INL/EXT-21-63525
Revision 000

Development of Bismuth and Platinum Bi-Metallic Nanoparticles to Enhance Melt Wire Temperature Resolution

July 2021

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Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

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ABSTRACT

Advanced manufacturing (AM) based on direct-write technologies has emerged as the predominant enabler for the fabrication of active and passive sensors for the harsh operating environments seen in a nuclear reactor. Recently, Idaho National Laboratory and Boise State University have established capabilities to incorporate AM methods to accelerate, modernize, and enhance the functionality of nuclear sensors and instrumentation to enhance the safety and efficiency of nuclear reactors. A significant thrust of this work includes the development of relevant nuclear feedstock materials compatible with a variety of direct-write processes for the development, fabrication, and testing of AM sensors for peak temperature detection and neutron flux monitoring. For this report, bismuth and bismuth-platinum (BiPt) bi-metallic nanoparticles were synthesized using wet chemical approaches to develop bi-metallic feedstock materials to enhance the sensitivity of melt wires for peak temperature detection. We performed nanoparticle characterization with transmission electron microscopy for nanoparticle composition and size, transmission x-ray diffraction fluorescence for nanoparticle composition, and differential scanning calorimetry to elucidate the melting point of BiPt bi-metallic nanoparticles. Preliminary results indicate bi-metallic BiPt nanoparticles as a viable pathway for fabricating high-resolution AM melt wires.

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ACKNOWLEDGEMENTS

This work was supported through the Department of Energy Nuclear Energy Enabling Technologies Advanced Sensors and Instrumentation program, under DOE Idaho Operations Office Contract Number DE-AC07-05ID14517. We would like to thank Kory D. Manning for his contributions towards melting point characterization and Karthik Chinnathambi of the Boise State Center for Materials Characterization his contributions towards TEM imaging and EDS analysis.

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ACRONYMS

AM	advanced manufacturing
BiPt	bismuth platinum
DEG	diethylene glycol
DSC	differential scanning calorimetry
DW	direct write
EDS	electron diffraction spectroscopy
INL	Idaho National Laboratory
PVP	polyvinylpyrrolidone
TEM	transmission electron microscopy
TXRF	total x-ray fluorescence

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1. INTRODUCTION

Advanced manufacturing (AM) has emerged as the predominant enabler for innovation and design as it significantly expands the design envelope in terms of materials, form, and functionality. Additionally, these technologies enable rapid prototyping, reduced production cost, and reduced material waste in comparison to classical fabrication methods. As part of the AM focus of the Nuclear Energy Enabling Technologies Advanced Sensors and Instrumentation Program, Idaho National Laboratory and Boise State University have recently established in-house capabilities to develop, fabricate, and test new advanced-manufactured sensors, such as those for measuring peak irradiation temperature within a nuclear test reactor. The exploration of novel technologies allows for the development of unique sensors that are not achievable with conventional fabrication processes, and the ability to produce miniature and robust sensors is made possible with additive-manufacturing techniques known as direct-write (DW) technologies such as aerosol jet printing, plasma-jet printing, inkjet printing, and micro-dispense printing. These technologies are capable of consistently producing device features from 10–25 μm, and these size ranges are advantageous for those instances where the miniaturization of sensors is required due to space limitations within an experiment.[1]

The limiting factor for implementing DW technologies in nuclear instrumentation fabrication is the current selection of commercially available feedstock materials that are compatible with these technologies. However, the database of materials available for DW technologies is rapidly expanding and benefitting greatly from emerging nanomaterials development, and efforts are currently being made to significantly expand the library of AM materials to include those that are more relevant to nuclear. These efforts provide the necessary path towards incorporating these novel methods for nuclear energy applications, and such material breakthroughs will revolutionize in-pile sensor development and deployment for the monitoring of nuclear fuel and material behavior during an irradiation experiment.

Methods for ink synthesis encompass both top-down and bottom-up methods. This process begins with nanoparticles of the metal, ceramic, or alloy of interest in the form of a powder or a dispersion. The key challenges of the top-down approach are found in obtaining a homogenous dispersion of the functional material with a solvent system compatible with DW technologies, limited control over particle size, and large particle size distributions. On the other hand, bottom-up methods for metallic nanoparticles require the synthesis of nanoparticles from their metallic precursors. A schematic for the bottom-up approach is in Figure 1. A capping agent, which induces steric stabilization to minimize agglomeration is employed to enhance suspension stability and is a critical factor in producing AM feedstock for DW technologies. The bottom-up approach is the preferred method, as it allows for greater control over particle size and size distribution, which are key properties of affecting the quality of the ink formulation. Key challenges associated with bottom-up methods include the development of an appropriate synthesis method, isolation of desired particle shape, particle size and distribution, and identification of an appropriate capping agent.

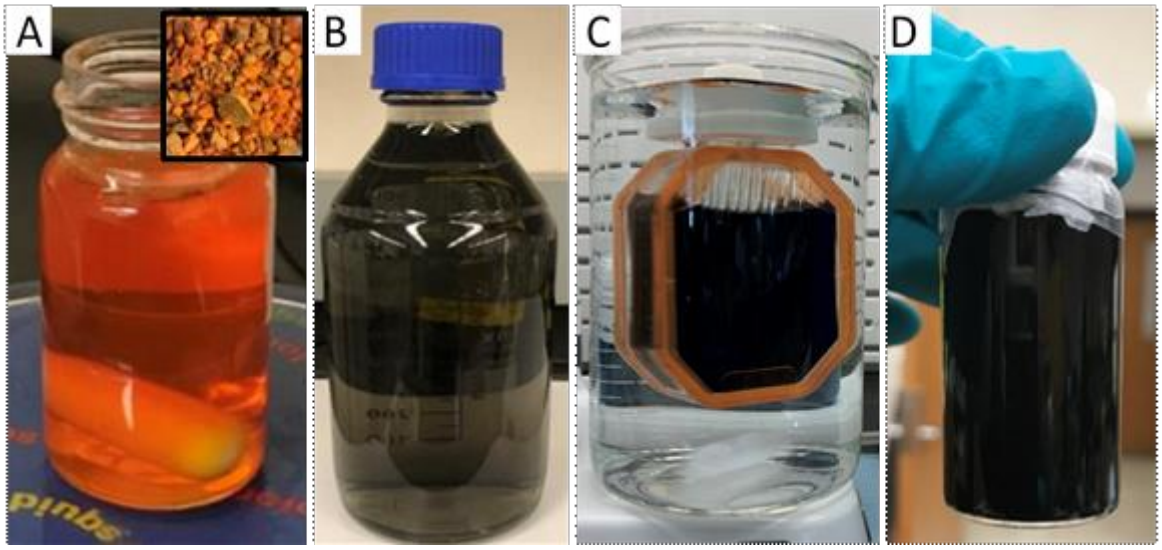

Figure 1. Schematic of the bottom-up ink synthesis method for platinum. (A) Utilizing a platinum-salt precursor, (B) a reduction method was used to synthesize platinum nanoparticles. (C) Platinum nanoparticles are purified via diafiltration and concentrated to form the (D) ink.

Irradiation testing is used to gain insight on a wide range of radiation-induced phenomena to understand the performance of fuels and materials in reactor environments. This understanding is critical for the assessment of potential materials for any nuclear reactor concept to ensure safety and reliability in operations. To enable an advance in sensor technology through AM methods, current activities involve an expansion of the database of the nuclear relevant feedstock available for DW technologies guided by the development of passive monitoring techniques, such as AM peak temperature sensors and advanced-manufactured neutron flux dosimeters.[2,3]

Temperature is a key parameter for irradiation tests, and temperature monitoring is accomplished through both passive and active monitoring techniques. Melt wires are a passive monitoring technique that enable experimenters to identify the peak temperature achieved during an irradiation test.[4,5] This method involves placing wires that have both a known composition and well-characterized melting temperature within a test. The peak test temperature is then inferred during a post-test examination or post-irradiation examination as the wire is inspected for visual signs of melting. Melting shows that the peak temperature during testing exceeded the melting point of wire material. On the other hand, the peak test temperature remained below the melting point of the wire material if the wire does not show signs of melting. Preferably, materials chosen for melt wires have a low neutron-absorption cross section while exhibiting distinct and reproducible melting behavior when they have been exposed to temperatures beyond their respective melting point.

The incorporation of classically fabricated melt wires can be limited due to space and temperature monitoring requirements of irradiation tests. This work is focused on expanding the temperature monitoring range to provide a greater temperature resolution than traditional melt wires. The current list of melt wire materials can be found in Table 1, and large gaps in measurable temperatures are highlighted.[5] To improve the temperature resolution of melt wires, we are investigating AM methods and the development of bi-metallic systems compatible with those AM methods. Our efforts are currently being focused towards demonstrating the ability to synthesize bi-metallic nanoparticles of bismuth and platinum from bottom-up methods. The successful synthesis of a variety of bismuth-platinum bi-metallics would enable peak temperature monitoring from 271°C to 1768°C (Figure 2).[6] This would enable the fine tuning of temperature resolution by tailoring the melt wire composition, which directly impacts passive peak temperature monitor performance.

Table 1. Current list of materials for classical melt wires

Material (wt% of components)	Melt Onset (°C)	
56.2Bi33.8Pb10Sn	85.0	
65Bi35In	110.6	
55.2Bi44.8Pb	126.4	
57Bi43Sn	139.4	Δ92.4 °C
100Sn	231.8	
95Sn5Sb	238.6	
90Pb10Sb	252.4	
80Au20Sn	279.5	
90Pb7.5Sn2.5Ag	290.0	
97.5Pb2.5Ag	302.9	
97.5Pb5Ag5Sn	304.0	
97.5Pb1.75Sn1.75Ag	309.3	
100Pb	327.5	
100Zn	479.6	
80Sb20Zn	507.8	Δ152.7°C
100Al	660.5	
49Ag16Cu23Zn7.5Mn4.5Ni	681.3	Δ169.4°C
40Ti20Zr20Cu20Ni	850.7	
98.2Cu1.8Be	865.1	
100Ge	938.3	
82Au18Ni	955.0	
100Ag	961.9	
65Cu35Au	995.6	
100Au	1064.0	
100Cu	1084.6	
70Cu30Ni	1191.0	Δ176.0°C
28Mo69Ni2Pe1Co1Cr	1370.0	
100Ni	1455.0	

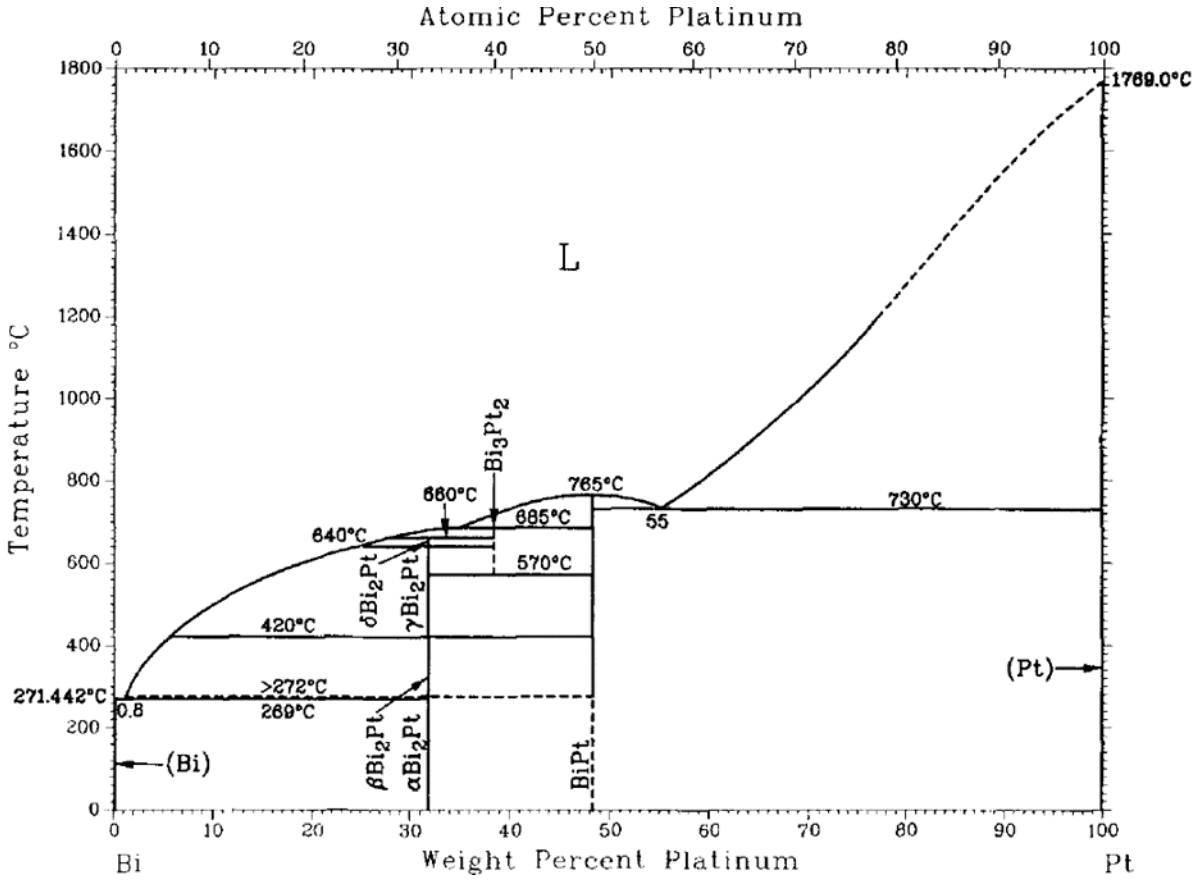

Figure 2. Assessed BiPt phase diagram. Dashed line corresponds to ideal solutions.[6]

This report highlights recent work in synthesizing a range of bismuth-platinum (BiPt) bi-metallic nanoparticle compositions with bottom-up methods to facilitate the inclusion of relevant nuclear materials within the AM library of materials. We synthesized and characterized four different bi-metallic BiPt compositions via transmission electron microscopy (TEM) with electron diffraction spectroscopy (EDS), total x-ray fluorescence (TXRF) and differential scanning calorimetry (DSC) to determine nanoparticle composition, particle size, and melting point. The ultimate goal of this work is to enhance the temperature resolution of melt wires for peak temperature detection used within irradiation tests.

2. BISMUTH AND BISMUTH-PLATINUM BI-METALLIC SYNTHESIS

2.1 Nanoparticle Synthesis

Bismuth and platinum bi-metallic nanomaterials were synthesized by using the following materials: diethylene glycol (DEG) (Reagent Plus 99%, Sigma Aldrich), tetraethylene glycol (99%, Sigma Aldrich), sodium borohydride (99.99% trace metals basis, Sigma Aldrich), chloroplatinic acid hydrate (99.995% trace metals basis 38–40% Pt, Sigma Aldrich), bismuth chloride (anhydrous 99.998% trace metals basis, Sigma Aldrich), and polyvinylpyrrolidone (Kollidon 25, BASF). All chemicals and reagents were used as received, without further purification or modification.

Four different compositions of bi-metallic BiPt nanoparticles were synthesized via a chemical reduction process. To begin, an appropriate amount of each precursor was determined for the series of BiPt bi-metallic nanoparticles. The target mass for each sample in the series was a combined total of 0.5 g of Bi or BiPt material. For this report, the following compositions were targeted: (100:0.00) Bi, (76.3:23.7) BiPt, (50.0:50.0) BiPt, and (37.0:63.0) BiPt. All bi-metallic concentrations are reported as

atomic percent (at.%), and the following procedure outlines the general synthesis method for each of the BiPt samples. After the appropriate amounts of metal-salt precursor were determined, 100 mL of diethylene glycol was degassed of excess oxygen within a three-neck round bottom flask while under reflux by bringing the solvent up to 180°C while purging under a high argon flow for one hour. The reaction was allowed to cool, and the argon flow was maintained throughout the entire synthesis. When the DEG reached 100°C, polyvinylpyrrolidone (PVP) and bismuth chloride ($BiCl_3$) were added. Then, the solution was put on ice to bring the reaction temperature down to 5°C. Chloroplatinic acid hydrate ($H_2PtCl_6 \cdot 6H_2O$) was added, and the solution was subjected to vigorous stirring for two hours to ensure an adequate mixing of the precursors. In parallel, 0.25 g of sodium borohydride ($NaBH_4$) was dissolved in tetraethylene glycol (TEG) and bath sonicated for 30 minutes. Finally, the tetraethylene glycol / $NaBH_4$ solution was quickly injected into the DEG, PVP, $BiCl_3$ and $H_2PtCl_6 \cdot 6H_2O$ solution and the reaction immediately turned from a yellow/orange to a black/brown to indicate nanoparticle formation. The reaction was allowed to stir overnight and was purified via centrifuge processing. Finally, the particles were dialyzed against a 30 kDa membrane filter to further remove any excess capping agent and reaction by-products.

2.2 Nanoparticle Composition and Size Analysis

After the purification step, suspended nanoparticles were analyzed both qualitatively and quantitatively via TEM/EDS and TXRF, respectively. TEM/EDS (Figure 3) images were obtained using a JOE JEM 2100 (Peabody, MA) and a 200 mesh lacey carbon copper grid (PELCO). Significant challenges in obtaining high quality TEM images were a result of an excessive amount of PVP, which is made apparent in each of the TEM images. As a result of the high concentration of organics that were decomposing under the beam, a large amount of carbon deposition occurred, which limited the amount of time that could be spent on each spot for imaging. The high concentration of PVP is a result of only performing purification via centrifuge prior to obtaining images, which is a common method for nanoparticle purification.[7–10] In the future, TEM imaging will be performed on samples that have been subjected to the final dialysis step for purification. However, the obtained TEM images depict particles that are spherical and well within the nano-regime (<100 nm), and the introduction of platinum appears to result in the formation of smaller particles when compared to that of the pure bismuth sample.

The EDS spectrum of each composition within the BiPt series was collected to provide a qualitative analysis towards bismuth and platinum concentrations within each sample, and Figure 4 provides the EDS spectrum of each different sample within the BiPt series. From Figure 4A to Figure 4D, there is an increase in platinum concentration, which is indicated by the shift in peak heights. Future work will include elemental mapping or line scans via TEM/EDS to elucidate the composition of individual bi-metallic particles to identify whether the individual particle compositions are in agreement with the bulk nanoparticle sample.

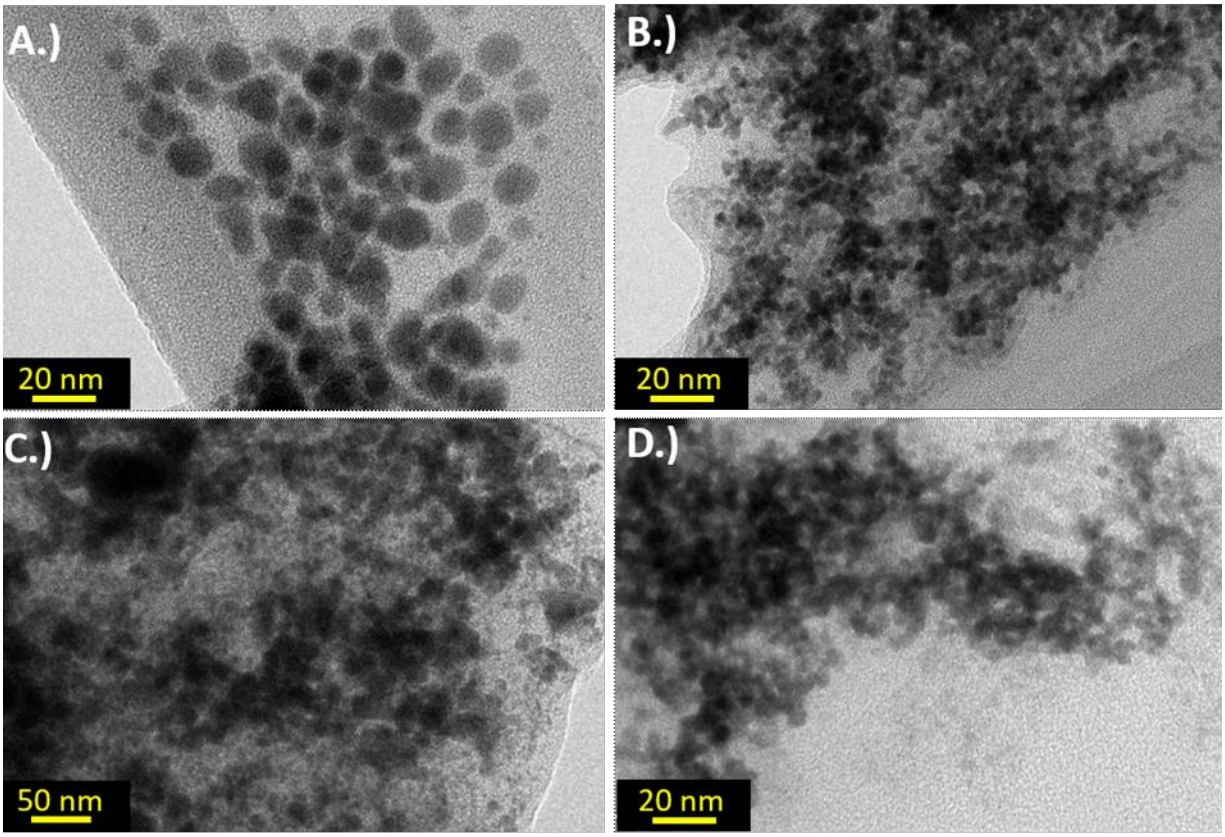

Figure 3. Transmission electron microscope images of BiPt series. Spherical nanoparticles were observed for A.) 100:0 BiPt, B.) 76.3:23.7 BiPt, C.) 1:1 BiPt, and D.) 37:63 BiPt, which indicates successful synthesis of BiPt nanoparticles.

The TXRF analysis was performed with a Bruker S2 Picofox, and the respective bi-metallic compositions can be found in Table 2. It is important to note that composition analysis was performed on the bi-metallic system and not on individual particles. Individual particle composition is critical in determining a target peak temperature for each bi-metallic system. The BiPt system is composed of both bismuth and platinum in amounts that are close to targeted concentrations. Any deviation can be attributed to experimental error, precursor concentration variations, and different reduction potentials associated with the two different elements.

Table 2. TXRF results

Sample	**Bismuth (%)**	**Platinum (%)**
100:0 BiPt	100	0
76.3:23.7 BiPt	76.5	23.5
1:1 BiPt	49.1	50.9
37.0:63.0 BiPt	39.4	60.6

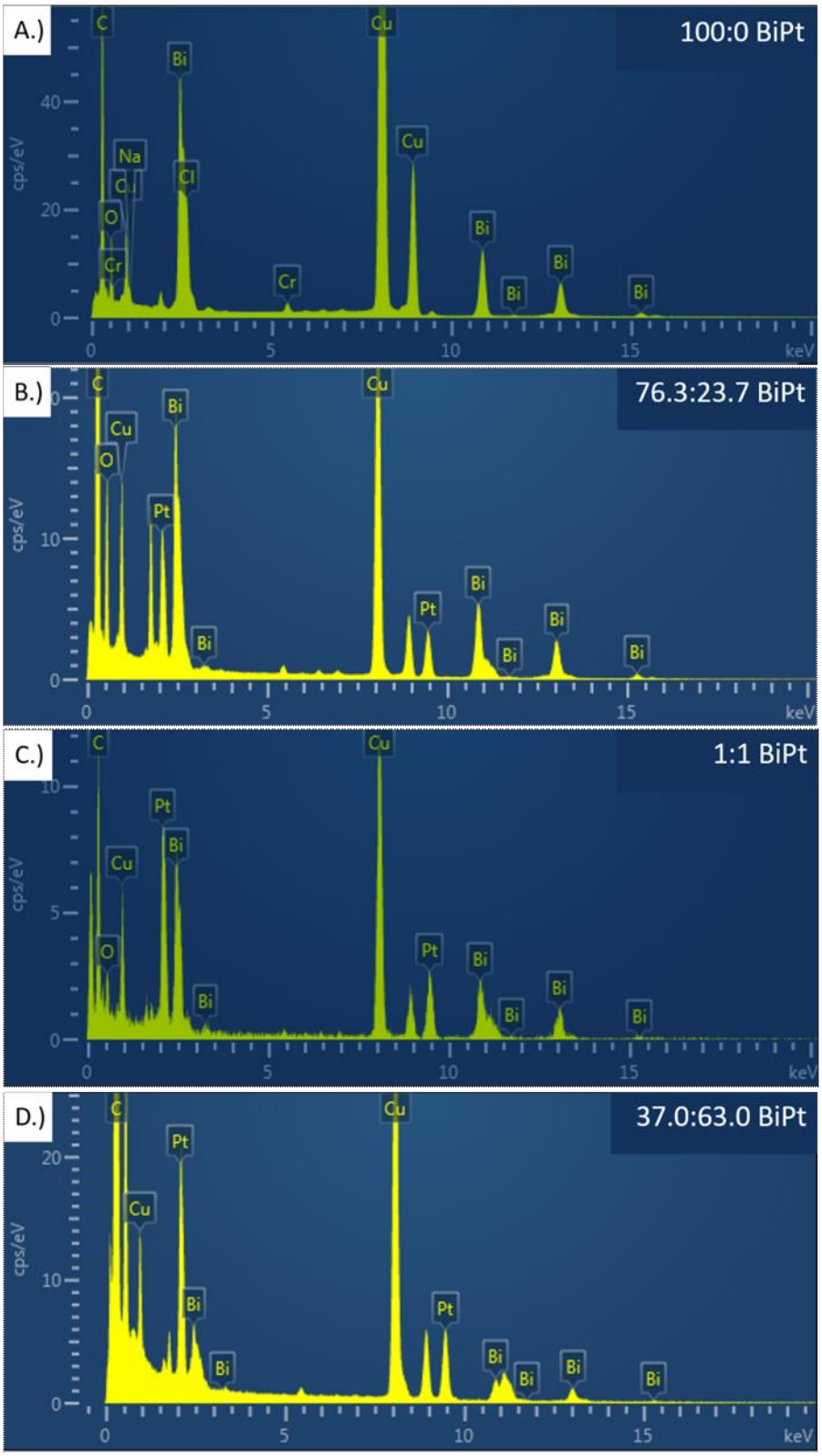

Figure 4. EDS of the BiPt series. Varying peak heights for A.) 100:0 BiPt, B.) 76.3:23.7 BiPt, C.) 1:1 BiPt, and D.) 37:63 BiPt indicate an increase in platinum concentration with each BiPt sample.

2.3 Melting Point Determination

DSC was used to determine the melting point of the PVP-capped bismuth and BiPt nanoparticles to evaluate the feasibility of integrating bottom-up synthesis methods to fabricate nanoparticle systems capable of enhancing the peak temperature resolution of melt wires. The results from the DSC evaluation can be found in Figure 4.

The theoretical melting point for each composition was estimated with the phase diagram provided in Figure 2. We expected the melting point for 100:0 BiPt to be 271.49°C, which is slightly higher than what was obtained for the nanoparticle system. This is a relatively small deviation from the expected melting point and can be reasoned to be in good agreement with the expected value. From Figure 5B, the expected melting point of the 76.3/23.7 BiPt was between 620–630°C, which is in good agreement with that obtained via DSC. A range of 10°C was used due to the level of uncertainty associated with estimating the melting point via the phase diagram. At higher platinum concentrations the detected melting point is lower than the estimated value. More specifically, the estimated melting point for 1:1 BiPt (Figure 5C) and 37.0:63.0 BiPt (Figure 5D) with estimated melting points were 760–770°C and 785–795°C, respectively. From DSC analysis, 1:1 BiPt melted at 713.6°C and 37.0:63.0 BiPt melted at 738.7°C. The reason for this deviation is unknown, but the melting point deviation from theoretical values indicates that the targeted concentration for the individual particles was not achieved and that further investigation is required to determine the cause at higher platinum concentrations.

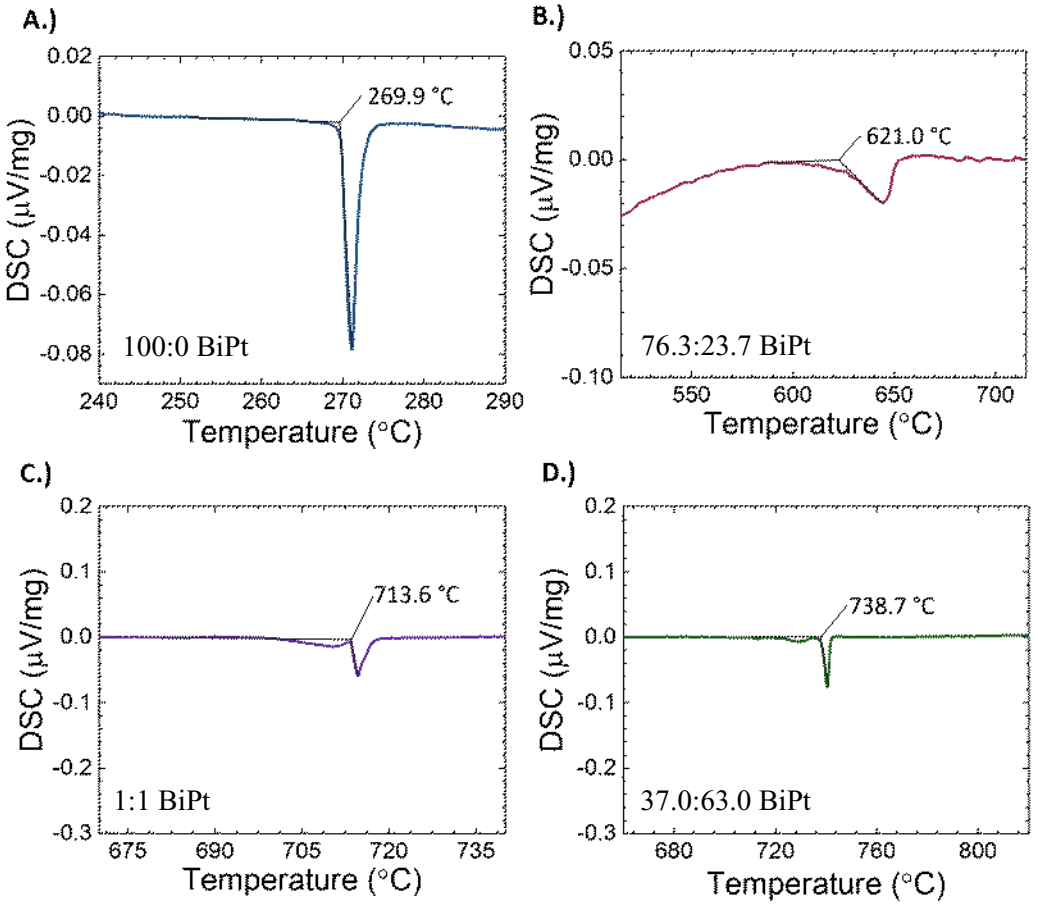

Figure 5. DSC of BiPt series. The melting point of each sample within the BiPt series is indicated by the onset of the phase change, where the onset for A.)100:0 BiPt was 269.9°C, B.) 76.3:23.7 BiPt was 621.0°C, C.)1:1 BiPt was 713.6°C, and D.) 37.0:63.0 BiPt was 738.7°C.

While slight deviations from theoretical melting point values occurred, the varying melting point for each of the different BiPt compositions show that the melting point of bi-metallic nanoparticles can be altered by varying the composition of the metal-salt precursors and ultimately the composition of the bi-metallic nanoparticle. Finally, the results from this study provide a feasible synthesis process for bi-metallic nanoparticles based on chemical reduction methods.

3. SUMMARY

Bismuth and bismuth-platinum bi-metallic nanoparticles have been synthesized using wet chemical approaches using a strong reducing agent. This goal of this work was to enhance the temperature resolution of melt wires for peak temperature detection within irradiation tests. With the use of DSC, preliminary results demonstrate significant promise towards tailoring the targeted peak temperature of melt wires with the development of bi-metallic nanoparticle systems. The BiPt series exhibited varying melting points that correlate to varying BiPt composition that is a direct result of varying the ratio of the metal precursors during synthesis.

Next steps will include minimizing any error associated with synthesizing bi-metallic nanoparticles of specific composition, and the exploration of additional bi-metallic systems to include indium/platinum and indium/silver. Furthermore, the samples within the BiPt series in this report will be formulated for a variety of DW technologies to be printed to provide an initial evaluation towards the melt behavior of printed bi-metallic wires and to determine their suitability for developing advanced-manufactured melt wire arrays. From the melting points obtained via DSC for the BiPt series, melt wires printed from these materials are expected to have better temperature resolution than those classically manufactured melt wires fabricated from bulk metals.

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