0.0018	–1023
5K5B900S	ST + R ^a + U ^a	37	0.0015	–876
5K5B900T	ST + R ^a	38	0.0026	–792
3K7B900	ST + R ^a	53	0.0019	–1283
10B900	ST + R ^a	50	0.0006	–1232

ST = SrTiO₃, R = TiO₂ (rutile), U = unidentified phases(s).

4. Conclusions

In $[\text{SrO} \cdot \text{TiO}_2] - [2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - [(1-y)\text{K}_2\text{O} \cdot y\text{BaO}]$ glass ceramic system (0–1), SrTiO_3 crystallized as the major phase. Trace amount of rutile was also found in some of the glass ceramic samples. It has been observed that presence of BaO favours glass formation whereas K_2O favours crystallization of perovskite phase. The lattice parameter of SrTiO_3 phase was found to be independent of crystallization temperature and also K_2O to BaO ratio. Fine crystallites uniformly distributed in the glassy matrix is the characteristic feature of the most of the glass ceramic samples. The temperature coefficient of dielectric constant (T_{ce}) was found to be negative for all the glass ceramic samples studied which is also an evidence for crystallization of SrTiO_3 as the major phase.

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