Application of Dielectric Mixtures Formulae to $PbTiO_3$ Based Glass-Ceramic Systems

J. Shankar[1,a)], G. Neeraja Rani[1] and V. K. Deshpande[2]

[1]*Geethanjali College of Engineering and Technology, Cheeryal, Hyderabad-501301*
[2]*Visvesvaraya National Institute of Technology, Nagpur-44 010*
[a)]Email:jshankar001@gmail.com.

Abstract: Glass samples with composition (50 - X) PbO - (25 + X) TiO_2 - 25 B_2O_3 (where X =0, 5, 10 and 12.5 mol %) were prepared using conventional quenching technique. These glass samples were converted to glass ceramics by following two stage heat treatment schedules. Transition temperature (T_g), crystallization temperature (T_c), density and Coefficient of Thermal Expansion (CTE) of glass and glass ceramic samples measured. T_g and T_c observed to decrease with increase in the content of TiO_2. The density values of glass ceramic samples are higher than those of corresponding glass samples. It was observed that there was good correlation between the density and CTE results of the glass–ceramics. The dielectric constant of glass ceramic samples is higher than those of corresponding glasses. Maxwell's dielectric mixture formula was used to correlate the theoretically predicted values of dielectric constant with experimentally observed values.

1. INTRODUCTION

The process of manufacturing a glass ceramic involves first, the preparation of a glass which is shaped in its molten state to produce materials of required size. The glass is next subjected to a controlled heat treatment cycle which brings about nucleation and crystallization of various phases so that the final product is a polycrystalline ceramic. This method of making a ceramic material represents a radical departure from conventional ceramic preparation processes and it offers a number of important advantages.

Since molten glass can be obtained in a homogeneous condition, uniformity of chemical composition can easily be achieved for glass ceramics. The homogeneity of the parent glass together with the controlled manner in which the crystals are developed results in ceramic materials having a very fine grained uniform structure free from porosity. This is beneficial in a number of ways since it favours the development of high mechanical strength and also results in good electrical insulating characteristics. An important feature of the glass ceramic process is that it is applicable to a wide range of compositions and this, together with the variations which can be applied in the heat treatment process results in the development of various crystal types in controlled proportions. As a result, the physical characteristics of glass ceramics can be varied in a controlled manner and this fact has an important bearing upon the practical applications of glass ceramics.

Grossman and Isard [1] have applied the dielectric mixture formulae to glass ceramic system. According to them the glass ceramic process provides the opportunity, in principle, of designing materials to specified properties by controlling separately the degree of nucleation and crystal growth. Mixture formulae may be used to study, theoretically, how a property of the material depends on the distribution of its component phases if their properties are known. In particular, the crystalline phases may be identified by x-ray diffraction, but this seldom gives adequate information about crystal size, shape, purity, defect content etc. on which many properties are critically dependent. Optical and electron microscopy may give information about the distribution of the phases present. The mixture formulae may then be used in a reverse calculation; that is, the properties of one constituent phase are found. When they are inserted in the mixture formula they give good agreement with the measured properties of the composite material, (the properties of all other phases are assumed to be known). This application of mixture formulae has been found useful in assessing glass-ceramic materials consisting of one ferroelectric crystalline phase in a matrix glass. In particular, it has been found that the dielectric properties of the composite material could be

explained on the assumption that the properties of the ferroelectric crystalline phase are similar to those of the same phase formed by normal ceramic sintering techniques.

2. EXPERIMENTAL

Glasses with composition (50-X) PbO – (25+X) TiO_2 - 25 B_2O_3 (where X = 0, 5, 10 and 12.5 mol %) were prepared from the high purity ingredients heated in an alumina crucibles at 1373 K-1523 K for 1 h. The melt was homogenized by stirring it before quenching into aluminium mould at room temperature. The resultant glass samples were annealed at 573 K for 4 hours to remove the residual stresses. T_g and T_c for the glass samples were determined from DTA (Perkin Elmer). The conversion of glass samples into glass ceramics was done using two stage heat treatment (i.e., 733 K for 14 hours and 793 K for 14 hours). The optimization of nucleation and crystallization schedule has been reported elsewhere [2] in detail for glass sample X = 0. The density of glasses and glass ceramics were measured using Archimedes principle with toluene as immersion liquid. Coefficient of Thermal Expansion (CTE) was measured using Orton Dilatometer. The dielectric measurements for different glass and glass–ceramic samples were carried out at different temperatures as a function of frequency by high resolution dielectric analyzer (Novo control systems) over a frequency range 1 mHz–1 MHz. Maxwell's dielectric mixture formula was used to correlate the theoretically predicted values of dielectric constant with experimentally observed values.

3. RESULTS AND DISCUSSION

The values of glass transition temperature (T_g), crystallization temperature (T_c), density of glass (ρ_{glass}) and glass ceramic($\rho_{glassceramic}$) CTE for glass and glass ceramic samples for the series (50-X) PbO- (25+X) TiO2 –B_2O_3 are given in the Table 1.

Table1.T_g, T_c, ρ, CTE for glass and glass ceramic of series (50-X) PbO- (25+X) TiO2 –B_2O_3

X (mol%)	T_g	T_c	ρ_{glass}	$\rho_{glassceramic}$	CTE_{glass}	$CTE_{glassceramic}$
0	731	875	4.98	5.62	8.44	5.21
5	704	870	5.08	5.67	7.81	5.10
10	702	868	5.13	5.73	7.61	5.05
12.5	716	865	5.28	5.78	6.32	4.74

It can be observed that the T_g decreases with increase in TiO_2 content up to 35 mol % and for glass sample with TiO_2 content 37.5 mol% the T_g increased. The T_g of all glass samples are below the Curie temperature (763 K) of lead titanate. This is of great advantage according to Lynch and Shelby [3], if the glass transition temperature is below the Curie temperature of $PbTiO_3$, then the crystal clamping can be avoided at crystal glass interface. The crystallization temperature is observed to decrease with increase of TiO_2 content. The T_c of all the glass samples are in between 865 K to 875 K. Bergeron and Rusell [4] have reported a T_c of 873 K for a composition similar to sample with TiO_2 25 mol% which supports the results obtained in the present work. The results of T_g and T_c were useful in deciding the heat treatment schedule for conversion of glass samples into glass ceramics. The density of glass as well as glass ceramic samples increases continuously with the addition of TiO_2. Also the density of glass ceramic samples is higher than that of corresponding glass samples. The increase in density may be attributed to an increase in crystalline phase in the glass ceramic samples.

It is also observed from Table 1 that the values of CTE for glass ceramic samples are lower than those of corresponding glass samples. It is also observed that there is a good correlation between the CTE and density results of glass ceramics. When the value of density increases for a glass ceramic sample, it indicates that the structure becomes more rigid and hence there is a decrease in the CTE value.

Table2: The room temperature (RT) dielectric constant and dielectric loss of glass and glass ceramic samples of series (50-X) PbO- (25+X) TiO2 –B_2O_3 at 1 kHz

X (mol %)	Glass		Glass ceramic	
	ε_{RT}	$Tan\delta_{RT}$	ε_{RT}	$Tan\delta_{RT}$
0	23	0.021	40	0.025
5	40	0.026	87	0.028
10	84	0.080	110	0.086
12.5	92	0.116	140	0.220

The room temperature (RT) dielectric constant and dielectric loss of glass and glass ceramic samples of series (50-X) PbO- (25+X) TiO2 –B_2O_3 at 1 kHz are given in Table 2. It is observed from this table that the dielectric constant and dielectric loss of glass ceramic samples are higher than those of corresponding glass samples. With increase in the content of TiO_2 both the values of ε and tanδ of glass ceramics are increased and this may be attributed to the increase in the volume fraction of major crystalline $PbTiO_3$ phase.

Based on the close agreement between the predicted and the experimentally measured values, it is the common practice that the dielectric properties of glass ceramics are adequately described by theoretical models. The Clausius – Mossotti formula for a dispersion of spheres is given by Reynolds and Hough [5] as:

$$\varepsilon_{eff} = \frac{(1-\delta_1)2\varepsilon_2^2 + (1+2\delta_1)\varepsilon_1\varepsilon_2}{(1-\delta_1)\varepsilon_1 + (2+\delta_1)\varepsilon_2} \quad (1)$$

When the dispersed phase occupies a significant volume fraction (>0.25), the spacing between the dispersed crystallites is small, allowance for electrostatic interaction between the crystallites must be made, while modeling the dielectric behaviour. Bottcher [6] and Bruggeman [7] incorporated interaction effects by assuming, in the calculation of the effective polarizing field, that the spheres of dielectric constant ε_1 are immersed in a medium of dielectric constant ε_2.

Odelevski has demonstrated the validity of such a formula for a mixture of two dielectric constituents with large difference (at least 1 order of magnitude) in their dielectric permittivity [8]. According to Lichtenecker's empirical mixing rule [9].

$$\log \varepsilon_{eff} = \delta_1 \log \varepsilon_1 + \delta_2 \log \varepsilon_2 \quad (2)$$

Maxwell's model which describes a two-phase dielectric mixture comprising of spherical particles with higher dielectric constant dispersed in a matrix of smaller dielectric constant. According to Maxwell's model, the effective dielectric constant of such a composite is given by

$$\varepsilon_{eff} = \frac{\varepsilon_2\delta_2(\frac{2}{3} + \frac{\varepsilon_1}{3\varepsilon_2}) + \delta_1\varepsilon_1}{\delta_2(\frac{2}{3} + \frac{\varepsilon_1}{3\varepsilon_2}) + \delta_1} \quad (3)$$

As mentioned in the above equation (3) the fraction of $PbTiO_3$ phase crystallized in a glass ceramic sample is denoted by δ_1. The fraction of remnant glass phase is denoted by δ_2. The room temperature dielectric constant of $PbTiO_3$ ceramic is taken from the literature [1] and the value is, ε_1= 200 (at 100 kHz). The dielectric constant of lead borate glass (experimentally measured) is ε_2 = 25 (at 100 kHz). In the present work the amount of volume fraction of crystalline phase $PbTiO_3$ δ_1 was calculated by comparison of integral intensities from X-ray diffraction patterns of amorphous, partially crystallized and completely crystalline samples using standard methods reported by Ilinsky et al. [10] and Alexander Karamanov et al. [11]

The Maxwell's dielectric mixture formula (equation 3) is applied in the present work to predict the effective dielectric constant ε_{eff} of the glass ceramic samples of series (50-X) PbO- (25+X) TiO2 –B_2O_3 at 100 kHz, The comparison of the predicted dielectric constant calculated using dielectric mixture formula with the experimentally measured values is given in Table 3.

Table 3: Comparison of the predicted dielectric constants with experimentally measured values for series (50-X) PbO- (25+X) TiO2 –B_2O_3.

X (mol%)	δ_1 ($PbTiO_3$ phase Crystallized)	δ_2 (remnant glass phase	Predicted dielectric constant (ε_{eff})	Expt. Measured dielectric constant
0	0.52	0.48	32.7	32.93
5	0.55	0.45	64.94	65.2
10	0.63	0.37	84.31	85.3
12.5	0.67	0.33	91.2	89.7

The agreement of the theoretically predicted values of dielectric constant with experimentally measured values suggests that the Maxwell's model is valid for the dielectric properties of $PbTiO_3$ based glass ceramics studied in the present work.

4. CONCLUSIONS

T_g and T_c of glass samples were observed to be decreased with increase in the content of TiO_2.Density ofglass ceramics were higher than those of corresponding glass samples. There exist a good correlation between density and CTE of glass ceramic samples Maxwell's dielectric mixture formula is valid for the dielectric properties of $PbTiO_3$ based glass ceramics studied in the present work.

REFERENCES

1. D. G. Grossman and J. O. Isard, J. Phys. D: Appl. Phys**., 3**, 1058 (1970).
2. V.K.Deshpande and J.Shankar, Ferroelectrics., **393**,63-70 (2009)
3. S. M. Lynch and J. E. Shelby, J. Am. Ceram.Soc. **67**, 424-430 (1984).
4. C. G. Bergeron and C. K. Russell, J. Am. Ceram. Soc. **48**, 115-120 (1965).
5. A. Reynolds and J. M. Hough, , Proc. Phys. Soc., **70B,** 769 (1957).
6. J. F.C. Bottcher, Rec. Trav. Chim. Pays-Bas*,* **64,** 47 (1945).
7. D. A. G. Bruggeman, Ann. Phys*.,* **24,** 636 (1935).
8. Odelevski, Zh. Tekh. Fiziki. 21**,** 675 (1951).
9. K. Lichtenecker, K. Rother, Phys. Z. **32,** 255 (1938).
10. A. G. Ilinsky, V. V. Maslov, V. K. Nozenko and A. P. Brovko, J. Mater. Sci.**35**, 4495-4501 (2000).
11. A. Karamanov and M. Pelino, Journal of European Ceramic Society **19,** 649-655 (1999).