

Rheological design of 3D printable all-inorganic inks using **BiSbTe-based thermoelectric materials**



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Introduction



We recently reported all-inorganic inks using BiSbTebased thermoelectric particles coupled with a chalcogenidometallate (ChaM) inorganic binder. In the current study, we analyzed the rheological behavior of the all-inorganic inks to assess printability and 3D structural retention with respect to the ChaM content. It is well known that an incorporation of organic binders such as cellulose acetate and poly(vinylidene fluoride) significantly enhances the viscoelasticity and corresponding extrudability of the colloidal inks, but such organics inevitably degrade the final performance of the printed objects due to the intrinsic limitation of electrical conductivity. We showed that using Sb₂Te₃ chalcogenidometallate (ChaM) ions as inorganic binder minimized the deterioration of the ultimate TE performance and improved the ink printability including extrusion behavior and shape retention of the 3D structure.

► Cylindrical thermoelectric generator by 3D printed thermoelectric materials

Research Result

Characterization of 3D Printed TE Materials



Printing Performance





► (a) Design of 3D printing process producing a series of diagonal grid layers to assess the layerby-layer stacking properties of TE inks and observation of 3D stacking behavior of (b) BST100, (c) ChaM12.5 and (d) ChaM25 TE inks with an increase in printing layers. The width of the single layer is 13 mm and the height of the five layers is about 140 µm. The layers were printed at an interval of 2 min. The dispensed pressure and X-Y motion speed of the nozzle were 0.34 MPa (about 50 psi) and 18 mm/s, respectively.

Zeta Potential (mV)

(a) Zeta potential curve of ChaM/ethylene glycerol solution and (b) Schematic presentation of enhanced electrostatic interaction and polar energy of TE particles due to adsorption of inorganic binder onto particle surface.

BST 100 \rightarrow 0% ChaM **BST 125** \rightarrow **25% Excess BST** BST 12.5, 25, $30\% \rightarrow BST + \%$ ChaM











OM images of one-layer grid constructs for assessing printability of (a) ChaM12.5, (b) ChaM25, and (c) ChaM37.5 inks. The black lines producing grid pattern is the printed TE inks, and the bridge part is the graphite substrate. The enlarged images for crossline of each construct confirmed higher printing resolution with the higher ChaM content.

(d) η' , (e) G', and (f) tan δ curves of TE inks were obtained after experiencing high stress up to 300 Pa

Outcome

Improvement of the viscoelasticity and phase stability of all-inorganic TE inks by adding the inorganic binder enabled the colloidal systems to yield high quality 3D products via continuous additive manufacturing. The surface property analysis confirmed that the anionic binder enhanced the polar surface energy of TE particles and then the chemical affinity with a polar solvent, glycerol. We believe that not only our results overcome a previously unresolved challenge for 3D printing of inorganic materials but they can also be widely extended into different types of ionic inorganic binders.