Supporting Information

Metal Matrix – Metal Nanoparticle Composites with Tunable Melting Temperature and High Thermal Conductivity for Phase Change Thermal Storage

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1. Details on Modified Effective Medium Approximation Calculations:

Our modified effective medium approximation is based upon the work by Minnich and Chen,[1] and was carried out as follows:

1. Due to the metallic nature of our composites, we only consider free electron contributions to thermal conductivity and neglect phonon contributions. To implement Minnich's formula, we need to specify the thermal conductivity of the host phase k_h, the thermal conductivity of the guest phase k_g, and the thermal interface conductance (TIC) between these two phases. These parameters are determined as described below.
2. The host phase in our nanocomposite is Ag prepared *via* the thermal decomposition of silver benzoate. Due to its polycrystallinity and porosity (see Figure S3), the thermal conductivity of silver prepared in this manner differs from literature values. Hence we prepared three Ag films and measured their thermal conductivity using the Wiedemann-Franz law.[2] We use the average of these three measurements as the thermal conductivity of the host phase in our calculations. In order to implement the modified effective medium approximation by Minnich and Chen, the thermal conductivity of the matrix needs to be further broken down into heat capacity, velocity and mean free path of the energy carriers (which are free electrons in our case). This approach allows the introduction of an effective mean free path that is a function of interface density, thereby accounting for nanoscale thermal transport effects. In our calculations we use the electronic heat capacity ($c_e = 1.8 \times 10^4$ J/m^3-K) and electron velocity ($v_e = 1.35 \times 10^6$ m/S) for bulk Ag.[2] We use our measured thermal conductivity for Ag to calculate a value of 33 nm for the electron mean free path, L (i.e. $k_e = c_e v_e L/3$). We use this value as the mean free path of Ag in our calculations.
3. We use the bulk thermal conductivity of Bi, 8 W/m-K, for the nanoparticle thermal conductivity k_g. We note that although thermal conductivity measurements on nanoparticles with similar structure imply lower thermal conductivities,[3] these measurements are on the thermal conductivity of the nanoparticles in combination with their surface ligands. In our model, the surface ligands are incorporated into the thermal interface conductance (see below) between the nanoparticle and matrix. We use the bulk thermal conductivity of Bi in our model to avoid double-counting the effect of the surface ligands. Importantly, we note that this parameter has a negligible effect on the composite's thermal conductivity. As shown in Figure S4a, the composite's effective thermal conductivity only varied ~ 0.03% as we changed k_g from 0.1 to 10 W/m-K.
4. In terms of the thermal interface conductance between the host and guest phases, we use a TIC of 34 MW/m^{2}K for the Bi-Ag interface. We note that this interface is not a typical solid-solid interface due to the presence of the Bi nanoparticle surfaces ligands and choose this TIC value based on experimental results on similar interfaces.[4, 5] Our analysis shows that the nanocomposite's thermal conductivity is insensitive to this parameter. (Figure S4b) The effective thermal conductivity increased by ~ 2% as we increased the TIC from 1 to 1000 MW/m^2-K.

2. Additional Figures:

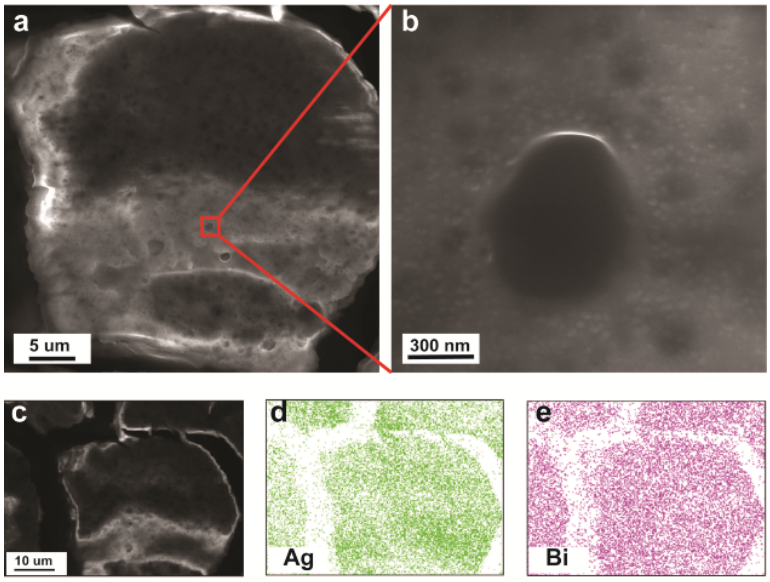

Figure S1. Scanning electron microscopy (SEM) image and corresponding energy-dispersive x-ray spectroscopy (EDS) results of a Bi nanoparticle-Ag matrix composite for phase change studies prepared by drop-casting into a differential scanning calorimetry (DSC) pan. (a) Low resolution SEM image of nanocomposite. (b) Zoomed-in image on the central area of the nanocomposite. (c) SEM image taken in EDS mode and chemical composition maps showing (d) Ag distribution and (e) Bi distribution.

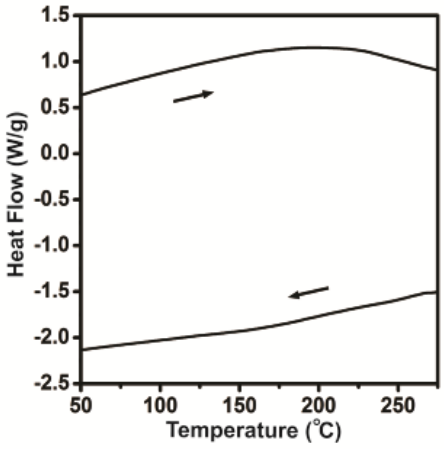

Figure S2. A heating and cooling DSC cycle on silver prepared *via* the thermal decomposition of silver benzoate.

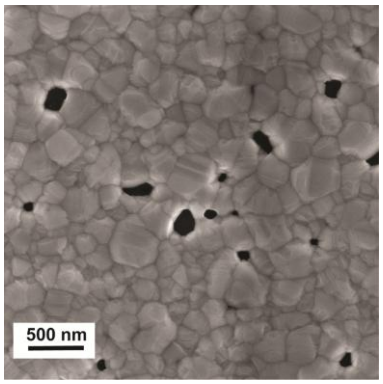

Figure S3. SEM image that illustrates the polycrystallinity and porosity of an Ag thin film prepared *via* the thermal decomposition of silver benzoate. This sample was prepared by spin-coating silver benzoate onto silicon substrates.

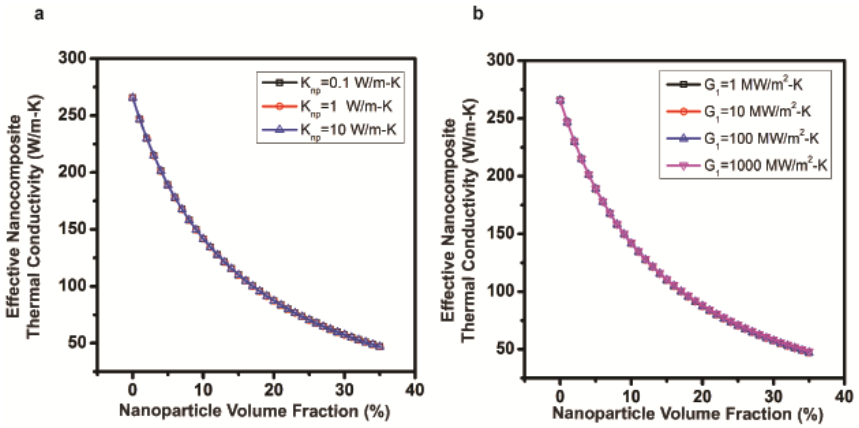

Figure S4. Modified effective medium approximation calculations on the thermal conductivities of nanocomposites containing 13 nm Bi nanoparticles with various nanoparticle volume fractions and (a) changing the Bi nanoparticles thermal conductivity from 0.1 to 10 W/m-K (b) setting the thermal interface conductance of Ag-Bi interface from 1 to 1000 MW/m^2-K.

References

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