An Experimental Study on Dielectric Relaxor Behavior of the System $(Pb_{1-x}Ba_x)\ ZrO_3$ (x = 0.25, 0.30, 0.35) Ceramics

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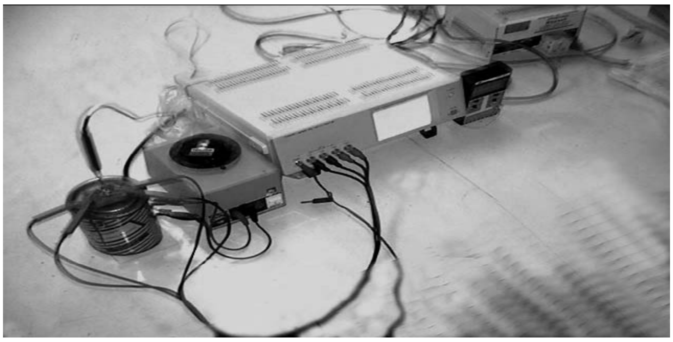
Introduction

$(Pb_{1-x}B_{ax})ZrO_3$ (x = 0.25, 0.30 and 0.35) (PBZ) powders are synthesized using a semi-wet route involving solid state thermo-chemical reaction in a mixture of $(Pb_{1-x}Ba_x)CO_3$ and TiO_2. The $(Pb_{1-x}Ba_x)CO_3$ precursors are obtained by a "forced" co-precipitation technique. The powders are sintered at 1050°C, which is 200 to 300°C lower than that of conventional dry route, to achieve about 95% of the theoretical density. It is observed that PBZ sample reveals dielectric anomaly around 127°C for x = 0.25, 84°C for x = 0.30 and 29°C for x = 0.35 in ferroelectric (FE) to paraelectric (PE) phase transition on heating. Real and imaginary part of the dielectric constant has a peak at this transition temperature. The peak value of the real part of the dielectric constant is higher during cooling mode than that of heating mode as per simple Landau Theory argument, which give thermal hysteresis of 10°C for PBZ (x = 0.25), 2°C for (x = 0.30) and 1°C for(x = 0.35).. From the resistance measurement, the range of PTCR (positive temperature coefficient of resistance)effect in R_P are 193 °C and 113 °C for PBZ x = 0.25 and x = 0.30 respectively. Analysis of impedance spectroscopic plots confirms that the sample PBZ is regular ferroelectric for x = 0.25, relaxor ferroelectric for x = 0.30 and reentrant relaxor ferroelectric for x = 0.35. This also confirms that the sample PBZ is polydispersive with double relaxation process. The feature of PBZ has great applications such as charge storage devices, capacitors, energy conversion device, microelectronic and micro-electromechanical devices.

The purpose of present work is to study the barium doped $PbZrO_3$ by using semi-wet route while the earlier workers except B.P. and Dutta have prepared such samples by dry route . The objectives of the present work are:

a) Dielectric studies of $(Pb_{1-x}Ba_x)ZrO_3$ ($0.20 < x \leq 0.35$) as a function of temperature and frequency.
b) Study of relaxor behaviour.
c) Resistance measurement.
d) Impedance spectroscopic analysis.

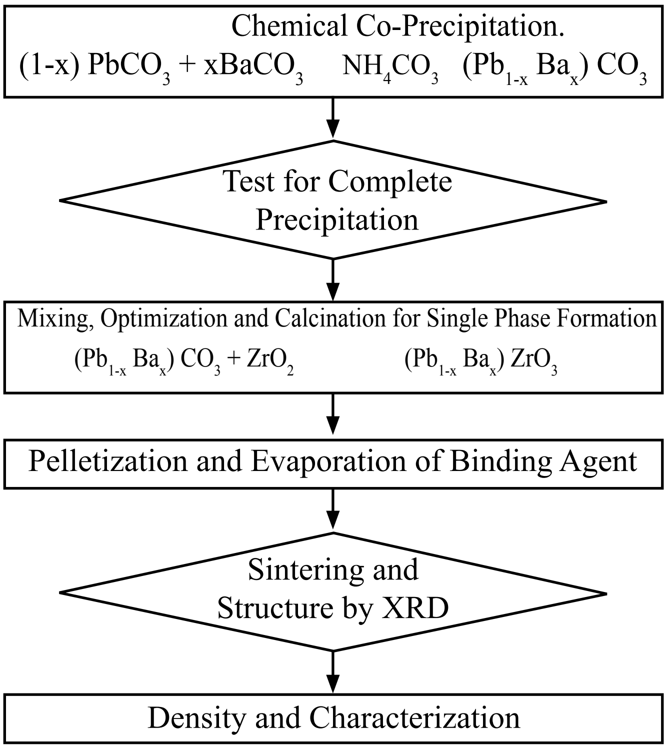
Instrument Used



Experimental setup of HIOKI LCR HiTESTER (3532-50)

Synthesis of the Sample (PBZ)

The sequence of the synthesis of the PBZ ceramics and characterization following the semi-wet route is outlined below in the figure



Details of synthesis of $(Pb_{1-x}Ba_x)ZrO_3$ Ceramics by semi-wet route.

Impedance Spectroscopic Analysis

Total impedance z* for the circuit containing one parallel RC component is given by ,

$$z^* = \frac{1}{i\omega C + \frac{1}{R}} = \frac{R}{1 + i\omega CR} = z' - iz'' \quad \text{.............. (1),}$$

$$\text{Where, } z' = \frac{R}{1 + \omega^2 C^2 R^2} \quad \& \quad z'' = \frac{\omega C R^2}{1 + \omega^2 C^2 R^2}$$

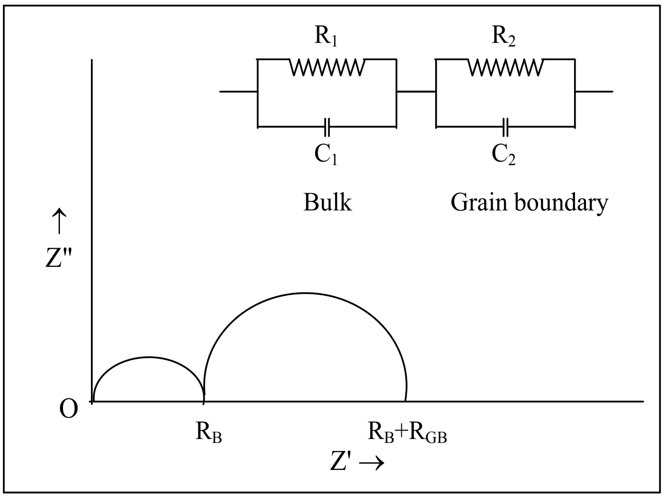
We get the relation between z' and z" by eliminating ω

$$\text{or, } \left(z' - \frac{R}{2}\right)^2 + (z'' - 0)^2 = \left(\frac{R}{2}\right)^2 \quad \text{... 4)}$$

This represent the equation of a circle with center coordinate $\left(\frac{R}{2}, 0\right)$ and radius equal to R/2, which passes through origin with its center on the real axis. The co-ordinate at the top of semi-circular arc, at a particular frequency ω_0, is $\left(\frac{R}{2}, \frac{R}{2}\right)$. Thus substituting z'=R/2 and z"=R/2 in equations S' and S" the relation $\omega_0 RC = 1$ is obtained, where $\omega_0 = 2\pi f_0$, where RC product is known as time constant i.e. relaxation time τ [1]. It should be noted that real and imaginary parts of these functions, referred as immittance functions, are always positive for dielectric or conductive materials [2]. Thus for a single crystal only one semi circular arc is obtained with single time constant. For a polycrystalline dielectric material, more than one semi circular arc or depressed circular arcs may be obtained depending on the number of processes having different time constants, τ's, such as τ, τ_2, τ_3 etc.

Table: Values of resistance and capacitance of equivalent RC circuit 7 at different temperatures for PBZ (25%, 30% and 35%) samples

Sample→	PBZ(25%)			
R&C↓ Temp(°C)→	50°C	70°C	90°C	110°C
R_1 (KΩ)	15.625	12.5	9.375	6.25
C_1(nF)	1.018	1.273	1.697	2.546
R_2(KΩ)	225	237.5	231.25	243.75
C_2(nF)	0.707	0.67	0.688	0.652
Sample→	PBZ(30%)			
R&C↓ Temp(°C)→	60°C	70°C	80°C	90°C
R_1 (KΩ)	4.5	2.857	7.894	26.667
C_1(nF)	3.536	5.57	2.016	0.596
R_2(KΩ)	63.3	26.42	39.473	46.667
C_2(nF)	2.514	6.024	4.032	3.41.
Sample→	PBZ(35%)			
R&C↓ Temp(°C)→	30°C	40°C	50°C	60°C
R_1 (KΩ)	7.5	9.615	8.75	10
C_1(nF)	2.122	1.655	1.818	1.59
R_2(KΩ)	92.5	153.846	100	97.5
C_2(nF)	1.72	1.034	1.818	1.632



Schematic representation of equivalent circuit and corresponding impedance plot for electrical transport through PBZ samples.

Temp.	Real part of dielectric constant at different temperatures				
	PBZ(25%)	Temp	PBZ(30%)	Temp	PBZ(35%)
	ε_r'		ε_r'		ε_r'
30	602.53	30	3323.98	25	1116.11
35	635.33	35	3917.92	26	1117.67
40	671.98	40	4183.63	27	1119.01
45	709.04	45	4642.11	28	1120.01
50	753.41	50	5163.11	29	1120.23
55	791.36	55	5978.48	30	1119.23
60	846.74	60	6786.03	31	1119.01
65	896.38	65	8171.89	32	1118.89
70	956.11	70	8989.86	33	1118.34
75	1017.34	75	9755.73	34	1118.00
80	1092.86	76	9961.52	35	1117.78
85	1184.43	77	10128.24	36	1117.45
90	1281.22	78	10185.55	37	1116.45
95	1389.16	79	10222.02	38	1115.22
100	1508.19	80	10261.10	39	1114.45
101	1528.48	81	10276.73	40	1112.89
102	1548.49	82	10326.22	41	1110.79
103	1581.60	83	10354.88	42	1111.88
104	1601.47	84	10370.51	43	1110.21
105	1625.85	85	10242.86	44	1109.02
106	1646.28	86	10237.65	45	1108.95
107	1670.37	87	10219.42	46	1105.49
108	1691.93	88	10146.48	47	1105.18
109	1715.32	89	10024.04	48	1104.54
110	1732.79	90	10013.62	49	1103.05
111	1753.08	91	9885.98	50	1100.90
112	1770.97	92	9773.96	52	1097.98
113	1783.79	93	9641.11	54	1097.33
114	1800.56	94	9599.43	56	1093.92
115	1814.09	95	9453.55	58	1090.96
116	1832.55	96	9307.67	60	1084.49
117	1850.02	97	9224.31	62	1079.70
118	1854.95	98	9101.87	64	1077.42
119	1858.19	99	8922.13	66	1073.34
120	1869.46	100	8750.20	68	1065.87
121	1879.47	101	8672.05	70	1059.93
122	1885.38	102	8502.72	75	1050.32
123	1887.50	103	8351.63	80	1032.51
124	1891.16	104	8260.46	85	1016.39
125	1889.75	105	8057.27	90	1000.70
126	1896.23	110	7413.83	95	982.53
127	1896.80	115	6903.25	100	963.16
128	1895.39	120	6350.99	110	923.03
129	1890.03	125	5861.25	120	883.29
130	1888.76	130	5441.85	130	837.40
131	1879.18	135	5025.05	140	795.87

The important results of present work are as follows:

1. The peak value of the dielectric constant is found at 127°C for PBZ (25%), at 84°C for PBZ (30%) and at 29°C for PBZ (35%) which are the transition temperatures of our samples.
2. The peak value of real and imaginary parts of dielectric constant is higher during cooling mode than that of heating mode. 3. The peak values of temperatures during heating and cooling modes are different, which give the thermal hysteresis of 10°C for PBZ (25%), 2°C for PBZ (30%) and 1°C for PBZ (35%). This shows that the value of hysteresis goes on decreasing with increasing the barium content in PBZ sample.
4. The transition temperatures for PBZ (25%) is 127°C, for PBZ (30%) is 84°C and for PBZ (35%) is 29°C. This shows the transition in PBZ (25%) and in PBZ (30%) is first order type.

5. From the measurement of capacitance it is found that the value of capacitance goes on increasing with increase of temperature and becomes maximum at a certain temperature called transition temperature and then starts decreasing with further increase in temperature at a particular frequency . Cs is slightly greater than Cp and the values of capacitances decreases with increasing frequency at a particular temperature.
6. From the measurement of resistance it is found that the series and parallel resistance of our sample show the PTCR (positive temperature coefficient of resistance) effect at a certain range of temperature. The range of PTCR in Rp for PBZ (25%) sample is 193 °C and for PBZ (30%) sample is 113 °C.
7. From the study of impedance spectroscopic plots, it is observed that the sample PBZ is polydispersive type ceramics. Double relaxation process are observed in each case. It is also observed that the sample PBZ (25%) is regular ferroelectric whereas the sample PBZ (30%) is relaxor ferroelectric and the sample PBZ (35%) is reentrant relaxor ferroelectric type.

References:

[1] R.K. Dwivedi, D.Kumar, O.Prakash,"Journal of Material Science",36 (2001)3657-3665

[2] W. Cao and R. Gerhardt,"Solid State Ionics",42 (1990)213

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