

## Specific heat of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Ti}_{1-y}\text{Zr}_y\text{O}$ ( $y = 0, 0.03, 0.05, 0.1$ ) ferroelectric ceramics obtained by the temperature relaxation method

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In the last few years great interest has developed around  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  (BST) or BST-based materials due to their great potential for technological applications such as integrated capacitors, ferroelectric memory and many others [1–3]. Thermal properties of materials used in the design and construction of electronic devices must be taken into account since heat will be unavoidably generated in a working electronic circuit. The behavior of the devices as their temperature change and their ability to store and dissipate heat will affect their performance and lifetime therefore their thermal properties cannot be neglected. Despite the extended use of the BST ceramic system, knowledge of the thermal properties is still scarce. For this reason a study of the heat capacity ( $C_p$ ) and specific heat ( $c_p$ ) of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$  ( $y = 0, 0.03, 0.05, 0.1$ ) ceramic samples obtained by the Temperature Relaxation Method (TRM) [4] is presented.

There are several methods reported in the literature to obtain the specific heat capacity of materials [5]. The TRM, also known as Temperature Increment Under Constant Illumination Method [6] selected among others, because of its effectiveness and simplicity, has been employed for thermal characterization of different type of materials such as semiconductors [7], zeolites [8], ceramics [9], woods [10] and foods [11] among others. It is based on the fact that the relaxation of a

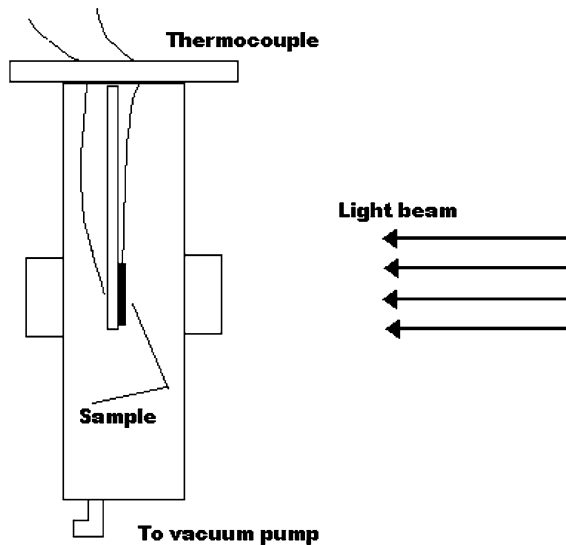
closed system can be studied by perturbing an initial equilibrium state and monitoring the behavior in time of the variable of interest, such as the absolute temperature  $T$ . If the deviation from equilibrium is small enough, the temperature relaxation will follow the exponential law  $T = T_0 e^{-(t/\tau)}$ , where  $t$  is the time,  $T_0$  is the initial value of the temperature  $T$ , and  $\tau$  is the relaxation time constant [12]. In the case presented here,  $\tau$  will depend on the specific heat capacity as will be evident in what follows.

The nominal composition of the samples is given by  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$  ( $y = 0, 0.03, 0.05, 0.1$ ). The samples were prepared using a traditional ceramic method [13] by mixing reagent grade  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  in an agate mortar for 2 h. The resulting powder was die pressed into 22 mm diameter, 10 mm thick pellets and calcined for 2 h at 1,100 °C in air. The calcined pellets were ground again for 3 h, die pressed into 10 mm diameter, 1 mm thick disks and sintered in air at 1,350 °C for 4 h.

To measure their specific heat, the samples were adiabatically suspended inside a stainless steel calorimeter at a working pressure of  $\approx 10^{-3}$  Torr. The calorimeter was provided with two glass windows. One was used to shine uniformly distributed white light on the sample while the second one was used for alignment and observation purposes. A chromel–alumel thermocouple was fixed on the back face of the sample for temperature control. Both surfaces of the samples were painted black to enhance light absorption and to push the emissivity ( $\epsilon$ ) as close as possible to one as stated in the calculations presented below. The temperature behavior of the samples with time was conveniently monitored with a temperature controller (Model 760 Eurotherm Controls Inc.) (Fig. 1).

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**Fig. 1** Schematic of the system used to measure specific heat

The heat ( $Q$ ) generated in the samples as a function of time ( $t$ ) due to the absorption of the incident light power  $P_0$  is given by:

$$\frac{\partial Q}{\partial t} = P_0 - L \tag{1}$$

where  $L = R + K$ , represents radiation ( $R$ ) and convection ( $K$ ) losses. Convection losses will be small and can be neglected at  $10^{-3}$  Torr. Radiation losses may be obtained from the Stefan–Boltzmann black body radiation law that, for temperature variations  $\Delta T$  around room temperature ( $T_0$ ) are given by:

$$R \approx 4A\epsilon\sigma T_0^3 \Delta T \tag{2}$$

The temperature variation and the heat generated in the sample by the incident radiation can be related by

$$Q = \rho c_p V \Delta T \tag{3}$$

where  $V$  is the volume of the sample. Since the specific heat capacity is related to the density  $\rho$  and the specific heat  $c_p$  of the material by:

$$C_p = \rho c_p \tag{4}$$

expression (3) becomes

$$Q = C_p V \Delta T \tag{5}$$

Taking the derivate with respect to time of Eq. (5) and substituting in Eq. (1) leads to

$$\frac{\partial \Delta T}{\partial t} + \frac{\gamma}{VC_p} \Delta T - \frac{P_0}{VC_p} = 0 \tag{6}$$

where

$$\gamma = 4A\epsilon\sigma T_0^3 \tag{7}$$

Assuming  $\Delta T(t = 0) = 0$  the solution to this equation is

$$\Delta T_{\uparrow}(t) = \frac{P_0}{\gamma} \left[ 1 - \exp\left(-\frac{t}{\tau}\right) \right] \tag{8}$$

where

$$\tau = \frac{dC_p}{8\sigma\epsilon T_0^3} \tag{9}$$

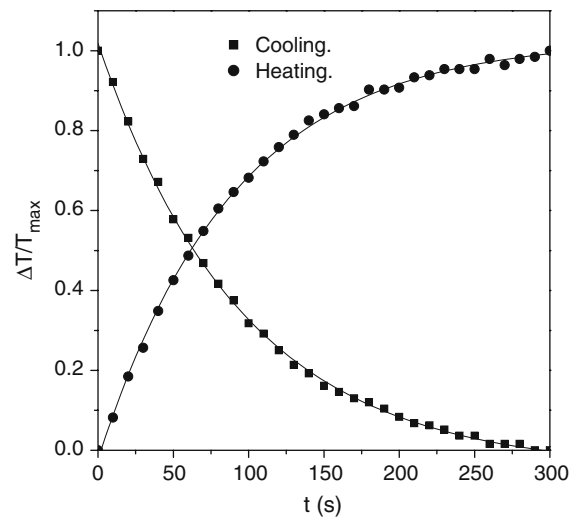
is the relaxation time and  $d$  is the sample thickness.

The temperature will reach a saturation value at thermal equilibrium. If at that point illumination is interrupted the dependence of temperature with time as the sample cools down will be:

$$\Delta T_{\downarrow}(t) = \frac{P_0}{\gamma} \left[ \exp\left(-\frac{t}{\tau}\right) \right] \tag{10}$$

By fitting the experimental data to Eqs. (8) and (10) the value of  $\tau$  may be determined and the calculation of  $C_p$  can be performed by means of Eq. (9). Knowledge of the sample’s density allows then the calculation of the specific heat capacity ( $c_p$ ) using Eq.(4).

In Fig. 2, the results of a typical measurement performed on a 5% Zr-doped sample are shown. For a better insight on the behavior of the sample, the curves



**Fig. 2** Normalized temperature variation as a function of time

taken during heating up and cooling down are presented. Continuous lines represent the fitting of Eqs. (8) and (10) to the experimental data with  $\tau$  as fitting parameter.

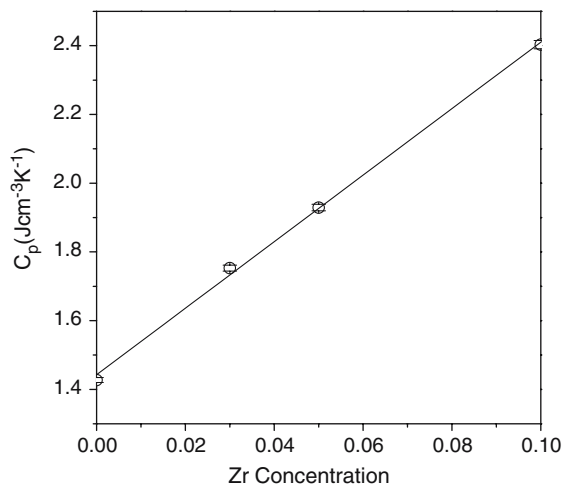
The heat capacity  $C_p$  was determined using Eq. (9) using the values of  $\tau$  obtained by the fitting procedure. Figure 3 presents a plot of the values of  $C_p$  as function of Zr content.

The resulting straight line shown in Fig. 3 represents a linear dependence of the heat capacity on Zr concentration and can be represented as the addition of two terms by  $C_p = C_0 + C_x$  where  $C_0 = (1.43 \pm 0.01) \text{ J cm}^{-3} \text{ K}^{-1}$  is the intercept with the ordinate axis at the origin and  $C_x = (9.8 \pm 0.3) \text{ J cm}^{-3} \text{ K}^{-1}$  accounts for the linear increase of  $C_p$  with temperature.

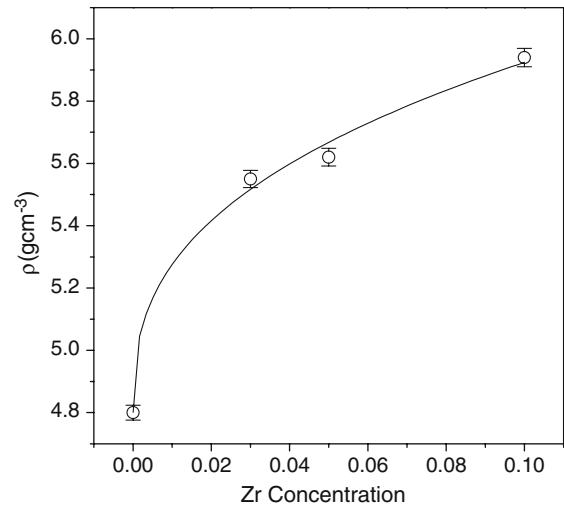
Figure 4 represents the density of the samples as a function of Zr concentration. The solid line is the best fit to the experimental data using an expression of the form  $\rho = \rho_{01} + \rho_{02} x^n$  with  $\rho_{01} = (4.8 \pm 0.06) \text{ g cm}^{-3}$ ,  $\rho_{02} = (2.7 \pm 0.6) \text{ g cm}^{-3}$  and  $n = (0.37 \pm 0.08)$ .

With the use of Eq. (4), the specific heat  $c_p$  can be determined for each Zr concentration. The results are shown in Fig. 5 where a linear increase of  $c_p$  with Zr content is observed for the studied concentration range. As far as we know, these are the first reported values for the specific heat of Zr-doped BST in these particular compositions.

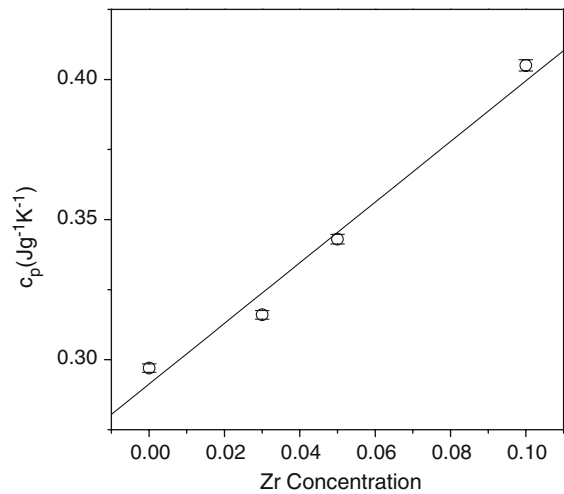
The usefulness of the temperature relaxation method for measuring the specific heat of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$  ferroelectric samples prepared by a traditional ceramic method, for different Zr concentrations has been demonstrated. The results show a strong dependence of the specific heat with the content of Zr. As far as we know, the results reported here using the relaxation method are the first reported values of the specific heat in the considered composition range.



**Fig. 3** Dependence of the heat capacity with Zr concentration



**Fig. 4** Density of the samples as a function of Zr concentration



**Fig. 5** Dependence of the specific heat with Zr concentration

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## References

- Zhang L, Zhong WL, Wang G (1998) Solid State Commun 10:761
- Zafar S, Chu P, Rimmel T, Jones RE, White BE, Gentile D, Jiang B, Melnick B, Taylor D, Zucher P, Gillespie S (1998) Mater Res Soc Symp Proc 43:15
- Reisinger H, Wendt H, Beitel G, Frisch E (1998) Symp on VLSI technology. Digest of Technical Papers 58
- Hatta L (1979) Sci Instrum 50:292
- Kraftmakher Y (2002) Phys Rev 356:1
- Mansanares AM, Bento AC, Vargas H, Leite NF, Miranda LCM (1990) Phys Rev B 42:4477
- Pichardo JL, Marin E, Alvarado-Gil JJ, Mendoza-Alvarez JG, Cruz-Orea A, Vargas H, Delgadillo I, Torres-Delgado G (1997) J Appl Phys A 65:69

8. Juárez GG, Angel OZ, Gil JJA, Vargas H, Dastore HDO, Barone JS, Velez MH, Baños L (1996) *J Chem Soc Faraday Trans* 92:2651
9. Alexandre J, Saboya F, Marques BC, Ribeiro MLP, Salles C, Da Silva MG, Sthel MS, Auler LT, Vargas H (1999) *Analyst* 124:1209
10. Balderas-López JA, Tomas SA, Vargas H, Olalde-Portugal V, Baquero R, Limón JMY, Alvarado Gil JJ, Hernández JF, Falconi C, Silva MD, Miranda LCM (1996) *Forest Prod J* 46:84
11. Rodríguez ME, Yáñez JM, Orea AC, Gil JJA, Angel OZ, Sinencio FS, Vargas H, De Dios Figueroa J, Bustos FM, De La Luz Martinez-Montes J, Hernández JG, Carlos De Moura L (1995) *Lebensmittel Untersuchung Und-Forschung*. Springer Verlag, Berlin Heidelberg New York
12. Krupska A, Krupski M, Konarski J (2001) *Eur J Phys* 22:133
13. Ring AT (1998) *Fundamentals of ceramic powder processing and synthesis*. Academic Press, New York