Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 1261–1265
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effects of PbO and SrO contents on crystallization and dielectric properties of PbO–SrO–Na_2O–Nb_2O_5–SiO_2 glass–ceramics system

W. Liu, Ch.H. Mao *, G.X. Dong, J. Du

Advanced Electronic Materials Institute, General Research Institute for Nonferrous Metals, Beijing 100088, PR China

Received 10 March 2008; received in revised form 25 March 2008; accepted 17 June 2008
Available online 16 July 2008

Abstract

PbO–SrO–Na_2O–Nb_2O_5–SiO_2 glass–ceramics were prepared via roll-quenching followed by controlled crystallization from 700 °C to 900 °C. The effects of PbO and SrO contents on crystallization and dielectric properties were investigated. The results show that $Pb_2Nb_2O_7$, $Sr_2Nb_2O_7$ and their solid solutions crystallize at 700 °C, $NaNbO_3$ is the primary phase at 800 °C, $Pb_2Nb_2O_7$ disappears and $PbNb_2O_6$ forms at 900 °C. The dielectric properties of the glass–ceramics formed through controlled crystallization has a strong dependence on the phase compositions that were developed during heat treatment. The highest dielectric constants (∼600) are found in samples with 6.0 mol% SrO annealed at 900 °C for 3 h. The dielectric–temperature characteristics of the samples show stability over the range from −60 °C to 180 °C, except the sample without SrO heated at 900 °C.

Keywords: B. X-ray diffraction; C. Dielectric properties; D. Glass–ceramics; Niobates

1. Introduction

Glass–ceramics are composites that are prepared through controlled crystallization of appropriate glass precursors [1,2]. Due to the excellent adjustability of composition and microstructure, glass–ceramics, containing high dielectric constant ceramic phases dispersed within glass phase, are strong candidates for the application in high energy storage density capacitors [3].

In contrast to conventional sintering techniques, controlled crystallization offers a tractable process to synthesize pore-free glass–ceramics [4], which begins with melt-casting of glass and then heat-treating of the as-quenched glass. High dielectric constant crystalline phases are precipitated from the glass matrix during heat treatments. The grain size and content of dielectric phases can be controlled through changing relative content of glass former and metal oxides before melt-casting. Consequently, the dielectric constant and breakdown strength of glass–ceramics are potentially very high [5], which will significantly improve energy storage density.

Studies on glass–ceramics for capacitor applications through controlled crystallization have been carried out by a number of researchers. In 2003, Pennsylvania State University and the Naval Research Laboratory (NRL) completed a feasibility study that had investigated the crystallization and dielectric behaviors of glass–ceramics in PbO–BaO–SrO–Nb_2O_5–B_2O_3–SiO_2 ($Sr_{0.33}Ba_{0.67}Nb_2O_6$ phase) and Na_2O–PbO–Nb_2O_5–SiO_2 ($Pb_2Nb_2O_7$, $NaNbO_3$ and $PbNb_2O_6$ phases) systems [6]. However, the volatilization of PbO during the preparation of glass precursor not only pollutes the environment, but also jeopardizes human lives. Therefore, in order to reduce the content of PbO, we substituted SrO for PbO to synthesize PbO–SrO–Na_2O–Nb_2O_5–SiO_2 glass–ceramics. The crystallization and dielectric characteristics of this system were investigated.

2. Experimental procedure

The compositions of the glass–ceramics were selected according to Table 1, by reducing PbO content from 10 mol% to 0 mol% and meanwhile, increasing SrO content from 0 mol% to 10 mol%.

The powder mixtures were milled for 7 h in a polyethylene bottle with alcohol for homogenous mixing. The slurry was then dried and the powder melted at 1400 °C in a platinum

* Corresponding author. Tel.: +86 10 8224 1247; fax: +86 10 8224 1246.
E-mail address: mao@grinm.com (C.H. Mao).

0272-8842/$34.00
doi:10.1016/j.ceramint.2008.06.002

Table 1
Composition of PbO–SrO–Na_2O–Nb_2O_5–SiO_2 glass–ceramics

Designation	SiO_2 (mol%)	Nb_2O_5 (mol%)	Na_2O (mol%)	PbO (mol%)	SrO (mol%)
S0	30	20	10	10	0
S2	30	20	10	8	2
S4	30	20	10	6	4
S6	30	20	10	4	6
S8	30	20	10	2	8
S10	30	20	10	0	10

crucible for 2 h. The melt was then quenched by a steel mold that had been preheated to 500 °C to form glass, followed by annealing at 500 °C for 2 h to remove residual stresses. Glasses from different batches were then ground into fine powder for X-ray diffraction (XRD) and differential thermal analysis (DTA) measurements. The crystallization processes were performed at temperatures of 700 °C, 800 °C and 900 °C for 3 h.

XRD investigations were performed by X' Pert PRO MPD diffractmeter (PANalytical, Netherlands) with Cu Kα radiation to verify the crystalline phases.

The microstructure of the crystallized samples was analyzed by Hitachi.S-4800 field-emission scanning electron microscope (SEM). The average grain size was determined by the linear intercept method from the SEM image of the surfaces of chemically etched samples.

The samples were ground down to a thickness of ∼500 μm using 400 and 600 grit SiC slurry to create flat parallel faces, which were then gold coated for capacitance measurements. The dielectric constants were measured by HP 41924A LF impedance analyzer at 100 kHz from −60 °C to 180 °C.

3. Results and discussion

3.1. Crystallization

Heat treatment protocols for the as-quenched glass are guided by DTA analysis. Fig. 1 shows the DTA curves of glass samples with varying contents of SrO. Three exothermic peaks are observed in S0 curve, and the other samples show only two peaks. With increasing SrO content, the first exotherm peak changes from 660 °C to 768 °C, while the second peak temperature shifts from 879 °C to 844 °C. The appearance of these exothermic peaks is associated with the crystallization of different phases from the glass matrix. Therefore, three temperatures are chosen to investigate the crystallization behavior of the glass–ceramics.

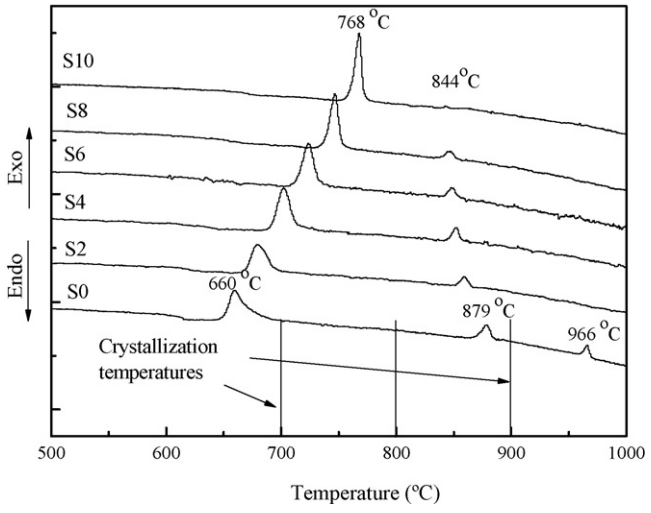

Fig. 1. DTA curves of glass samples with various SrO contents.

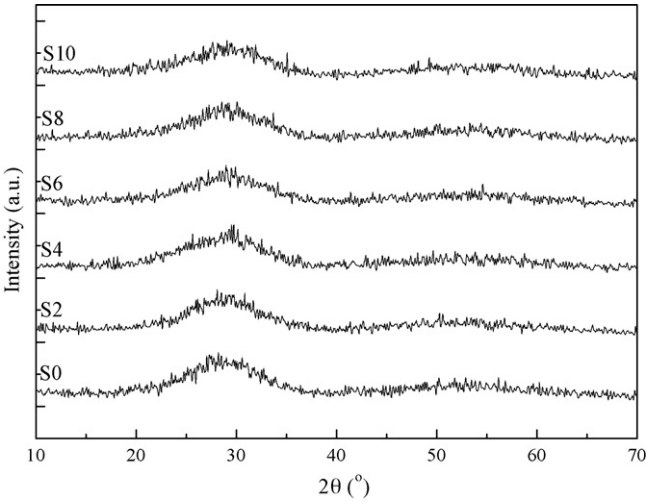

Fig. 2. XRD patterns of the as-quenched glass.

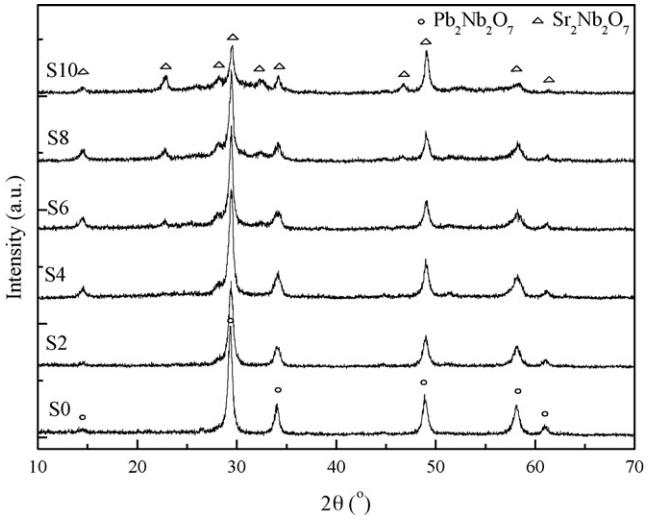

Fig. 3. XRD patterns of glass–ceramics with various contents of SrO annealed at 700 °C.

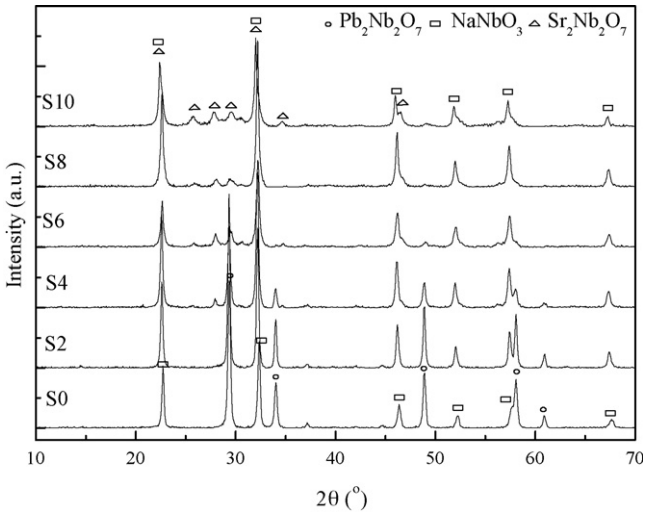

Fig. 4. XRD patterns of glass–ceramics with various contents of SrO annealed at 800 °C.

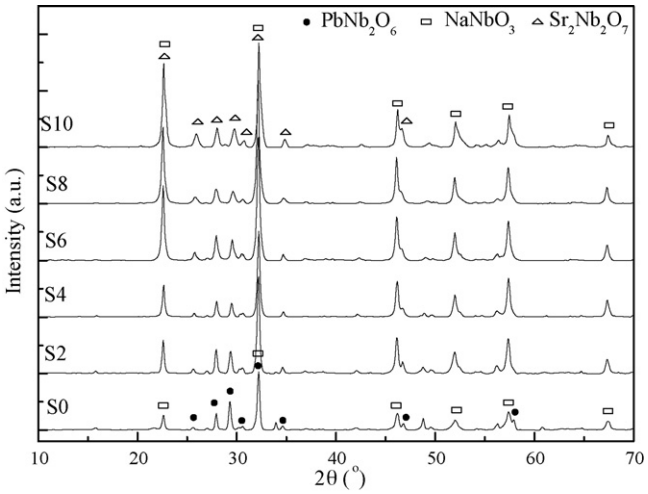

Fig. 5. XRD patterns of glass–ceramics with various contents of SrO annealed at 900 °C.

A typical amorphous feature of the as-quenched glass with a broad X-ray diffraction peak is shown in Fig. 2, which indicated a fully glassy structure after melt-casting. Figs. 3–5 show the XRD analysis of the samples crystallized at three temperatures. When the glass is heat-treated at 700 °C (Fig. 3), $Pb_2Nb_2O_7$, which has rhombohedra pyrochlore structure [7,8] appears in the sample without SrO (S0), and $Sr_2Nb_2O_7$ with orthorhombic structure shows in the sample without PbO (S10). In the other samples (S2, S4, S6 and S8), according to Satoshi Nanamatsu's research [9], we suppose that $Pb_2Nb_2O_7$ and $Sr_2Nb_2O_7$ form solid solutions, which are consistent with the DTA exothermic peaks at 660–760 °C (Fig. 1). For the samples annealed at 800 °C (Fig. 4), a large amount of $NaNbO_3$ crystallizes from the glass precursor, which is consistent with the second exothermal peaks in the DTA curve. For the samples with high Pb content (S0, S2 and S4), the crystalline phases mainly show rhombohedra structure ($Pb_2Nb_2O_7$), and with increasing SrO content (S6, S8 and S10), the phases mainly show orthorhombic

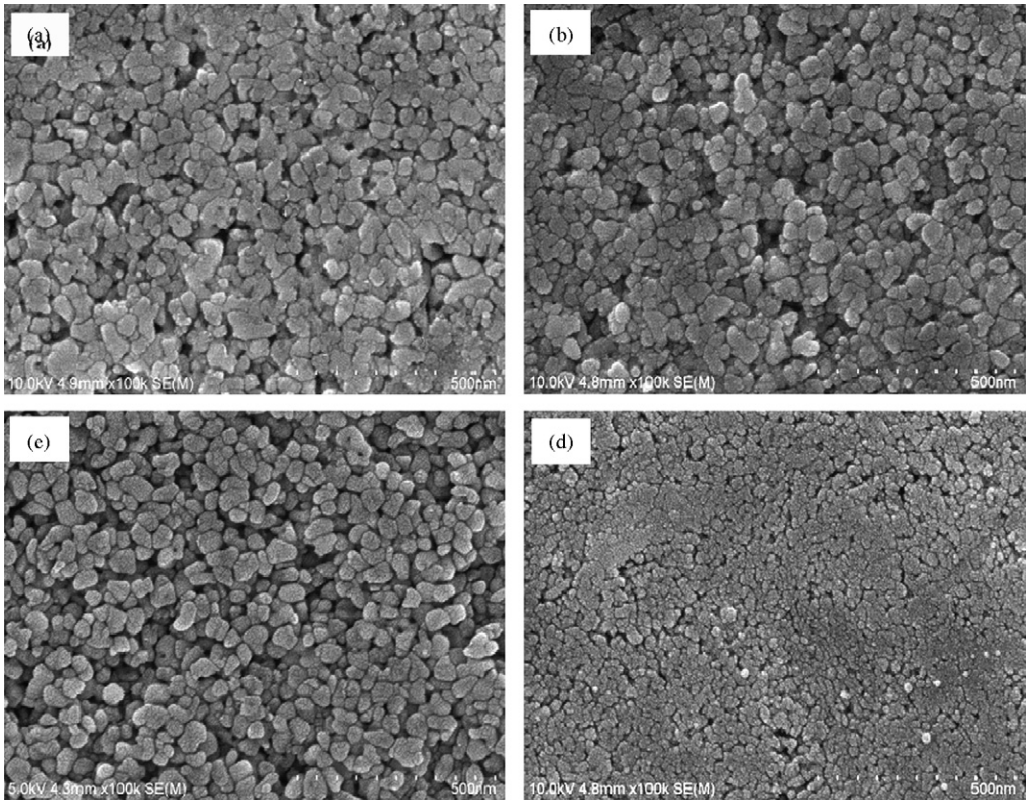

Fig. 6. SEM images of glass–ceramics crystallized at 900 °C with SrO content: (a) 0 mol%; (b) 2 mol%; (c) 6 mol%; (d) 10 mol%.

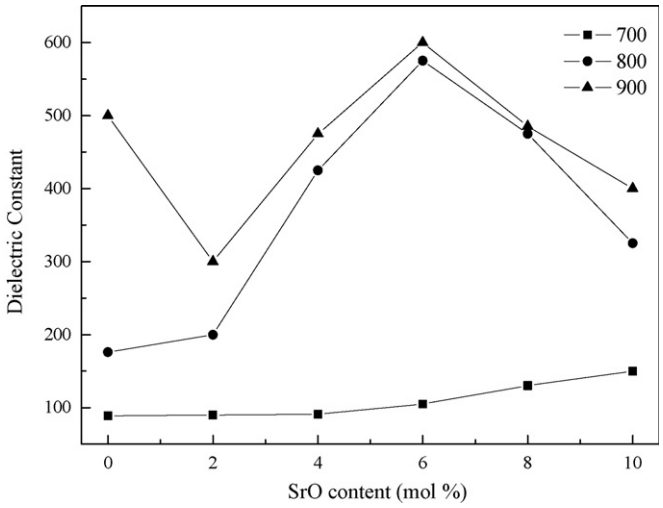

Fig. 7. Dielectric constant of glass–ceramics as a function of SrO content (100 kHz).

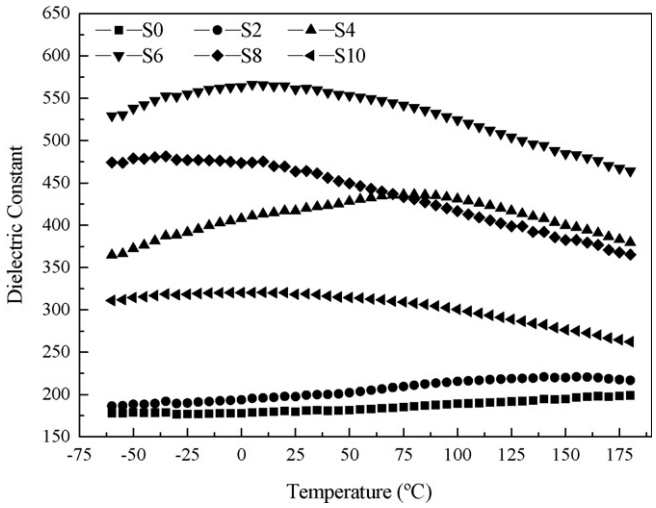

Fig. 9. Dielectric constant vs. temperature heated at 800 °C (100 kHz).

structure ($Sr_2Nb_2O_7$). When the temperature is further increased to 900 °C (Fig. 5), in S0, $Pb_2Nb_2O_7$ transforms to $PbNb_2O_6$ with orthorhombic tungsten bronze structure [10], which is consistent with the third exothermal peak in the DTA curve. In S10, $Sr_2Nb_2O_7$ is still the primary phase.

The microstructure of the samples crystallized at 900 °C is shown in Fig. 6. The average grain size of the samples with different SrO content is about 50 nm. The ceramic grains are uniformly dispersed, suggesting that the rate of nucleation be relatively high.

3.2. Dielectric properties

Fig. 7 shows the variation of the dielectric constant as a function of SrO content at 100 kHz. When the glass is heat-treated at 700 °C, the dielectric constant values of the samples are mainly attributed to the formation of $Pb_2Nb_2O_7$, $Sr_2Nb_2O_7$ and their solid solutions. The dielectric constant increases significantly with increase in crystallization temperature up to 800 °C. This is mainly attributed to the crystallization of $NaNbO_3$ with high-ε_r (500–600) [11,12]. At this crystallization temperature, the maximum value of dielectric constant is ~550 when the content of SrO is 6 mol%. The dielectric constant is continuously improved as the temperature further increases to 900 °C, which is attributed to the increase in crystallization volume fraction. Due to the crystallization of $PbNb_2O_6$ and $NaNbO_3$, the dielectric constant of the S0 sample annealed at 900 °C gets a sharp increase. The high dielectric peak may be related to the morphotropic phase boundary (MPB) between $Pb_2Nb_2O_7$/$PbNb_2O_6$ and $Sr_2Nb_2O_7$ [13,14].

The dielectric–temperature characteristics of the glass–ceramics with various amounts of SrO are shown in Figs. 8–10. It can be found that the dielectric properties of the samples are almost independent with the measured temperature (−60 °C to 180 °C), except S0 heat-treated at 900 °C. The stronger temperature dependence of dielectric constant for S0 annealed at 900 °C may be attributed to the lower ferroelectric phase transition temperature of $PbNb_2O_6$ (550 °C) [10].

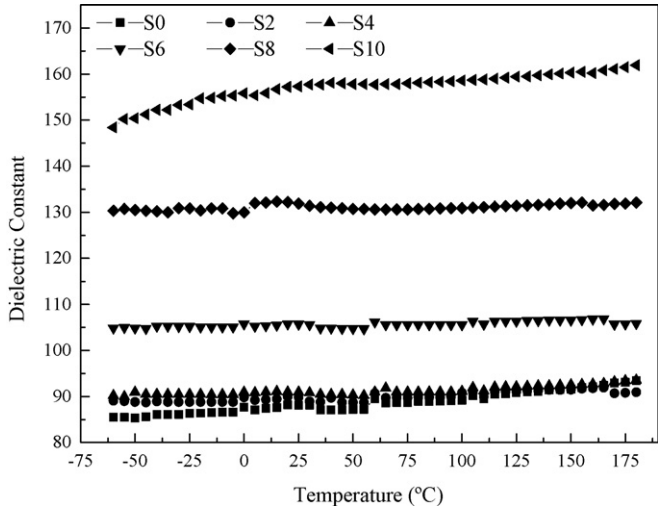

Fig. 8. Dielectric constant vs. temperature heated at 700 °C (100 kHz).

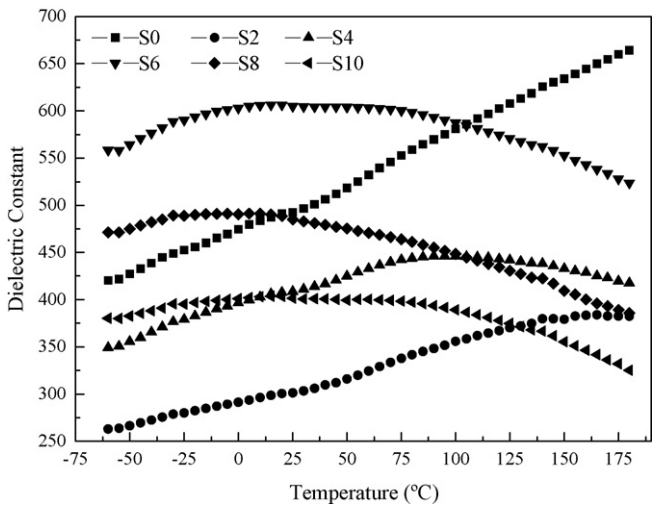

Fig. 10. Dielectric constant vs. temperature heated at 900 °C (100 kHz).

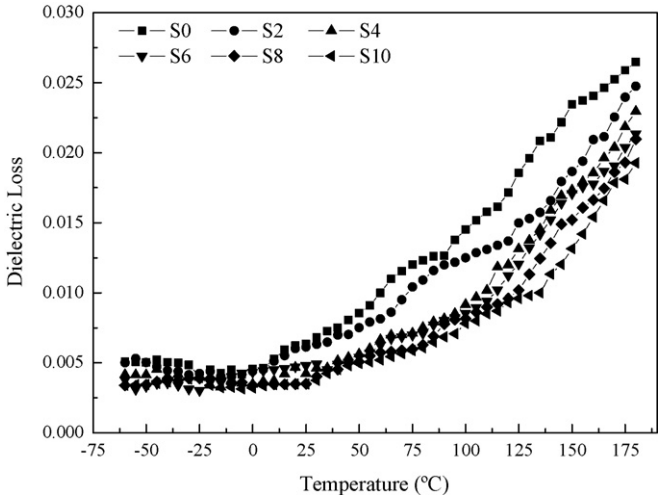

Fig. 11. Dielectric loss vs. temperature heated at 700 °C (100 kHz).

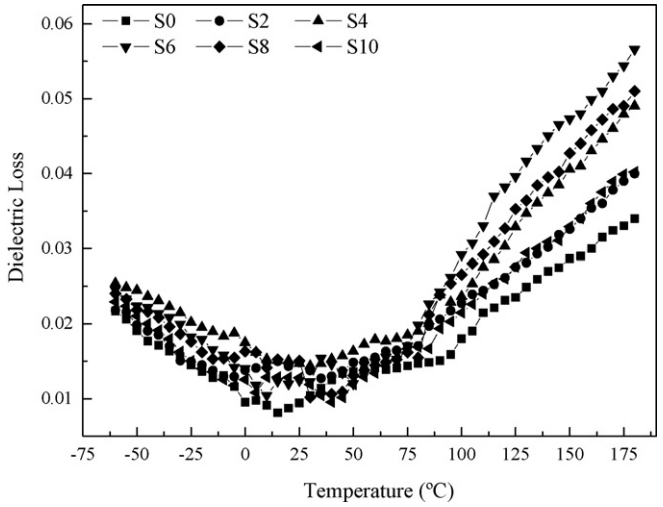

Fig. 12. Dielectric loss vs. temperature heated at 800 °C (100 kHz).

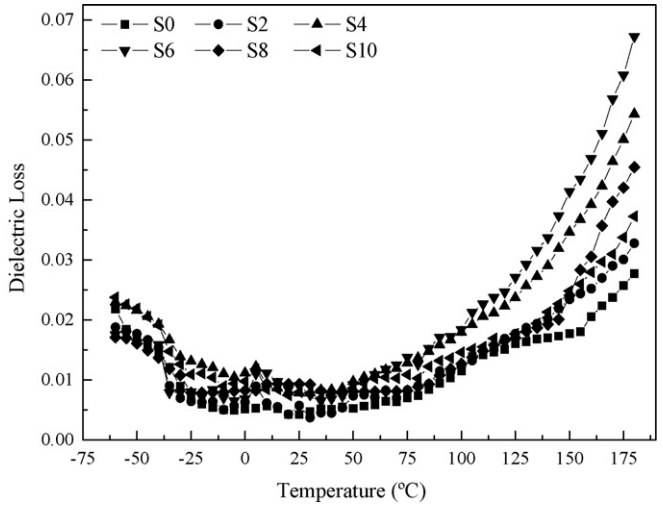

Fig. 13. Dielectric loss vs. temperature heated at 900 °C (100 kHz).

Figs. 11–13 show the temperature dependence of the dielectric loss of different glass–ceramics at frequency of 100 kHz in the range from −60 °C to180 °C. In general, the dielectric loss values of the samples increase with measurement temperatures. The sample treated at 700 °C, that has the lowest dielectric constant, shows the lowest dielectric loss value around room temperature.

4. Conclusion

PbO–SrO–Na_2O–Nb_2O_5–SiO_2 glass–ceramics had been synthesized by melt-quenching process. The effects of PbO and SrO contents on crystallization and dielectric properties were investigated in this study. The results show that,

(1) $Pb_2Nb_2O_7$, $Sr_2Nb_2O_7$ and their solid solution crystallizes at 700 °C and exhibits low dielectric constant.
(2) Large amounts of $NaNbO_3$ form at 800 °C which contribute to the significant increase in dielectric constant values.
(3) At 900 °C, $Pb_2Nb_2O_7$ disappears and transforms into $PbNb_2O_6$, which improves the dielectric constant but degrades the temperature-stability.
(4) Glass–ceramic doped with 6.0 mol% SrO and heat-treated at 900 °C for 3 h shows a high dielectric constant.

References

[1] S.D. Stookey, Catalyzed crystallization of glass in theory and practice, Ind. Eng. Chem. 51 (7) (1959) 805–808.
[2] P.W. Mcmillan, Glass–ceramics, Academic Press, London, 1979.
[3] A. Herczog, Applications of glass–ceramics in electronic components and circuits, IEEE Trans. PHP 9 (4) (1973) 247–256.
[4] A.J. Moulson, J.M. Herbert, Electroceramics—Materials, Properties and Applications, Wiley, England, 2003.
[5] E.P. Gorzkowski, M.-J. Pan, Glass–ceramics of barium strontium titanate for high energy density capacitors, J. Electroceram. 18 (3–4) (2007) 269–276.
[6] J. Du, B. Jones, Preparation and characterization of dielectric glass–ceramics in Na_2O–PbO– Nb_2O_5–SiO_2 system, Mater. Lett. 59 (22) (2005) 2821–2826.
[7] J.D. Siegwarth, W.N. Lawless, A.J. Morrow, Dielectric and thermal properties of $Pb_2Nb_2O_7$ at low temperature, J. Appl. Phys. 47 (9) (1976) 3789–3791.
[8] G. Shirane, R. Pepinsky, Dielectric properties and phase transitions of $Cd_2Nb_2O_7$ and $Pb_2Nb_2O_7$, Phys. Rev. 92 (2) (1953) 504.
[9] S. Nanamatsu, M. Kimura, T. Kawamura, Crystallogragrphic and dielectric properties of ferroelectric $A_2B_2O_7$ (A = Sr, B = Ta, Nb) crystal and their solid solutions, J. Phys. Soc. Jpn. 38 (3) (1975) 817–824.
[10] G. Goodman, Ferroelectric properties of lead metaniobate, J. Am. Ceram. Soc. 36 (11) (1953) 368–372.
[11] L.A. Reznitchenko, A.V. Turik, E.M. Kuznetsova, V.P. Sakhnenko, Piezoelectricity in $NaNbO_3$ ceramics, J. Phys.: Condens. Matter 13 (17) (2001) 3875–3881.
[12] G. Shirane, R. Newnham, R. Pepinsky, Dielectric properties and phase transitions of $NaNbO_3$ and $(Na,K)NbO_3$, Phys. Rev. 96 (3) (1954) 581–588.
[13] J.R. Oliver, R.R. Neurgaonkar, G.L. Shoop, Structural and ferroelectric properties of morphotropic phase boundary systems in the tungsten bronze family, in: Proceedings of the Sixth International IEEE Symposium, Bethlehem, PA, (1986), pp. 485–489.
[14] J.R. Oliver, R.R. Neurgaonkar, Ferroelectric properties of tungsten bronze morphotropic phase boundary systems, J. Am. Ceram. Soc. 72 (2) (1989) 202–211.