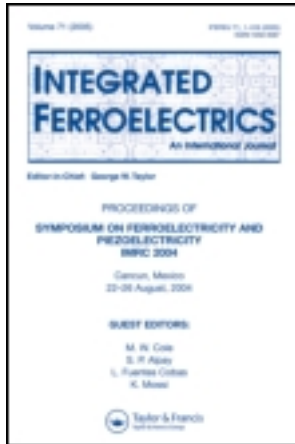


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S. Reddy^a, A. K. Dubey^b, B. Basu^b, R. Guo^a & A. S. Bhalla^a

^a Department of Electrical and Computer Engineering, University of Texas at San Antonio, San Antonio, TX-78249, USA

^b Laboratory for Biomaterials, Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur-208016, UP, India

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Thermal Expansion Behavior of Biocompatible Hydroxyapatite-BaTiO₃ Composites for Bone Substitutes

S. REDDY,¹ A. K. DUBEY,² B. BASU,² R. GUO,¹
AND A. S. BHALLA^{1,*}

¹Department of Electrical and Computer Engineering, University of Texas at San Antonio, San Antonio, TX-78249, USA

²Laboratory for Biomaterials, Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur-208016, UP, India

In the present study, the thermal expansion behavior of biocompatible pure Hydroxyapatite (HA) and HA-BaTiO₃ composites were studied in the temperature range of –150 to 300°C. The composites were optimally processed by conventional pressure-less sintering at 1250°C for 2 hrs. The measured coefficients of thermal expansion (CTE) values in the temperature range close to the human body temperature were ranging from $11 \times 10^{-6}/^{\circ}\text{C}$ to $12 \times 10^{-6}/^{\circ}\text{C}$. It was observed that the CTE values are almost stable in the entire temperature range of measurement and closely resembled with the values for natural human bone.

Keywords Hydroxyapatite; BaTiO₃; Thermal expansion

1. Introduction

Hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂], HA] being analogous to mineral component of bone, has been recognized as potential material for orthopedic implant applications [1, 2]. However, the poor mechanical and electrical properties of HA has necessitated to the development of HA-based composites with various reinforcements, like mullite [3, 4], CaTiO₃ [5], BaTiO₃ [6]. In view of significant electrical properties (piezoelectricity [7], pyroelectricity [8] etc.) possessed by bone, the potentiality of BaTiO₃ (BT) as an implant material has been proved in both, soft and hard tissues [9]. In the *in vivo* study involving implantation of BT in the femora of dogs for the time period of upto 20 weeks, the suitability of BT has been demonstrated by the absence of any inflammation or adverse effect at the implant (BT)-tissue interface [10]. In addition, the piezoelectric secondary phase in the composite has been shown to improve the fracture toughness [11, 12].

In order to integrate the biological, mechanical and electrical response, a composite of HA-BaTiO₃ (HA-BT) with varying amount of BT (0, 20, 40, 60, 80 wt%) in HA has been optimally processed using conventional sintering route.

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*Corresponding author. E-mail: amar.bhalla@utsa.edu

The aim of the present study is to examine the thermal expansion behavior of the developed composites in the temperature range of -150 to 300°C and to compare the results with the reported values of the thermal expansion coefficient for the natural bone.

2. Experimental

For the present work, HA is synthesized by suspension-precipitation route [13, 14] using CaO (M/s SD Fine-Chem Lit., Product No. 37614) and H_3PO_4 (M/s Merck, CAS No. 7664-38-2) as precursors. The H_3PO_4 solution (0.17M) was added drop wise in hot (80°C) and stirred CaO solution. Following this, the pH of the solution was maintained at 10 using 25% NH_4OH solution (M/s Qualikems, Product No. A025112). The reaction product was precipitated and dried. The powders were calcined at 800°C for 2 hrs and the phase verification was done using XRD. For the synthesis of BaTiO_3 , stoichiometric amounts of BaCO_3 (Himedia, RM 1340) and TiO_2 (Himedia, RM 3065) were ball milled for 6 hrs using agate jar and balls as grinding media and acetone as a milling medium. The ball milled powders were calcined at 1000°C in air for 6 hrs in a platinum crucible. For the preparation of composites, HA- x wt.% BT ($x = 0, 20, 40, 60, 80$) were ball milled for 16 hrs to ensure the homogeneous mixing with reduced particle size. These composites will be abbreviated as HA, HA-20BT, HA-40BT, HA-60BT, and HA-80BT, respectively. The powder compacts were consolidated at temperature of 1200°C for 2 hrs in air atmosphere. In order to avoid decomposition of HA, sintering temperature was kept low. The synthesized samples were cut into the rectangular strips ($\sim 1.5 \text{ mm} \times 5 \text{ mm}$) using a cutting saw. The samples were placed between the specimen push rod. The thermal expansion measurement of the samples were performed in the temperature range of -150 to 300°C , while heating and cooling at a constant rate ($3^{\circ}\text{C}/\text{min}$), using dual push rod dilatometer [Theta Industries; Dilatronic VIII].

3. Results and Discussion

The coefficients of thermal expansion (CTE) measured in the temperature range of -150 to 300°C for all the developed dense composites ($\rho_{\text{th}} \sim 95\%$) are shown in Fig. 1. Figure 2 represents the variation in instantaneous coefficient of thermal expansion (CTE) with temperature. As these composites have been developed for orthopedic implant applications, the thermal expansion behavior of both the constituents of composite under *in vivo* environment (37°C) is the matter of significant concern. The calculated CTE values for pure HA, HA-20BT, HA-40BT, HA-60BT, HA-80BT in the temperature range of 0 to 50°C are $12.52 \times 10^{-6}/^{\circ}\text{C}$, $10.95 \times 10^{-6}/^{\circ}\text{C}$, $11.9 \times 10^{-6}/^{\circ}\text{C}$, $12.06 \times 10^{-6}/^{\circ}\text{C}$, and $10.96 \times 10^{-6}/^{\circ}\text{C}$, respectively. Table 1 summarizes the values of CTE in different temperature range of measurements. From these results, it is clear that the dispersion in CTE values for the developed composites in the temperature range close to the human body temperature is almost negligible. Apart from the biocompatibility and significant electrical activity, the stability in CTE values over a wide range of temperature further confirms the suitability of HA- BaTiO_3 composites as a potential orthopedic implant material.

Pal and Saha [15] reported the CTE value for the human tibia bone measured in the temperature range of -20°C to 20°C was $23 \times 10^{-6}/^{\circ}\text{C}$ to $32 \times 10^{-6}/^{\circ}\text{C}$. The value of CTE for pure HA obtained in this study is in well agreement with the values reported in literatures [16–20]. The CTE values for pure BT have been reported in the range of $6 \times 10^{-6}/^{\circ}\text{C}$ to $12 \times 10^{-6}/^{\circ}\text{C}$ [21, 22].

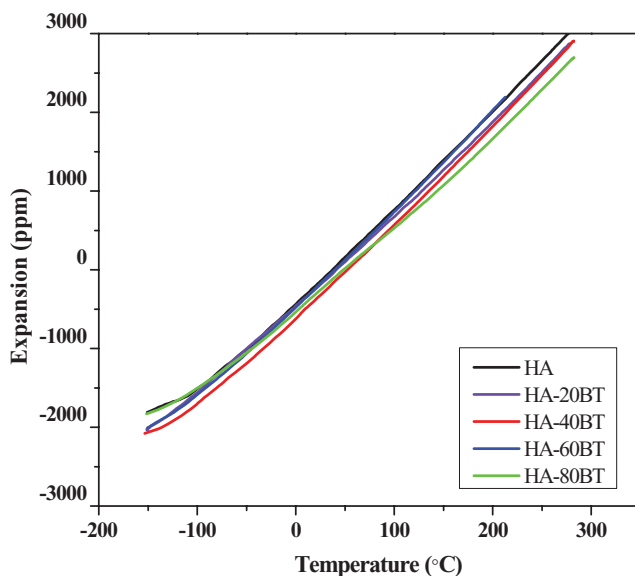


Figure 1. Variation of thermal expansion with temperature for the developed composites.

An important aspect associated with the thermal expansion behavior of HA-BT composites is the ferroelectric phase transitions in BT. For example, the cubic to tetragonal phase transition in the present case seems to vary around 90°C–140°C (Table 1) depending upon the BT content in HA matrix and mode of thermal operation (heating or cooling). From the Table 1, it can be inferred that lower is the BT content (~12 vol.%), more is the

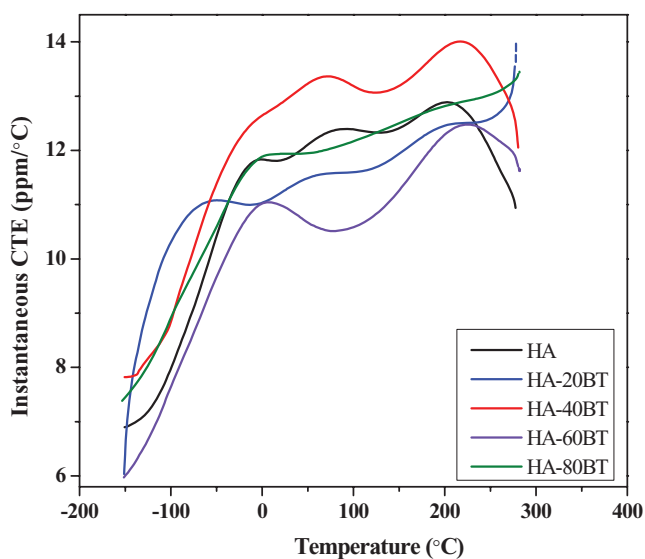


Figure 2. Variation of instantaneous coefficient of thermal expansion (CTE) with temperature for the developed composites.

Table 1
Coefficients of thermal expansion measured in different temperature ranges and corresponding phase transitions for the developed composites

Material	Temperature (°C)	Heating CTE $\times(10^{-6}/^{\circ}\text{C})$	Cooling CTE $\times(10^{-6}/^{\circ}\text{C})$	Transition Temperatures (°C)	
				Heating Run	Cooling Run
HA	100 to 280	13.59	14.20	No phase transitions	No phase transitions
	0 to 50 (-150) to (-50)	12.52 7.94	13.02 8.88		
HA-20BT (HA-12 vol.% BT)	100 to 280	12.36	13.25	(-100), (-22),106	(-121), (-65), 90
	0 to 50 (-150) to (-50)	10.95 8.84	11.85 9.64		
HA-40BT (HA-26 vol.% BT)	100 to 280	12.81	13.24	(-130), (-27),113	(-123), (-77),100
	0 to 50 (-150) to (-50)	11.9 8.75	13.5 9.65		
HA-60BT (HA-44 vol.% BT)	300 to 100	13.21	13.43	(-128), (-24),129	(-128), (-44),111
	0 to 50 (-150) to 100	12.06 11.87	12.23 10.72		
HA-80BT (HA-68vol.% BT)	300 to 100	11.87	12.13	(-115), (-35),147	(-117), 0.2,126
	0 to 50 (-150) to (-50)	10.96 7.63	10.47 7.81		

matrix constraint towards the phase transformation of BT which might resulting the phase transition of BT at relatively higher temperatures. For higher BT content (≥ 26 vol.%), the transition temperature is close to that of pure BT.

4. Conclusions

The experimental results confirm stable linear thermal expansion behavior of both HA and HA-BaTiO₃ composites. Pressureless sintered HA and HA-BaTiO₃ composites exhibited almost stable values of thermal expansion coefficients ($\sim 10 \times 10^{-6}/^{\circ}\text{C}$) in the entire temperature range of measurement. The phase transition in BaTiO₃ seems to be affected by the structural constraints imposed by HA in the developed composite. The measured

values of coefficients of thermal expansion for these composites are similar to the human cortical bone.

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References

1. B. D. Ratner, A. S. Hoffman, F. J. Schoen, and J. E. Lemons, *Biomaterials Science: An Introduction to Materials in Medicine*. Elsevier Academic Press, London; 2004.
2. Jeffrey O. Hollinger, Thomas A. Einhorn, Bruce A. Doll, and Charles Steir, *Bone Tissue Engineering*, CRC Press LLC, 2005.
3. S. Nath, B. Basu, M. Mohanty, and P. V. Mohanan, In vivo response of novel calcium phosphate-mullite composites: results upto 12 weeks of implantation. *J. Biomed. Mater. Res. B: Appl. Biomater.* **90B**, 547–557 (2009).
4. S. Nath, A. K. Dubey, and B. Basu, Mechanical properties evaluation of novel calcium phosphate-mullite biocomposites. *J. Biomat. Appl.* (In press, 2010) (DOI: 10.1177/0885328210393292).
5. Ashutosh Kumar Dubey, Garima Tripathi, and Bikramjit Basu, Characterization of hydroxyapatite-perovskite (CaTiO₃) composites: Phase evaluation and cellular response. *J. Biomedical Materials Research Part B: Applied Biomaterials* **95B**, 320–329 (2010).
6. Ashutosh Kumar Dubey, Shourya Dutta Gupta, and Bikramjit Basu, Optimization of electrical stimulation conditions for enhanced fibroblast cell proliferation on biomaterial surfaces. *J. Biomedical Materials Research Part B: Applied Biomaterials* In Press (2011) (DOI: 10.1002/jbm.b.31827).
7. I. Yasuda, *J. Japan Arthrop. Surg. Soc.* **28**(3), 4 (1954) (In Japanese).
8. S. B. Lang, *Nature* **212**, 704 (1966).
9. J. B. Park, A. F. von Recum, G. H. Kenner, B. J. Kelly, W. W. Coffeen, and M. F. Grether, Piezoelectric ceramic implants: A feasibility study. *J. Biomed. Mater. Res.* **14**(3), 269–277 (1980 May).
10. J. B. Park, B. J. Kelly, G. H. Kenner, A. F. von Recum, M. F. Grether, and W. W. Coffeen, Piezoelectric ceramic implants: in vivo results. *J. Biomed. Mater. Res.* **15**(1), 103–110 (1981 Jan).
11. X. M. Chen and B. Yang, A new approach for toughening of ceramics. *Materials Letters* **33**, 237–240 (1997).
12. B. Yang and X. M. Chen, Alumina ceramics toughened by a piezoelectric secondary phase. *Journal of the European Ceramic Society* **20**, 1687–1690 (2000).
13. Rathje W. Zur Kenntnis de Phosphate, *I. Uber. Hydroxyapatite. Bodenk Pflernah.* **12**, 121–128 (1939).
14. M. H. Santos, M. Oliveira, L. P. F. Souza, H. S. Mansur, and W. L. Vasconcelos, Synthesis control and characterization of hydroxyapatite prepared by wet precipitation process. *Mater. Res.* **7**, 625–630 (2004).
15. S. Pal and S. Saha, *Coefficient of Thermal Expansion of Bone. Biomechanics*. Wiley, 1989. 52–60.
16. Miyazaki Hidetoshi and Isao Ushiroda, Thermal Expansion of Hydroxyapatite between –100 °C and 50 °C. *Materials Science and Engineering C* **29**, 1463–1466 (2009).
17. S. Zhang, Z. Xianting, W. Yongsheng, C. Kui, and W. Wenjian, *Surf. Coat. Technol.* **22–23**, 6350 (2006).
18. J. Brems, Y. Zhou, and L. Groh, *Biomaterials* **16**, 239 (1995).
19. G. Jiang and D. Shi, *J. Biomed. Mater. Res.* **43**, 77 (1998).

20. S. Zhang, Z. Xianting, W. Yongsheng, C. Kui, W. Wenjian, *Surf. Coat. Technol.* **22–23**, 6350 (2006).
21. Y. He, Heat capacity, thermal conductivity, and thermal expansion of barium titanate-based ceramics. *Thermochimica Acta* **419.1-2**, 135–141 (2004).
22. M. V. Radhika Rao, and A. M. Umarji, Thermal expansion studies on ferroelectric materials. *Bull. Mater. Sci.* **20**, 1023–1028 (1997).