Thermal Properties of BaTiO₃/Ag Composites at Different Temperatures

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Abstract:

This study examines the thermal properties, i.e. thermal expansion, specific heat, and thermal conductivity, of active composites comprising of barium titanate (BaTiO₃) and silver (Ag). BaTiO₃/Ag composites with varying silver composition were fabricated by powder metallurgy technique. The coefficient of thermal expansion (CTE) was measured within -50 to 250 °C temperature range using thermal mechanical analyzer (TMA). Differential scanning calorimeter (DSC) was used to measure the specific heat of the composites at a constant pressure within -50 to 200 °C temperature range, while, thermal conductivity and thermal diffusivity were measured by HotDisk technique. The effect of silver content on various thermal properties was investigated experimentally and numerically. The experimental results were also compared with some available experimental data from literature. As for the numerical investigations, 2-D and 3-D micromechanical models were constructed from realistic and randomly generated microstructures in order to predict the effective CTE and thermal conductivity of the composite, and investigate the local field fluctuations. The micromechanical models were implemented in finite elements. The effects of loading direction, porosity, particle shape and dispersion, and material properties of constituents were also studied. Numerical results for 2-D micromechanical models and 3-D generated microstructural models were compared to the experimental data.

1. Introduction

Barium titanate (BaTiO₃) has perovskite type crystalline structures with the Currie temperature around 120 °C. Above the Currie temperature, the perovskite crystalline structure is cubic and non-polar, while below its Currie temperature, BaTiO₃ undergoes a phase transformation to a tetragonal phase, in which a spontaneous polarization occurs. When further cooling BaTiO₃, another phase transformation occurs around 0 °C, at which the crystalline structure changes to an orthorhombic [Forsbergh, 1949; Frazer, 1955; Zhong, 1994; Jaffe, 2012]. Due to its relatively high dielectric constants BaTiO₃ based ceramics have found many applications. **For example, it can be used as reinforcement to improve the dielectric constant of the composite [Wang, Li et al. 2011, Goyal, Katkade et al. 2013].** It is also widely used in electronic industry like multilayer ceramic capacitors (MLCCs) [Hennings, 1987; Sakabe, 1997; Kishi, 2003]. MLCCs nowadays are widely used in electronic industry because of their high capacitance, relatively small size, and

good reliability. For instance, MLCCs are key parts of integrated circuit (IC), which are either embedded in or bonded to the surface of a substrate [Setter, 2000]. The key challenge in such applications is the thermal management because large amount of heat would be generated during service. The mismatch in the thermal properties between MLCC materials and substrates would introduce thermal stresses, which, if large enough, would lead to debonding at the interface or crack in the materials during cycling operations [He, 2004]. BaTiO₃ based ceramics are also preferred for actuator and sensor applications because they do not contain lead as some other piezoelectric ceramics [Takenaka, 1991; Karaki, 2007]. Due to the large heat generation during cycling service, good thermal management is also a key issue for the integrity and reliability of those devices. In order to improve the durability of BaTiO₃ ceramic based devices under harsh thermal environment, metal phase were doped in BaTiO₃ matrix in order to fabricate ceramic/metal composite [Ikushima, 1965; Chen, 1999; Halder, 1999; Chen, 2000; Panteny, 2006; Panteny, 2006; Kojima, 2009; Sánchez-Jiménez, 2010]. Compared to monolithic ceramics, the mechanical properties, such as fracture strength and fracture toughness, of the composite containing metallic phase were also greatly enhanced. On the other hand, the introduction of metal phase to BaTiO₃ ceramics also can increase its dielectric constants, which is beneficial to the miniaturization of MLCC [Hennings, 1987]. This study focuses on the thermal properties of BaTiO₃/Ag composite that are investigated at various temperatures, both experimentally and numerically.

Several sintering techniques have been considered to obtain bulk and dense BaTiO₃ ceramics with desired microstructures. The most widely used technique is the conventional powder metallurgy method [Jaffe, 2012], which is a relatively easy and inexpensive way to produce bulk ceramics with good density. The disadvantage of this method is that it is difficult to control the grain size, which significantly influences the macroscopic properties of BaTiO₃, especially its dielectric properties [Arlt, 1985]. To overcome this drawback, Chen and Wang [Chen, 2000] introduced a novel two-step sintering technique, in which the mechanisms of grain boundary controlled densification and grain boundary controlled grain growth were exploited to suppress the rapid grain growth in the final stage of sintering. Several authors successfully utilized this technique to fabricate dense BaTiO₃ ceramics with nano grain size [Polotai, 2005; Deng, 2006; Karaki, 2007]. Another method to obtain dense BaTiO₃ ceramic with small grain size is spark plasma sintering (SPS). Spark plasma sintering combines hot-pressing and electrical current. Compared with the conventional sintering, in SPS process the powder can be sintered at a lower temperature and in a much shorter sintering time, which is favorable for suppressing the undesired grain growth [Li, 2003; Zhao, 2004; Deng, 2006].

Metal phase doped ferroelectric ceramics, such as BaTiO₃ and lead zirconate titanate (PZT), were extensively studied by researchers. The doping by Ag can lower the starting temperature of densification and enhance the densification rate. [Chen, 1999; Panteny, 2006]. In addition, a small amount of silver would increase the relative density, since they can fill the pores within the ceramic [George, 2009]. It was reported that Curie temperature would decrease as silver content increase due to the substitution of silver in

A-site of the perovskite crystal structure [Ikushima, 1965; Maher, 1983]. However, as reported in [Hwang, 1998], the addition of silver increases the Curie temperature of PZT due to the relaxation of transformation-induced internal stress in the “soft” silver phase. Since silver is much softer than BaTiO₃, the hardness and stiffness are reduced by adding silver phase [Panteny, 2006]. Silver particles are located at either BaTiO₃ grain boundary junctions or within individual BaTiO₃ grains [Chen, 1999; Panteny, 2006]. They can increase the toughness of the ceramic by crack bridging or crack deflection mechanisms [Chou, 1995; Panteny, 2006]. On the other hand, adding silver phase may introduce more defects and pores, which reduces the fracture toughness. Silver inclusion in the ceramic also forms conductive phase and increases the electric field intensity, which significantly increases the dielectric constants [Panteny, 2006; Kojima, 2009]. The thermal properties of monolithic BaTiO₃ ceramics have been studied in several literatures [Sawada, 1949; Shirane, 1952; Rao, 1997; He, 2004]. However, limited studies are available on the influence of silver reinforcement on the thermal properties of the composites.

The effective CTE and thermal conductivity (λ_{eff}) of different composites have been determined from various micromechanical models. An early development of micromechanics models considers idealized microstructures, such as spherical or ellipsoidal inclusions dispersed in homogeneous matrix, linear thermo-elastic behaviors of the constituents, perfect bonding at the interfaces, etc. Based on such simplifications analytical formulas can be derived for the effective CTE and λ_{eff} , for example [Turner, 1942; Kerner, 1956; Schapery, 1968; Fahmy, 1970; Rosen, 1970] for CTE and [Cheng, 1969; Davis, 1986; Sangani, 1988; Verma, 1991; Klemens, 1990; [Andrianov et al. 2013](#); [Yu et al. 2013](#)] for λ_{eff} . Benveniste, 1986 and Hasselman, 1987 also considered the effect of thermal barrier at phase boundaries. Khan, 2010, Khan, 2011, and Muliana, 2012 developed unit cell models to numerically predict the effective CTE and thermal conductivity of two phase composites. Though simplified microstructural geometry were assumed, these models can be applied to composites consisting of nonlinear constituent with field dependent material properties [[Lin and Muliana 2015](#)]. Another type of micromechanics models were based on detailed microstructures of the composite. The detailed microstructures can either be randomly generated by computer algorithms, [Böhm, 2002; Segurado, 2002; González, 2004; Lévesque, 2004], or obtained from the experiments using scanning electronic microscopy (SEM), [Bakshi, 2010; Chawla, 2002; Langer, 2001; Wang, 2003; Gudlur et al. 2014 a,b,c]. Finite element methods are often employed to solve a boundary value problem, from which the effective properties can be calculated. Advantages of such model are nonlinear constituents and complex reinforcement shapes can be easily incorporated. It can simulate the detailed local field fluctuations, such as thermal residual stresses, stress concentrations, and heat flux path. However, to accurately represent the phase boundaries very fine finite element meshes are need, which make it computationally expensive. When the reinforcement volume fraction and the ratio of thermal conductivity of the particles to the matrix are relatively small the above micromechanics model can give reasonable predictions of λ_{eff} . However, as the volume fraction of reinforcement and differences between the properties of the constituents increase significant mismatches in micromechanics predictions and

experiments were observed as shown by [Khan, 2010]. This is due to the formation of thermal conductivity chains by the reinforcement particles with high thermal conductivity [Agari, 1985; Agari, 1986; Zhang, 2005]. Heat can flow following such high conductivity chains much easier compared to other parts of the composites, which significantly increases the effective thermal conductivity [Zhou, 2007].

In this study, we investigated the influence of silver phase on the thermal properties of the BaTiO₃/Ag composite, both experimentally and numerically. BaTiO₃/Ag composite samples with varying silver compositions were made by powder metallurgy technique. Thermo-mechanical analysis (TMA) within the temperature range of -50 to 250 °C and differential scanning calorimetry (DSC) within the temperature range of -50 to 200 °C were conducted to determine the CTE and heat capacity of the composites. The temperature ranges were selected in order to induce the two-phase transformations in the BaTiO₃. We also measured the thermal conductivity and thermal diffusivity at higher temperatures using HotDisk technique. Two micromechanics models based on detailed microstructures were constructed to predict the effective CTE and thermal conductivity. One model is 2-D based on experimental obtained microstructures from SEM images and the other is 3-D based on randomly generated microstructure using random sequential addition algorithm. The influence of microstructural morphologies, such as particle shapes, distribution, and pores, on the effective thermal properties were also investigated. The numerical predictions were compared with the experimentally measured values.

2. Experimental procedures

2.1. Materials and sample preparation

Powder metallurgy method was used to prepare BaTiO₃/Ag composite samples. 99.95% pure BaTiO₃ powder (Inframat Advanced Materials) with an average particle size of 100 nm and 99.9% pure silver power (Alfa Aesar) with an average 4-7 μm particle size were used as starting powders. Two different fabrication procedures were employed to manufacture samples for various thermal testing. For thermal expansion and heat capacity testing samples (procedure A), 0.5 wt% of polyvinyl alcohol binder was added to the BaTiO₃/Ag powder mixture to avoid cracking during cold-pressing. To uniformly mix the binder with BaTiO₃/Ag powder, polyvinyl alcohol was first dissolved into distilled water, then added to BaTiO₃/Ag powder mixture that was subsequently ball-milled for 30 min. The ball-milled powder was dried in a heating oven and further grinded in a mortar. The final powder was poured into a cylindrical die of 1/2 inch in diameter and a hydraulic press was used to cold-press the powders at room temperature under a pressure of 100 MPa. The binder was burned out at 600 °C for 2 hours. For thermal conductivity testing samples (procedure B), firstly the mixture of BaTiO₃/Ag powder was shaped by cold-pressing at 20 MPa using a split sleeve pressing die (Across International) of 1 inch in diameter. Secondly, the shaped cylindrical body was pressed under hydrostatic pressure using cold isostatic pressing (CIP, American Isostatic Presses,

Inc.) with a pressure of 200 MPa. The cold-pressed cylindrical green bodies were sintered at 1250 °C for 6 hours in air atmosphere. The heating/cooling rates were 3 °C/min. SEM images of typical BaTiO₃/Ag composite samples with 10 vof% silver are shown in Figure 1.

Figure 1 SEM images of typical 10 vof% BaTiO₃/Ag composite samples from different fabrication procedures: left, procedure A; right, procedure B.

2.2 Density

Density was measured by Archimedes' principle, and more details can be found in ASTM standard C 20 [2010]. 200% proof ethanol was used as the immersion liquid. The density ρ of the sample is given by the following equation:

$$\rho_{sample} = \frac{m_{dry}\rho_{ethanol}}{m_{wet} - m_{suspended} + m_{wire}} \quad (1)$$

where m_{dry} is the mass of the sample before immersed in ethanol liquid, $m_{suspended}$ is the mass of the sample measured when suspended in ethanol liquid, m_{wet} is the mass of the sample after soaking in the ethanol, m_{wire} is the mass of suspending system, and $\rho_{ethanol}$ is the density of the ethanol at certain temperature which was measured during the testing. The relative density of the sample is then determined by

$$\text{Relative density} = \frac{\rho_{sample}}{\text{Theoretical density}} \quad (2)$$

In addition, the open and closed porosity of the sample can be calculated by the following:

$$\text{Open porosity} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{wet}} - m_{\text{suspended}} + m_{\text{wire}}} \quad (3)$$

$$\text{Closed porosity} = 100\% - \text{Relative density} - \text{Open porosity} \quad (4)$$

2.3 Thermal expansion

The coefficient of thermal expansion of BaTiO₃/Ag composite was measured using a thermal mechanical analyzer (TA Q400, TA instruments, UT), within a temperature range from -50 to 250 °C. The height of the cylindrical samples was between 7 and 10 mm and the diameter was about 9 mm. The top and bottom surfaces were carefully polished to make them parallel. A preload of 0.1 N was applied to ensure perfect contact between the probe and the sample surfaces. To ensure repeatability of the tests two samples were tested for each composition in three heating/cooling cycles each. The heating and cooling rates were 5 °C/min and 4.6 °C/min, respectively, according to ASTM standard E831 [2014]. Changes in height of the specimen were recorded as a function of temperature. The thermal strain was calculated by dividing the change of height by the original height of the specimen at room temperature. The slope of thermal strain versus temperature curve gives the CTE of the composite.

2.4 Heat capacity

The specific heat at constant pressure, C_p , was measured by a differential scanning calorimetry (DSC; TA Q20, TA Instrument, DE). The composite samples were machined into small disk to fit them into the specimen holder, i.e. alumina pan. A synthetic sapphire disk (α -aluminum oxide, TA Instruments) was used as the standard reference material. The scanning was conducted within a temperature range from -50 to 200 °C with a heating/cooling rate of 10 °C/min. The heat flow of BaTiO₃/Ag composite during heating/cooling cycles was monitored and recorded as a function of temperature, from which the heat capacity can be calculated. To ensure repeatability of the tests two samples were tested for each composition and two heating/cooling cycles were carried out for each specimen. To accurately determine the heat capacity the recommended procedure given by ASTM standard E1269 [2011] was followed. First, the heat flow curve of an empty aluminum pan was measured which would be used as a baseline. Then, the standard sapphire sample was put in the aluminum pan and a reference heat flow curve was measured. Finally, the heat flow curve of the composite was measured using the same aluminum pan. The specific heat of the composite can be determined by the following formula:

$$C_p(s) = C_p(st) \cdot \frac{D_s \cdot W_{st}}{D_{st} \cdot W_s} \quad (5)$$

where $C_p(s)$ and $C_p(st)$ are the specific heat of the specimen and sapphire sample, respectively; D_s and D_{st} are the net heat flow of the specimen and sapphire sample at a given temperature; W_s and W_{st} are the mass of the specimen and sapphire sample.

2.5 Thermal conductivity and thermal diffusivity

Hot disk technique (TPS 2500 S, Hot Disk AB), a transient plane source technique, was used to measure the thermal conductivity of the composites at ambient and elevated temperature up to 175 °C. During the measurement, a hot disk sensor made of double spiral of nickel wire embedded in Kapton polyimide film was used to generate heat and, at the same time, monitor the temperature changes. It was sandwiched between two cylindrical samples with diameter of 20 mm and height of 9 mm. The recorded temperature change ΔT determined from the electrical resistance change of the nickel sensor is related to the thermal properties of surrounding samples by the following equation [Gustafsson, 1991; He, 2005]:

$$\Delta T(t) = \frac{F(\tau)}{K} \quad (6)$$

where K is the thermal conductivity of surrounding samples, F is a function depending on $\tau = \sqrt{\kappa t}/r^2$ and other parameters, κ is the thermal diffusivity of surrounding samples, and r is the radius of the nickel sensor. Thermal conductivity, K , of the samples can be calculated by fitting equation (6). Since thermal diffusivity is related to thermal conductivity by $K = \rho C_p \kappa$, once we know the density and specific heat of the sample, we can also obtain its thermal diffusivity. To arrive equation (6) infinite domain was assumed, since our samples have finite size we need to make sure that the ambient atmosphere would not affect the transient heat transfer in the nickel sensor, which can be achieved by setting the measurement time $t < r^2/(4\kappa)$ [Gustafsson, 1986]. In this study, the measurement time was set between 2.5 to 7 seconds depending on the sample size and thermal diffusivity. The radius of nickel sensor is 3.189 mm and the output power to the sensor was 0.2 W. To ensure the repeatability four measurements were conducted for each silver composition.

3. Experimental Results

3.1 Density

The density of composite samples made using procedures A and B are shown in Table 1. The relative density, open porosity and closed porosity were also calculated. There is no significant difference in relative densities between samples made using procedure A and procedure B, which means the final density is more controlled by sintering process rather

than cold compaction. The relative density almost stays unchanged for different silver compositions.

Table 1 Density and porosity of BaTiO₃/Ag composite made by procedure A and B

	Procedure A				Procedure B		
Volume Fraction	0 vol%	5 vol%	10 vol%	15 vol%	0 vol%	5 vol%	10 vol%
Density ρ (g/cm ³)	5.75±0.02	6.03±0.01	6.18±0.01	6.42±0.01	5.80±0.01	6.03±0.01	6.22±0.01
Relative density (%)	95.44	96.61	95.56	96.01	96.39	96.57	96.11
Open porosity (%)	1.83	0.13	0.31	0.21	0.26	0.06	0.09
Closed porosity (%)	2.73	3.26	4.13	3.78	3.35	3.36	3.80

3.2 Thermal expansion

The engineering thermal strain as a function of temperature is shown in Figure 2 for different silver compositions. Both heating and cooling curves were drawn from the second running cycle. Thermal hysteresis exists during each heating/cooling cycle, which is due to the energy dissipated during phase transformations. Within the temperature range from -50 to 250 °C two phase transitions occur around 0 °C and 120 °C, i.e. orthorhombic phase to tetragonal phase and tetragonal phase to cubic phase. Around phase transformation temperatures there are obvious shrinkage during the heating cycles and expansion during the cooling cycles, which can be attributed to the contractions or elongations of crystalline lattices. Phase transformation temperatures obtained from the thermal expansion measurement are listed in Table 2Table 1. The phase transformation temperatures are slightly lower during the cooling cycles (T-O and C-T) than those in the heating cycles (O-T and T-C). The reason for this is that the thermal sensor in TMA measures the ambient temperature. However, the actual temperature in the sample might show certain lag with the ambient temperature. As a result, the actual temperature in the sample might be slightly lower than the recorded one during heating, while slightly higher during cooling. We noticed that the two phase transformation temperatures are slightly different from the previous reported values, namely 0 °C and 120 °C [He, 2004]. The slope of the thermal strain versus temperature curve gives the CTE of BaTiO₃/Ag composite. Within each phase the thermal strain versus temperature curve shows a nearly straight line, which means the CTE of BaTiO₃/Ag composites is constant at each individual phase. However, as shown in Figure 3 the CTE significantly increases from the orthorhombic phase to the tetragonal phase and from the tetragonal phase to the cubic phase. The CTEs calculated during heating and cooling are slightly different. The relative difference, however, is no more than 10.24%. The CTE slightly increases with the increase of silver content because the CTE of silver is significantly higher than that of BaTiO₃. Table 3 compares the CTE of BaTiO₃ ceramic at different crystalline phases with reported data in literature. For all crystalline phases the CTE of BaTiO₃ measured in this work is slightly higher than the value previously reported in [Shirane, 1952]. In the work of [He, 2004] the phase transformation around 0 °C was not detected and the CTE of monolithic BaTiO₃ ceramic calculated between 0 and 50 °C is $6 \times 10^{-6} \text{ K}^{-1}$ which is between the CTE values measured at orthorhombic phase and tetragonal phase in this

work. The CTE of BaTiO₃ at cubic phase is $10.51 \times 10^{-6} \text{ K}^{-1}$, which is close to the value of $11.35 \times 10^{-6} \text{ K}^{-1}$ reported in [He, 2004]. The CTEs of BaTiO₃/Ag composites with different silver content for each individual phase are listed in Table 4.

Table 2 Phase transformation temperatures obtained from TMA tests and DSC tests, respectively.

Volume fraction	TMA results (°C)				DSC results (°C)			
	O-T	T-O	T-C	C-T	O-T	T-O	T-C	C-T
0 %	33.0	3.5	120.7	102.8	20.6	6.5	126.8	122.6
5 %	27.7	1.3	119.7	104.1	18.7	9.4	129.1	125.6
10 %	27.8	3.2	117.9	103.9	17.5	9.8	128.3	124.7
15 %	31.2	6.9	122.7	106.7	18.9	10.6	128.6	124.4

O-T: orthorhombic to tetragonal

T-O: tetragonal to orthorhombic

T-C: tetragonal to cubic

C-T: cubic to tetragonal

Table 3 Comparison of CTE for BaTiO₃ with literature data

Crystalline phase	BaTiO ₃ (10^{-6} K^{-1})		
	Present work	He ^a	Shirane et al. ^b
Orthorhombic phase	5.30	-	4.60
Tetragonal phase	7.52	6.00	6.50
Cubic phase	10.51	11.35	9.80

^a [He, 2004]

^b [Shirane, 1952]

Table 4 Coefficient of thermal expansion (CTE) for BaTiO₃/Ag composite.

Crystalline phase	CTE for different silver VF (10^{-6} K^{-1})			
	0 vol%	5 vol%	10 vol%	15 vol%
Orthorhombic phase	5.30	6.23	6.76	7.19
Tetragonal phase	7.52	8.35	9.04	9.65
Cubic phase	10.51	11.03	11.52	11.79

Figure 2 Engineering thermal strain as a function of temperature for BaTiO₃/Ag composites

Figure 3 Coefficients of thermal expansion for BaTiO₃/Ag composites

3.3 Heat capacity

Typical heat flow curves for BaTiO₃/Ag composite obtained from differential scanning calorimetry (DSC) are shown in Figure 4. It consists of one baseline curve of an empty aluminum pan, one reference curve of a standard sapphire sample and one heat flow curve of a BaTiO₃/Ag specimen. The specific heat capacity of the composite can be calculated by using the vertical distances from the heat flow curves of sapphire sample and BaTiO₃ specimen to the baseline curve. The phase transformation temperatures obtained by DSC measurement are listed in Table 2. They do not change as the silver content increases, similar to what has been observed in the results of thermal expansion. The phase transformation temperatures measured during heating are slightly higher than those measured during cooling, though such discrepancy is smaller compared with the one from the thermal expansion test. Phase transformation temperatures obtained by DSC measurement are slightly different from those by TMA measurement most likely due to different heating/cooling rate. The heat capacities of BaTiO₃/Ag composite as a function of temperature for each individual phase are shown in Figure 5. In contrast with CTE, the heat capacity continuously increases as the temperature increases. An increase in silver contents slightly decreases the heat capacity due to its relatively smaller content in the composites. The large standard deviation in the measurements may be due to the fact the sample used in the testing is very small. As a result it cannot adequately represent the macroscopic property of the composites due to its inhomogeneity. In this study the measured heat capacity for pure BaTiO₃ at room temperature is 0.456 J/g.K which is consistent to previously reported values, 0.434 J/g.K in [He, 2004] and 0.439 J/g.K in [Touloukian, 1970].

Figure 4 Heat flow curves for empty pan, sapphire standard and BaTiO₃ specimen

Figure 5 Heat capacity of BaTiO₃/Ag composites as a function of temperature

3.4 Thermal conductivity and thermal diffusivity

The thermal conductivity of BaTiO₃/Ag composite at room and elevated temperatures was measured by Hot Disk technique, as shown in Figure 6. For a fixed silver composition the thermal conductivity of the composite remains nearly constant below its tetragonal to cubic transformation temperature, which is around 120 °C, then slightly decreases and stays constant after that up to 175 °C. As the silver content increases, the thermal conductivity of the composite is greatly enhanced due to the formation of conductive particle chains [Agari, 1985; Agari, 1986], which is enhanced by the high contrast of the thermal conductivities between silver and BaTiO₃. Heat can flow easily following such conductive chains which greatly enhances the effective thermal conductivity. The measured thermal conductivity of monolithic BaTiO₃ ceramic at room temperature is 3.672 W/(mk) which is larger than the value of 2.85 W/(mk) previously reported in [He, 2004] but is within the range of 1.3 to 6 W/(mk) reported in [Touloukian, 1970]. Possible reasons for the variation of thermal conductivity are due to different manufacturing procedures, different dopants added to the material and different measurement techniques used. The thermal diffusivity decreases with an increase of silver content, as shown in Figure 7. In this work the room-temperature value of monolithic BaTiO₃ ceramic is 1.438 mm²/s, which is higher than 1.03 mm²/s and 1.18 mm²/s reported in [He, 2004]. **Thermal conductivity and thermal diffusivity of BaTiO₃/Ag composites at ambient and elevated temperatures are listed in Table 5 for reference.**

Figure 6 Thermal conductivity of BaTiO₃/Ag composite as a function of temperature

Figure 7 Thermal diffusivity of BaTiO₃/Ag composite as a function of temperature

Table 5. Thermal conductivity and thermal diffusivity of BaTiO₃/Ag composites at elevated temperatures

		Temperature					
		25 °C	75 °C	100 °C	125 °C	150 °C	175 °C
Thermal conductivity (W/mK)	0 vol%	3.672	3.657	3.572	3.450	3.297	3.277
	5 vol%	4.623	4.569	4.417	4.283	4.140	4.129
	10 vol%	6.077	6.142	5.969	5.825	5.688	5.664
Thermal diffusivity (mm ² /s)	0 vol%	1.438	1.231	1.164	1.085	1.076	1.055
	5 vol%	1.814	1.635	1.545	1.418	1.426	1.408
	10 vol%	2.713	2.380	2.261	2.116	2.167	2.132

4. Finite element analyses and discussion

Numerical analyses based on micromechanical models were carried out to determine the effective thermal properties of BaTiO₃/Ag composites. Two types of microstructural models implemented in finite element (FE) were considered. The first model was constructed from 2-D microstructural of the composite obtained using scanning electron microscope (SEM) images that were further converted into finite element meshes using OOF software as it is described in more details in [Gudlur et al. 2014 a,b,c]. The second model was based on 3-D representative volume element (RVE) of randomly generated solid spherical inclusions dispersed in homogeneous matrix. An advantage of micromechanical models is that it allows investigating the influence of detailed microstructures (particle shape, size, and distribution) on local field fluctuations, such as thermal residual stresses and heat fluxes, on the overall performance of composites. The overall properties of the thermal properties determined from the two different models were compared to each other, as well as to experimental results.

4.1. Finite element microstructural models

For the 2-D microstructural models of the composite samples, four FE models (FE model #1-4) were generated for each composition to study the reliability of the microstructural representation. The SEM images of these four FE models were taken at different locations of the same sample. The physical sizes of the SEM images range from 415 µm to 547 µm, which were selected based on the following reasons: (1) big enough to represent the overall behavior of the composites; (2) different constituents can be clearly identified; (3) considerations of computational costs. The meshes were generated using the open source software OOF [Langer S, 2007] and the finite element analyses were carried out using ABAQUS.

Typical microstructures and FE models for 10 vol% BaTiO₃/Ag composite are shown in Figure 8. Figure 8(a) shows the SEM images, in which white colored phase is silver, while gray colored phase is BaTiO₃. Pores can be seen as black areas on the same figure. To study the influence of pores on the effective thermal behaviors, FE models with and without pores were created. A FE mesh generated by OOF2 is shown on Figure 8 (b)-(c). Inside of each phase the meshes are relatively uniform while at the phase boundaries it is refined to generate a more accurate representation. The meshes for different FE models contain 70,000 to 100,000 elements depending on their detailed microstructures. Silver and pore volume fractions for various FE models are listed in Table 6. The listed values for each composition are averaged from four different models. The standard deviations for these four models are also included.

Figure 8 Selected but typical microstructure and 2-D FE models for 10 vol% BaTiO₃/Ag composites: (a) SEM image with size 547 x 547 μm ; (d) FE meshes; (c) Enlarged meshes of part of the model.

Table 6 Silver and pore volume fractions of 2-D FE models for effective CTE and λ_{eff} analysis

Samples	Phase volume fraction in 2-D FE models for effective CTE analysis		Phase volume fraction in 2-D FE models for effective λ_{eff} analysis	
	Silver VF (vol%)	Pores VF (vol%)	Silver VF (vol%)	Pores VF (vol%)
0 vol%	-	-	-	1.01±0.06
5 vol%	5.02±0.29	-	5.41±0.25	0.87±0.10
10 vol%	10.20±0.47	0.93±0.14	12.26±0.61	0.53±0.02
15 vol%	16.11±0.27	-	-	-

A 3-D finite element microstructural model was created by modified random sequential addition algorithm, which can generate statistically isotropic spatial dispersion of particles [Böhm, 2001]. The model consists of a cubic volume that contains 30 random and homogeneous distributed identical spherical particles. The radius r of each spherical particle can be calculated by the volume fraction of reinforcement particles and the number of particles generated within the cube. Overlapping between particles was excluded by the method of separating axis [Eberly, 2001]. A minimum distance between different particles and between particles and surfaces was enforced to avoid distortion of finite element meshes. The minimum distance was selected to make sure that at least two layers of elements were generated between particles. The particles intersecting with side surfaces of the cube were copied to appropriate opposite surfaces to make the unit cell symmetric. Since the number of randomly generated spherical particles in the cube is large enough, it is safe to treat the unit cell model as a representative volume element (RVE). A typical 3-D model with the finite element meshes is shown in Figure 9.

Figure 9 3-D FE model and meshes for typical 10 vol% BaTiO₃/Ag composites: (a) FE meshes of the composite; (b) FE meshes of silver particles.

Commercial software ABAQUS is used to perform the analyses of heat conduction and deformation due to temperature changes. The effective CTE is calculated from the thermal expansion analysis, while the effective thermal conductivity is calculated from a steady state heat transfer analysis. Boundary conditions and constraints applied to the 2-D FE model are given below, and those for the 3-D model can be derived similarly. For the thermal expansion analysis the following boundary conditions were employed,

$$\begin{aligned} u_x(0, y) &= 0; & 0 \leq y \leq L \\ u_y(x, 0) &= 0; & 0 \leq x \leq L \end{aligned} \quad (7)$$

Multipoint constraints were applied as follows to other edges to ensure their straightness after deformation,

$$\begin{aligned} u_x(L, y) &= u_{right}; & 0 \leq y \leq L \\ u_y(x, L) &= u_{top}; & 0 \leq x \leq L \end{aligned} \quad (8)$$

In ABAQUS thermal expansion analysis is implemented by defining temperature as a predefined field. If the initial temperature is T_i and the final temperature is T_f , the effective CTE was calculated by

$$\begin{aligned} \alpha_x &= \frac{\bar{\varepsilon}_{xx}}{\Delta T}, \quad \bar{\varepsilon}_{xx} = \frac{u_{right}}{L}, \quad \Delta T = T_f - T_i \\ \alpha_y &= \frac{\bar{\varepsilon}_{yy}}{\Delta T}, \quad \bar{\varepsilon}_{yy} = \frac{u_{top}}{L} \end{aligned} \quad (9)$$

To calculate the effective thermal conductivity in the x direction the following boundary condition and loading were employed,

$$\begin{aligned} T(0, y) &= 0; & 0 \leq y \leq L \\ q_x(L, y) &= q_{right}; & 0 \leq y \leq L \end{aligned} \quad (10)$$

where q_x is the external heat flux applied on the right edge.

A multipoint constraint was apply to enforce uniform temperature on the right edge during the analysis,

$$T(L, y) = T_{right}; \quad 0 \leq y \leq L \quad (11)$$

The thermal conductivity in x direction was given by

$$\lambda_x = \frac{q_x}{\bar{\beta}_x}, \quad \bar{\beta}_x = \frac{T_{right}}{L} \quad (12)$$

In addition to the above mixed boundary conditions (BCs) various other boundary conditions, such as constant temperature gradient, uniform flux and periodic BCs, were considered to understand their influence on the effective thermal conductivity. With respect to periodic BCs, since our microstructures and meshes are not periodic, polynomial functions are used to approximate the field fluctuations on the boundaries [Nguyen, V.-D., et al. 2012]. In ABAQUS polynomial functions and reference points are used as constraints to the boundaries. For example, the 2nd order polynomial approximation is defined by the following equations:

$$\begin{aligned} T(0, y) &= T_{x0} + T_{x1} \left(\frac{y}{L} \right) + T_{x2} \left(\frac{y}{L} \right)^2, & T(L, y) &= T(0, y) + \langle \bar{g} \rangle \cdot \bar{p}_x; \\ T(x, 0) &= T_{y0} + T_{y1} \left(\frac{x}{L} \right) + T_{y2} \left(\frac{x}{L} \right)^2, & T(x, L) &= T(x, 0) + \langle \bar{g} \rangle \cdot \bar{p}_y \end{aligned} \quad (13)$$

where $T_{x0}, \dots, T_{y2}$ are the temperatures at reference points; $\bar{p}_x = (L, 0)^T$ and $\bar{p}_y = (0, L)^T$; and $\langle \bar{g} \rangle$ are the applied macroscopic temperature gradients. It was shown [Jiang et al. 2002] that the effective thermal conductivities obtained by applying periodic BCs are bounded between those obtained from applying uniform flux and constant temperature gradient BCs, where the uniform flux BC leads to a lower bound and the constant temperature gradient BC leads to an upper bound. In addition, they showed that if the thermal conductivity of the particulate reinforcement is larger than that of the matrix, which is the case in this study, then the convergence rate of uniform flux BC is similar to that of periodic BC and is much faster than that of constant temperature gradient BC. The mixed BC gives a close prediction to the lower bound (uniform flux BC), see section 4.4. A constraint (equation (11)) in the mixed BC was applied to impose constant temperature on the edges. Then the corresponding temperature gradient is calculated from equation (12) instead of determining the volume average by numerical integration, which significantly reduces the computational cost. The predictions from the mixed BC are very close to uniform flux BC because such a constraint is very weak. As a result, in the following simulations the mixed BC are employed except a comparison of various BCs in section 4.4.

The finite element simulations for determining the overall thermal properties were conducted by prescribing fixed temperatures, discussed in Eqs. (9)-(12). For example, to calculate the effective thermal conductivity of the composite at 25 °C, the inputs are the thermal conductivities of the two constituents (BaTiO₃ and Ag) at 25 °C, while the thermal conductivities of the two constituents at 100 °C serve as the inputs for the predictions at 100 °C. The mechanical and thermal properties of BaTiO₃ and Ag used in this study are listed in Table 7. In the temperature range we studied (-50 to 250 °C) the elastic constants, CTE and thermal conductivity of silver only slightly change [Andrews 1924, Powell, Ho et al. 1966, Ross 2013]. For example, the thermal conductivity is 428 W/mK at 0 °C, while it slightly reduces to 413W/mk at 227 °C. So in the simulation we

used those values at ambient temperature. The CTE and thermal conductivity of BaTiO₃ at ambient and elevated temperatures are listed in Table 4 and Table 5, respectively. Its elastic constants significantly change with temperatures even within each phase [Cheng, 1996]. However it only slightly affects the effective CTE of the composites as shown later.

Table 7 Material properties of BaTiO₃ and Ag at room temperature

	Modulus (GPa)	Poisson's ratio	Yield Strength (MPa)	CTE (10 ⁻⁶ K ⁻¹)	Thermal conductivity (W/mK)
BaTiO ₃ ^a	119.86	0.323	-	- ^b	- ^c
Ag ^d	76.0	0.370	55.0	19.6	419.0

a: This work

b: See table 4

c: See table 5

d: [Andrews 1924, Powell, Ho et al. 1966, Ross 2013]

4.2. Effects of microstructures and material properties

In this section we examine the significance of possible microstructure-introduced anisotropy and inhomogeneity, and also the influence of porosity and material properties on the effective CTE and thermal conductivity. In the 2-D real microstructure based FE models, four FE models were created for each composition to study the influence of microstructural dispersion. Table 8 shows examples of variations in silver contents for different FE models with around 10 vol% silver content, which were calculated from the pixel fraction of silver phase in the SEM images. The calculated effective CTE and thermal conductivity are plotted in Figure 10 (a)-(b). By comparing Table 8 with Figure 10(a)-(b) it is seen that the calculated effective CTE and thermal conductivity increased with the increase of silver content, which is expected since silver has higher CTE and thermal conductivity than BaTiO₃. For all FE models and both loading directions, the effective CTE varies between 8.52 to 8.77 $\mu\text{m/mK}$ and the thermal conductivity varies between 4.960 to 5.401 W/mK. The relative difference for the effective CTE is 2.87%, while 8.17% for the thermal conductivity. This suggests that thermal conductivity is more sensitive to microstructure of the composite than the CTE. One possible reason is that the elastic moduli of BaTiO₃ and Ag are comparable which introduces small internal stresses between these two phases. Thermal conductivity of Ag, however, is much larger than that of BaTiO₃, which leads to significant local heat flux concentration between phases, and large differences in thermal conductivity of the composites with only slight differences in phase compositions. While this investigation shows the dispersion of effective thermal properties is relatively small, it also validates the necessity of statistical treatment of results. Figure 10(c)-(d) shows the effective CTE and thermal conductivity averaged from four FE models as a function of silver composition. It is clear that the averaged values are less sensitive to loading directions.

Figure 11 shows the effect of porosity on the effective CTE and thermal conductivity. The volume fractions of silver and pores are given in Table 6. While the influence of pores on CTE is negligible, porosity reduces the effective thermal conductivity. The reason is due to the small thermal conductivity of the pores, which serve as thermal barriers and interrupt the heat-flow path in the composite. For the thermal expansion analysis, the mismatch of the CTE for different phases introduces thermal residual stresses within each phase. The magnitude of such thermal stress depends on the differences in CTEs between individual phases, the mechanical property of each phase, and the geometry of the reinforcements. For BaTiO₃/Ag composite the thermal residual stress may even exceed the yield limit of the silver phase. Furthermore, as shown in [Cheng, 1996] the Young's modulus of BaTiO₃ increases significantly from tetragonal phase to cubic phase, which may influence the effective CTE of the composite. The effects of yielding of silver phase and the increase of Young's modulus of BaTiO₃ from tetragonal to cubic phase on the effective CTE of the composite were examined in this study, as shown in Table 9. The yielding stress of silver is 55.0 MPa and the Young's modulus of BaTiO₃ in cubic phase is 189.357 GPa [Cheng, 1996]. The yielding of silver phase decreases the calculated effective CTE, and so as the increase of the Young's modulus of the BaTiO₃. However, the relative difference is small. For example the largest relative difference due to the increase of Young's modulus is 2.17%, while only 0.81% due to the yielding of silver phase. **At high temperatures silver may experience creep. However, based on data available in literature [Price 1966], creep strain under stress 77.2 MPa at 250 °C increases by less than 2% for a loading period of about 30 minutes. In this study, the thermal expansion test is conducted up to the highest temperature is 250 °C. The time period when the samples experienced a temperature change between 150 °C and 250 °C is approximately 30 minutes, and it is expected that the creep strain due to this period of temperature increase is much smaller than 2%. It is noted that the thermal stresses developed in the composites gradually increase with increasing temperatures, and the maximum thermal stresses occur at 250 °C and these stresses decrease when the temperature is immediately brought back to the initial temperature. Thus, we neglected the creep behavior of silver at elevated temperatures during thermal expansion analysis.**

Table 8 Silver volume fraction of 2-D FE model for 10 vol% BaTiO₃/Ag composite.

	FE Model #1	FE Model #2	FE Model #3	FE Model #4
Silver VF in effective CTE analysis (vol%)	10.13	11.55	9.54	9.59
Silver VF in effective λ_{eff} analysis (vol%)	12.25	11.16	11.70	13.95

Figure 10 Effects of microstructure and loading direction on effective CTE and λ_{eff} : (a) CTE for 10 vof% BaTiO₃/Ag; (b) λ_{eff} for 10 vof% BaTiO₃/Ag; (c) CTE at tetragonal phase; (d) λ_{eff} at room temperature.

Figure 11 Effects of pores on effective CTE and λ_{eff} : (a) CTE for 10 vof% BaTiO₃/Ag; (b) λ_{eff} at room temperature.

Table 9 Effects of silver yielding and temperature dependent Young's modulus on the effective CTE (10^{-6} K^{-1}).

FE model	Effect of Ag yielding		Difference	Effect of E		Difference
	Elastic	Elastoplastic		Room temp. E	High temp. E	
#1	8.60	8.53	0.76%	8.60	8.43	1.98%
#2	8.76	8.68	0.81%	8.76	8.57	2.17%
#3	8.54	8.47	0.74%	8.54	8.38	1.88%
#4	8.54	8.48	0.72%	8.54	8.38	1.92%

4.3. The effective CTE

The effective CTEs are averaged from the predictions of four FE models to reduce the dispersion of microstructures. Firstly we will investigate the dispersion of simulated effective CTEs. The highest recorded standard deviation of the effective CTEs is $0.06 \mu\text{m/mK}$, which is very small compared to the magnitude of average CTEs (approximately two orders of magnitude lower than the average CTEs). Furthermore, the values of standard deviations are comparable for all cases, suggesting that the chosen 2-D FE models can reasonably represent the microstructures of composites in terms of thermal behaviors. In other words, for the thermal expansion analysis the microstructural models are statistically homogeneous and can represent the homogenized macroscopic behavior of the composite. In addition, among all phases and compositions the largest relative difference between effective CTEs in x and y directions ($|\lambda_x - \lambda_y|/\lambda_x$) is 0.61%, which suggests the simulated effective CTEs for our models are almost isotropic, i.e. the effective strains are insensitive to the loading directions.

Figure 12 Effective CTE for BaTiO₃/Ag composite: comparison between experiment and simulated results from 2-D and 3-D models.

Figure 12 shows the comparison of CTEs from 2-D and 3-D microstructural models and experimental results for all phases and silver compositions. For the 2-D models the plotted values are calculated by averaging results from four FE models, two loading directions, and heat/cooling cycles. Except for the composite with 15 vol% Ag content at orthorhombic and cubic phases, the simulated results are slightly smaller than those of measured data. The largest deviation of the simulated CTEs from the measured ones is for the composite with 10 vol% Ag content at the tetragonal phase, which is 4.84% in relative error. Among all three phases the largest difference happens at the tetragonal phase since the dispersion in the measured CTEs and the difference between heating and cooling at the tetragonal phase is larger than at other two phases. The simulated effective CTEs from the 3-D FE models based on randomly generated microstructures are very close to those of the 2-D FE models which are based on realistic microstructures. The largest relative difference is shown for the orthorhombic phase for the composite with 10 vol% Ag content, which is 1.6%. As a result, it is more desirable to use 2-D realistic microstructure based FE model, because the computational cost for the 2-D models are much less than 3-D model meanwhile the accuracy of the calculated effective CTEs are comparable. However, the detailed thermal residual stress and stress concentrations for 2-D and 3-D FE models are quite different as shown later. It is also concluded that the predicted effective CTEs are insensitive to the shape and size of the silver particles.

One advantage of the microstructural based modeling is that we can examine the local field fluctuations in the composite and their effects on the overall performance/properties of the composite. For the thermal expansion analysis one of the most important local fields are the residual (thermal) stresses. The BaTiO₃/Ag composite samples were manufactured by powder metallurgy method. After cold-pressing the green body was heated up to 1250 °C and then cooled down to room temperature. As a result, at room temperature the composite sample might experience significant internal thermal residual stresses. The effective thermal properties might be insensitive to the internal residual stress introduced during sintering. Its effect on the mechanical properties, however, usually cannot be neglected, as reported in [Gudlur, 2014 b]. Figure 13 presents the simulated thermal residual stress for the 2-D and 3-D finite element analyses. The thermal stresses for composites with 5 vol% and 10 vol% silver contents are shown. In the simulation we assume BaTiO₃ is at tetragonal phase. The initial temperature is set at room temperature, i.e. 25 °C. Then the composite is heated up to 120 °C. The selected temperature range for the simulation approximately is within the temperature span of the tetragonal phase for BaTiO₃ ceramic. Most of the residual stresses are located within and around the silver particles. Composites with 5 vol% silver contents have smaller regions with noticeable thermal stresses, compared to the ones with 10 vol% silver contents. The yield strength for silver is about 55 MPa as listed in Table 7. Figure 13 indicates that the residual thermal stress in the silver is greater than 60 MPa, which would result in yielding of silver. However, as shown in Table 9 the yielding of silver phase has little influence on the calculated effective CTEs. In addition, the simulated effective CTEs are in good

agreement with experimentally measured values, which further validates that the effect of plastic deformation of silver is insignificant in case of thermal expansion analysis. It can be seen that smaller distance between two adjacent silver particles leads to larger stress concentration. As shown in Figure 13(c)-(d) the stress concentration in 3-D model is lower than that in 2-D real microstructure based FE models, which is due the spherical silver particle approximation used in the 3-D FE models.

Figure 1 Simulated residual thermal stress for BaTiO₃/Ag composite. (a)-(b), 2-D results for 5 vol% and 10 vol% composite, respectively; (c)-(d), 3-D results for 5 vol% and 10 vol% composite, respectively. The unit for stress is MPa.

4.4 The effective thermal conductivity

To make sure that the 2-D micromechanical models can approximate the macroscopic behavior of the composite in heat transfer analysis, again firstly we will investigate the dispersion of simulated effective thermal conductivities. The analyses at all temperatures and silver compositions showed that the largest difference in effective thermal conductivities measured in the x and y directions is 0.7%, indicating a reasonable isotropic assumption. The largest dispersion is 0.10 W/mK at 25 °C and 75 °C for

composite with 10 vol% silver. This value is small compared with the magnitude of the effective thermal conductivity itself.

Figure 14 shows the effective thermal conductivities by using polynomial functions up to 5th order. Note that the linear polynomial approximation (1st order) is equivalent to the constant temperature gradient BC. As expected increasing the polynomial order decreases the prediction of the effective thermal conductivities but the rate is slow due to the inefficiency of polynomial approximation to approximate highly fluctuated functions. As shown in literature [Nguyen, V.-D., et al. 2012], a polynomial of order over 20 or even 30 is needed to reach convergence for mechanical properties. In this study, it seems that the effective thermal conductivities from periodic BCs reach convergence at 5th order polynomial. In addition, the mixed BC gives a close prediction to the lower bound (uniform flux BC). The predictions from mixed and constant temperature gradient BCs for 2D and 3D micromechanics models are plotted in Figure 15. Under the mixed BC the predictions from 2D and 3D are very close, and the largest relative difference is 1.29%. In contrast, under constant temperature gradient BC the predictions from 2D and 3D models differ significantly. The predictions from 3D models are much larger than those from 2D models because the number of particles in 3D models is less than that in 2D models (based on SEM images).

Comparison of experimental results and the effective thermal conductivities from 2D micromechanics models with constant temperature gradient BC and mixed BC is given by Figure 16. The predictions from the constant temperature gradient BC (1st order periodic BC) give upper bounds and are close to the experiment results. On the other hand, the predictions from mixed BC underestimate the experiment results. The percent difference in the thermal conductivities from the mixed BC is 7.23-8.93% for 5 vol% composite and 15.22-18.71% for 10 vol% composite. One possible reason for the discrepancies is the high contrast in thermal conductivity between silver and BaTiO₃, which leads to high heat flux concentrations, which cannot be captured in the mixed BC. Figure 17 shows that the heat flux concentration for composites with 10 vol% silver is higher than the one with 5 vol% silver. In this study we did not take into consideration eventual effects of the thermal contact resistance between constituents since that information pertinent to the contact behaviors between BaTiO₃ and silver is not available in the open literature. Thermal contact resistance is usually determined experimentally due to its complex influencing factors, such as the thermo-physical and mechanical properties of the constituents, the presence of gaseous or nongaseous interstitial media, the apparent contact pressure, etc. [Fletcher 1988].

Figure 14 Effective thermal conductivities predicted by various boundary conditions for 2D micromechanical models at 25 °C.

Figure 15 Comparison of predictions between 2D and 3D micromechanics models: left, mixed BC; right, constant temperature gradient BC.

Figure 16 Comparison of experiment results to predictions from 2D micromechanics models with constant temperature gradient BC and mixed BC.

Figure 17 Simulated heat flux for BaTiO₃/Ag composite. (a)-(b), 2-D results for 5 vol% and 10 vol% composite, respectively; (c)-(d), 3-D results for 5 vol% and 10 vol% composite, respectively. The unit for heat flux is $\mu\text{W}/\mu\text{m}^2$.

Detailed local heat flux fields for composites with 5 vol% and 10 vol% silver contents are shown in Figure 17 for 2-D and 3-D models. In the simulation right edge ($x=L$) of the model is prescribed with a temperature of 0 °C and the left edge ($x=0$) with 100 °C. Since it lies in the temperature span of tetragonal phase of BaTiO₃ ceramic within which its thermal conductivity almost stays constant, thermal conductivity for BaTiO₃ at room temperature is used as the input in the simulation. The heat transfer is assumed to be steady state. As shown in Figure 17 (a)-(b) only a very small part has heat flux in the ranges from 2.5 to 28.5 $\mu\text{W}/\mu\text{m}^2$ for composites with 5 vol% silver and from 2.5 to 56 $\mu\text{W}/\mu\text{m}^2$ for the composite with 10 vol% silver. The composite with 10 vol% silver has higher heat flux concentration compared to the one with 5 vol% silver. Higher heat flux is seen in the silver constituent. Lowest magnitude of heat flux happens at the interfaces between BaTiO₃ and silver constituents. When heat flows in the x direction and approaches phase boundaries it is attracted by silver phase due to its much higher thermal conductivity. Heat flux concentration also occurs in the regions between adjacent silver particles with small spacing because heat flows following a passage of higher conductive constituent. Heat flux concentration in 3-D model is lower than that in 2-D model, as shown in Figure 17 (c)-(d), due to its smoother spherical silver particles. The heat flow paths in the matrix are clearly observed in Figure 17 (c)-(d) as indicated by the green contours connecting silver particles.

5. Summary and conclusion

In this work, the influence of silver phase and temperatures (-50 to 250 °C) on the effective thermal properties of BaTiO₃/Ag composite was experimentally and numerically investigated. BaTiO₃/Ag composites with various silver compositions were made by powder metallurgy method. BaTiO₃ showed two phase transformations within the temperature range of interest. Thermal-mechanical analysis (TMA) shows the addition of silver in BaTiO₃ matrix has little influence on the phase transformation temperatures. CTE stays constant at each crystalline phase, but increases as BaTiO₃'s crystal structure changes from orthorhombic to tetragonal phase further to cubic. In addition, CTE slightly increases as the increase of silver content. Differential scanning calorimetry (DSC) was conducted to determine the heat capacity of BaTiO₃/Ag composites. Our results show that heat capacity increases as the temperature increases and decreases as silver content increases. Phase transformation temperatures from DSC test stay constant as silver content increases, but are slightly different with that from the TMA measurement. Thermal conductivity and thermal diffusivity were measured by HotDisk technique. Thermal conductivity is nearly constant at tetragonal and cubic phases, respectively, but smaller at cubic phase than that at tetragonal phase. Increase of silver content significantly enhanced the thermal conductivity of the composite due to the formation of thermal conductivity chains. 2-D and 3-D microstructure

based finite element models were created to determine the effective CTE and thermal conductivity. 2-D FE models were constructed by directly meshing the real microstructure from the SEM images of BaTiO₃/Ag samples, while 3-D FE models were generated by random sequential addition algorithm. Numerical results showed that microstructure introduced anisotropy is negligible and the effective properties are independent of loading directions. Our micromechanical models achieved macroscopic homogeneity. Effective CTE were shown to be insensitive to the yielding of silver phase and the elastic modulus of BaTiO₃ matrix. The prediction of effective CTE was in a good agreement with experimental results. The effective thermal conductivity with a constant temperature gradient BC gives a close predictions of experimental data. An investigation of local field shows that high stress and heat flux concentration exist in the thermal expansion and steady state heat transfer analyses, respectively.

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