Combining Ultrafast Calorimetry and Electron Microscopy: Reversible Phase Transformations in SeTeAs Alloys

Paul A. Vermeulen, Joost Calon, Gert H. ten Brink, and Bart J. Kooi

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, Groningen 9747 AG, The Netherlands

Supporting Information

ABSTRACT: Reversible amorphous—crystalline phase transitions are studied using complementary ultrafast differential scanning calorimetry and transmission electron microscopy techniques, which together allow a wealth of thermal and structural properties to be determined. The SeTe(As) system is investigated because these chalcogenide-based materials have favorable properties as a phase-change memory material and in optical systems. Using calorimetry, we find that the addition of 10 at. % As to SeTe alloys strongly increases their glass forming ability, increasing both glass transition and crystallization temperatures while reducing critical quench rate. Ex situ investigation of Se$_{60}$Te$_{40-x}$As$_{x}$ using electron microscopy and elemental mapping reveals a two-phase lamellar segregation mechanism, where a trigonal SeTe-phase and an amorphous As-rich phase are formed. These findings demonstrate the power of combining thermal and structural analysis techniques.

INTRODUCTION

Many modern industrial manufacturing processes rely on rapid cooling and heating to obtain materials in their desired state, phase, or form. Prominent examples are the production of polymers, steels, and nonferrous metal alloys based, for instance, on aluminum or titanium but also in the production of bulk metallic glasses. It is crucial to carefully control and characterize the thermal treatment to obtain a functional material. During device operation some materials undergo rapid thermal transformations as well, for example, in the so-called phase-change memories (PCM); where a rapid (nanosecond) heat pulse or melt-quench can set and reset the state of a small material. During device operation some materials undergo rapid thermal transformations as well, for example, in the so-called phase-change memories (PCM); where a rapid (nanosecond) heat pulse or melt-quench can set and reset the state of a small material.

Recently, a commercial ultrafast differential scanning calorimeter (UFDSC), which can reach relevant heating and cooling rates of $10^5$ K/s, was introduced. This has led to the discovery of new crystal phases and extended the knowledge of thermal stability of glasses and crystallization rates within a wide range of materials. While already increasing our knowledge of phase transformations, the UFDSC technique lacks any structural information accompanying those transitions. Solutions to this shortcoming were mostly sought using thermal and structural analysis techniques, to match the XRD and Raman capabilities, while also allowing local microstructural and compositional analysis.

Our material system of choice is SeTeAs alloys, which are prototypical chalcogenide-based PCMs, displaying clear contrast between amorphous and crystalline phases. Much interest from this field of research is on the crystal growth rate, energy required for switching operation, long-term stability of the alloy in either phase, and reversibility of the phase change. Using Kissinger analysis, the crystallization kinetics can be characterized, while determining the glass transition temperature and critical quench rate gives a measure of stability of the amorphous phase. By reversibly heating and cooling, a switching application is replicated. The glassy state of the alloy is used for fiber-optic communications because of its favorable transmissivity at IR wavelengths and stability of the amorphous phase. Many reports in literature focus on high-As content SeTe glasses, e.g., to determine optical losses due to inhomogeneity. Furthermore, the chosen alloys are melt-quenchable within the UFDSC limitations (melting below 450 °C, cooling rate $\sim 10^4$ K/s), and the binary SeTe was already studied before, offering direct comparison.

The article will be presented in two parts: first the thermal analysis using ultrafast DSC is shown, and then microscopy

Received: March 26, 2018
Revised: May 1, 2018
Published: May 14, 2018
data is used in order to elucidate and extend the knowledge of the structure of thermally treated and analyzed SeTeAs alloys.

**RESULTS**

Using UFDSU Se$_x$Te$_{100-x}$As$_{10}$ flakes are heated and melted, and then cooled at various rates. During these reversible cycles the composition of flakes slowly varies due to Se evaporation as we have already demonstrated for our earlier work on SeTe alloys. This can be considered as a disadvantage because it prevents studying a perfectly reversible system; however, it is also a clear advantage. Since the change in composition is very gradual, it provides an elegant method to determine phase diagrams in which glass transition, crystallization temperature (for various heating rates), and the melting temperature can be measured as a function of alloy composition. An important point, therefore, is the determination of the actual composition of the Se$_x$Te$_{100-x}$As$_{10}$ flake in the UFDSU. As shown in the methods section at the end of this article and in the first section of the Supporting Information (SI), the onset of melting can be used as an adequate estimator of the alloy composition. This is a convenient method to keep track of the composition in UFDSU because this measurement can be readily performed for these sample types.

To show the strength of this method, we first present the critical quench rate as a function of composition, i.e., the cooling rate needed to obtain a fully amorphous (glassy) phase from the melt. When the cooling rate becomes sufficiently high, no crystallization peak is visible in the trace of the heat flow. The critical quench rate over a range of compositions is shown in Figure 1c. Compared to SeTe alloys, the addition of 10 at. % As to Se$_x$Te$_{100-x}$As$_{10}$ leads to a shift of over three orders of magnitude while effectively leaving the general trend of decreasing glass forming ability when exchanging Se by Te unaffected. This indicates that the crystallized phase itself is of similar nature, but its formation rate is strongly retarded by the added As content.

Employing the critical quench rate to regain a fully amorphous sample, we use a temperature program to reversibly switch the specimen between melt-quenched and crystalline phases. Representative heating traces of Se$_x$Te$_{100-x}$As$_{10}$ flakes are shown in Figure 1a. The first exothermal peak, which indicates crystallization, is clearly visible. The samples also exhibit a glass transition that is visible as a step in the heat flow (inset of Figure 1a). The melting (endothermal) is visible as a clear dip around 400 °C. The crystallization peak temperature ($T_c$), glass transition ($T_g$), and melting onset temperature ($T_m$) are used for analysis in Figure 1b,d. The slope of the heat-flow traces is related to the heat conduction losses to the sample surroundings. Generally, a lower heating rate leads to higher losses to the environment and thus a steeper slope. Furthermore, crystalline samples are good heat conductors, followed by the glassy and finally undercooled liquid states: this is also reflected in their respective heat-flow slope.18

The Se$_x$Te$_{90-x}$As$_{10}$ phase diagram in Figure 1b shows a decrease of $T_c$ and $T_g$ for increase of at. % Te (albeit rather modest for $T_g$). Increasing the heating rate dramatically increases the $T_g$, as well as to a much lesser extent the $T_c$. This increase in transition temperatures cannot be ascribed to systematic thermal lag, which is estimated to be below 1 °C for heating rates below 1000 K/s.18 A remarkable feature of the Se$_x$Te$_{90-x}$As$_{10}$ crystallization is the appearance in the heat flow of a broad shoulder at the higher temperature side of the (initial) crystallization peak when the $T_c$ drops below 200 °C, as is visible for the slowest three curves in Figure 1a. The points corresponding to heating rates where a two-peak transition was observed are circled in the phase diagram. This two-peak character is not observed for the binary SeTe and hints at a more intricate crystallization behavior for SeTeAs than for SeTe.

Figure 1d compares $T_c$ and $T_g$ values as a function of Te composition for Se$_x$Te$_{100-x}$As$_{10}$ and Se$_x$Te$_{90-x}$As$_{10}$. The region of overlap is small; due to the extremely slow crystallization of SeTeAs, no crystallization is observed for lower Te content. Adding As increases both $T_c$ and $T_g$ dramatically: like for the critical quench rate, it shows As serves as a strong glass stabilizer or crystallization retardant. Nevertheless, for both alloys, $T_c$ is found to decrease as the Te content increases. Finally, we note that the $T_g$ of SeTe increases, while that of SeTeAs decreases for increasing Te concentration. When instead the reduced glass transition ($T_{rg} = T_g/T_m$) is inspected, it decreases for both alloy systems for increasing Te concentration, as is expected when the material becomes a poorer glass-former.19

Kissinger analysis was performed on Se$_x$Te$_{90-x}$As$_{10}$ alloys with a wide range of compositions (Figure 2a) to elucidate the crystallization kinetics. A clear non-Arrhenius behavior was observed due to the fragility of the undercooled liquid. This effect becomes particularly observable at higher heating rates,
where the data points clearly deviate from a straight line. This was also previously found for other phase-change materials.\textsuperscript{6,7,18} The activation energy of crystallization was calculated for the lower heating rates \textless 100 K/s\textsuperscript{,} where the crystallization can be approximated by Arrhenius behavior, and the result is shown in Figure 2b. The results bear a great similarity to those obtained for SeTe. Although the measurements are performed in only slightly overlapping regions, trends are similar and seem to even match quite well. This indicates that the crystallized (part of the) sample resembles SeTe.

At this point we have gained a good understanding of the thermal response of the alloy. It is clear that the material behaves as a phase-change material, possessing non-Arrhenius characteristics. We have found that the addition of As strongly stabilizes the glass phase. We will now present structural analysis using various microscopy techniques, which will add crucial information on sample inhomogeneity, chemical composition, and crystal structure. To investigate the crystalline state of the alloys, samples were crystallized in various ways: (1) from a closed quartz tube ingot slowly cooled from the melt, (2) slowly heated (1 K/s) from the amorphous phase in a regular DSC, and (3) using UFDSC heated with 100 K/s. For this last sample, a novel method involving simple components and lab materials was developed to transfer the submillimeter ingot (part of the) sample. Microscopy images of these three samples are shown in Figure 3. As is immediately obvious, an increase in heating rate significantly reduces the size of several features of the alloy. For the ingot (Figure 3a), optical microscopy suffices to image the clearly faceted crystals (features, \textasciitilde 10 \mu m). SEM is used for the slowly heated samples that feature \textasciitilde 1 \mu m thick lamellae (Figure 3b), and TEM is required to resolve the lamellae in the quickly heated samples (Figure 3c) where the lamellae have widths of only \textasciitilde 0.1 \mu m. The slowly heated sample shows distinct grain boundaries, providing microstructuring on a 100 \mu m length scale, while within the grain, lamellar structures without clear facets can be observed. In the quickly heated sample (100 K/s), a morphology similar (albeit on a smaller scale) to that for the slower heated (1 K/s) sample is observed. While for SEM/ optical images, the lighter color indicates high conductivity and hence a crystalline phase; in TEM, the darker lamellae, which indicate strong scattering contrast, indicate crystalline phase. Sharp boundaries are observed, and the back-scattered electron (BSE) imaging, which is sensitive to the elemental-weight distribution, shows that both phases are relatively homogeneous. The diffraction pattern (Figure 3d) taken from the (part of) sample shows several crystals with a common crystallographic orientation and a small tilt gradient, indicating that the lamellae originate from one grain center.

To investigate this two-phase lamellar structure, which appears after rapid crystallization upon heating of the supercooled liquid structure more closely, small-area diffraction patterns (SADPs) were taken on a dark and a bright region within the lamellar structure (Figure 4a). By selecting a dark lamella, a sharp diffraction pattern is observed, which conforms to the trigonal structure of SeTe (Figure 4b).\textsuperscript{29} When a bright area is selected, diffuse rings characteristic of an amorphous phase are visible, along with some spots due to the aperture selecting a small part of the adjacent lamella (Figure 4c). The two-phase structure consists of one crystalline and one amorphous compound. The same can be concluded from an HRTEM image shown in Figure 4e, which shows a lamella edge and a rather sharp boundary between amorphous and crystalline phases.

Electron dispersive X-ray spectroscopy combined with scanning transmission electron microscopy (EDS-STEM) is
performed, which maps the elemental composition of the alloy. Figures 4f–i show the mapping of an area consisting of crystalline and amorphous materials. The crystalline phase, which has a diameter of ~150 nm, is rich in Te, while the amorphous phase is rich in Se and As.

The histogram in Figure 4d shows the average composition of several amorphous and crystalline areas in the specimen and shows a trend similar to the mapping scans. For comparison, the composition of an ingot slowly cooled from the melt, representing an (nearly) equilibrium distribution, is shown hatched. The ingot shows no As in the crystalline phase, which is consistent with As as a glass former. The crystalline part of the ingot contains more Se and less Te than the heated alloy, but this can also be explained by slight selective Se evaporation due to thermal cycling in the DSC (cf. SI section 3). So, during the phase separation, which results in alternating crystalline and amorphous lamellae, the predominant diffusing species are As toward the amorphous phase and Te toward the crystalline phase. These observed elemental compositions upon phase separation are consistent with the thermal properties of the alloy: a higher Te/Se ratio reduces the glass forming ability, while the addition of As significantly increases the glass forming ability. This is also consistent with literature descriptions of these materials’ binary alloys; where SeAs is frequently listed as a glass, whereas AsTe and SeTe are mostly reported as crystalline.21–23

## DISCUSSION

The observed microstructures show that the ternary alloy has a strong tendency to separate into two phases, which was not the case for the perfectly mixable SeTe binary alloy (cf. SI section 5).24 The formation of a crystalline lamellar microstructure within a matrix of grains is a known phenomenon in many materials and has been well described by many sources.25,26 The process occurs when, due to a change in temperature, the alloy segregates into two separate compounds. Due to the expulsion of one constituent from the compound, an advancing front rich in expelled constituent is created, which slows the propagation of the phase boundary. The observed lamellae are created due to this self-slowed segregation reaction.25 In such
processes, it is obvious that the time scale involved in crystallization, e.g., the heating rate, directly affects the attainable lamella spacing. In the present case, we observed that an increase of heating rate from 1 to 100 K/s results in a 10-fold reduction in lamella spacing (from about 1 to 0.1 μm). Although our data are very limited, a lamella spacing showing a square root dependence on heating rate is a reasonable first approximation result because the phase separation into lamellae is a diffusional process where the spacing λ depends on the square root of the effective diffusion coefficient D (mainly involving As) multiplied by time t allowed for this process: 
\[ \lambda \approx \sqrt{Dt}. \]

Another interesting feature to elucidate is how the observed microstructure, in particular the decomposition into two phases, relates to the double peak observed in the DSC traces. The initial sharp exothermal peak observed on heating from the undercooled liquid clearly relates to crystallization. Since we have identified the second phase as amorphous using EM, the broad shoulder is not a second crystallization effect. It must therefore be understood in the context of an exothermic relaxation or reorganization effect. This is corroborated by the fact that the transition effect is not a reversible process (cf. SI section 6), unless the sample is returned to a fully molten state. At relatively low crystallization temperatures (heating rates 1—100 K/s), the driving force for crystallization is high, while mobility is still extremely low: the typical behavior of a fragile liquid PCM. This leads to crystallization into a highly unfavorable phase where As is partly incorporated into the SeTe structure. We speculate several thermal reorganization effects take place after this initial crystallization. The amorphous As-rich phase, stressed by the partial crystallization of the alloy, might undergo a structural relaxation. Alternatively or concurrently, a redistribution of elemental species throughout both phases may take place, removing As from the crystalline phase and redistributing all expelled As within the glassy phase. At the lower heating rates, substantially more time is available for these processes, resulting in a more pronounced shoulder.

The phase segregation as observed using TEM also implies that the initial determination of the specimen composition using the melting point will overestimate the Te content and is in fact based on an incorrect assumption since the sample segregates into two phases. As shown in SI section 1, however, the \( T_m \) can still be used as a reasonable estimator of composition. Nevertheless, as shown by the microscopy data, one should be careful in interpreting the data in terms of absolute composition. The segregated phases (undercooled liquid and crystal) are expected to be fully remixed when the whole sample returns to the melt. The segregation, melting, and quenching, therefore, represent a reversible phase change system.

From our analysis, we can extract several implications for functional application in phase-change materials. Since almost complete phase separation with respect to As occurs, the system can be treated as a pseudobinary alloy, where the amorphous As\(_x\)(Se/Te)\(_{1−x}\) severely hampers the SeTe crystallization (three orders of magnitude lower quench rate). The crystallization, while slower (or at higher temperature), still proceeds in similar fashion, as shown in Figures 1 and 2. TEM analysis confirms the SeTe phase still crystallizes into the trigonal phase. For application into optics, the alloy is to remain stable in the amorphous phase, however. We have shown that even the addition of 10 at. % As is enough to stabilize the alloy into the amorphous phase with modest cooling rates of a few K/s.

The results presented above clearly indicate the merit of combining powerful thermal techniques with well-established electron microscopy methods to obtain a full understanding of the material.

### CONCLUSIONS

Ultrafast differential scanning calorimetry and transmission electron microscopy were performed to form a comprehensive understanding of the reversible crystallization behavior of SeTeAs alloys. Using ultrafast DSC, extended phase diagrams showing glass transition and crystallization as a function of elemental composition were presented, and we showed that the addition of 10 at. % As reduced the critical quench rate by three orders of magnitude. Kissinger analysis was performed, and the alloys were found to show non-Arrhenius fragile behavior, which is common for phase-change materials. Using a novel technique to transfer ultrafast-DSC specimens to TEM, we investigated the two-phase lamellar microstructure, which was formed upon crystallization. It was found that feature size reduces by orders of magnitude when rapid heating was used. Using electron diffraction and elemental mapping, we found coexisting crystalline Te-rich and amorphous As/Se-rich lamellae. The observed microstructure allows explanation of an exothermic shoulder after the initial crystallization in the DSC traces at lower heating rates. These phenomena make compelling arguments to combine ultrafast thermal analysis with in-depth structural analysis using TEM.

### METHODS AND EXPERIMENTAL DETAILS

Se\(_{40}\)Te\(_{36}\)As\(_{24}\) alloys were prepared by mixing their pure constituents into a quartz ampule and melting them in an oven at 450 °C for 8 h. The resulting alloy was slowly (~1 K/min) cooled to room temperature. The resulting ingot was shattered into smaller parts for investigation in (ultrafast-) differential scanning calorimetry using a PerkinElmer DSC and a Mettler Toledo Flash DSC 1. For regular DSC, 10 mL Al pans were used, while for the ultrafast DSC UFS-1, chip sensors were used with an active area of 500 μm in diameter. The samples are molten to the heater area and are approximated as a half-sphere with diameter of 100 μm and sample mass of 1−2 μg. Measurements were performed in a 20 mL/min nitrogen flow environment. Single flakes of Se\(_x\)Te\(_{1−x}\)As\(_{10}\) and Se\(_{10}\)Te\(_{36}\)As\(_{24}\) were deposited on the calorimetry sensor. These samples were heated at different rates to capture their crystallization behavior and consecutively quenched into the amorphous phase by cooling with 4000 K/s. The heat-flow traces are recorded for all heating and cooling steps. The composition of the sample shifts rather slowly through evaporation, allowing for many measurements on a single starting sample. For each crystallization run, the composition is approximated from the observed melting peak temperature, as was also described in ref 18 and SI section 1. The cyclic heat treatment eliminates sample to sample variations and shows the applicability of these alloys to be reversibly switching phase-change systems.

SEM images were made using a Philips/FEI ESEM XL30 FEG. Specimen transfer from ultrafast DSC to TEM was performed by transferring the sample using paper and a hair, and embedding the samples in an epoxy resin membrane suspended on a copper ring. The samples were polished to electron transparency by ion polishing using a Gatan PIPS II. (S)TEM analysis was performed using a JEOL JEM2010, and images were analyzed using a digital micrograph (Gatan). EDS/STEM analysis was performed using a Thermo-Fischer detector attached to the JEM2010 and analyzed using NSS3.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.8b00450.

Additional composition analysis, TEM sample preparation methods, analysis of SeTe using TEM, and DSC analysis of two - peak transition (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: p.a.vermeulen@rug.nl.

ORCID

Paul A. Vermeulen: 0000-0003-2035-3383

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Pogatscher, S.; Leutenegger, D.; Hagmann, a.; Ugogowitz, P. J.; Levi, J. F. Characterization of bulk metallic glasses via fast differential scanning calorimetry, Thermochim. Acta 2014, 590, 84−90.
(2) Chokshi, R.; Zia, H. Hot-Melt Extrusion technique: A Review, Iran. J. Pharm. Res. 2004, 3, 1−6.
(3) Wuttig, M.; Yamada, N. Phase-change materials for rewriteable data storage, Nat. Mater. 2007, 6 (11), 824−32.
(4) van Herwaarden, S.; Iervolino, E.; van Herwaarden, F.; Wijffels, J.; Leeuwen, A.; Mathot, V. Design, performance and analysis of thermal lag of the UFS1 twin-calorimeter chip for fast scanning calorimetry using the Mettler-Toledo Flash DSC 1, Thermochim. Acta 2011, 522 (1−2), 46−52.
(5) Schawe, J. E. K. Influence of processing conditions on polymer crystallization measured by fast scanning DSC, J. Therm. Anal. Calorim. 2014, 116 (3), 1165−1173.
(6) Orava, J.; Greer, a L.; Gholphour, B.; Hiewak, D. W.; Smith, C. E. Characterization of supercooled liquid Ge2Sb2Te5 and its crystallization by ultrafast-heating calorimetry, Nat. Mater. 2012, 11 (4), 279−83.
(7) Chen, B.; Momand, J.; Vermeulen, P. A.; Kooi, B. J. Crystallization kinetics of supercooled liquid Ge-Sb based on ultrafast calorimetry, Cryst. Growth Des. 2016, 16, 242.
(8) Chen, B.; de Wal, D.; ten Brink, G. H.; Palasztas, G.; Kooi, B. J. Resolving Crystallization Kinetics of GeTe Phase-Change Nanoparticles by Ultrafast Calorimetry, Cryst. Growth Des. 2018, 18, 1041.
(9) Rosenthal, M.; Doblas, D.; Hernandez, J. J.; Odarchenko, Y. I.; Burghammer, M.; Di Cola, E.; Spitzer, D.; Antipov, A. E.; Aldoshin, L. S.; Ivanov, D. A. High-resolution thermal imaging with a combination of nano-focus X-ray diffraction and ultra-fast chip calorimetry, J. Synchrotron Radiat. 2014, 21 (1), 223−228.
(10) Wei, L.; Jiang, J.; Shan, M.; Chen, W.; Deng, Y.; Xue, G.; Zhou, D. Integration of ultrafast scanning calorimetry with micro-Raman spectroscopy for investigation of metastable materials, Rev. Sci. Instrum. 2014, 85 (7), 074901.
(11) Schawe, J. E. K.; Vermeulen, P. a.; van Drongelen, M. Two processes of α-phase formation in polypropylene at high supercooling, Thermochim. Acta 2015, 616, 87−91.
(12) Orava, J.; Greer, a L.; Gholphour, B.; Hiewak, D. W.; Smith, C. E. Characterization of supercooled liquid Ge 2 Sb 2 Te 5 and its crystallization by ultrafast-heating calorimetry, Nat. Mater. 2012, 11, 279.
(13) Simpson, R. E.; Fons, P.; Kolobov, A. V.; Fukaya, T.; Krchal, M.; Yagi, T.; Tomimaga, J. Interfacial phase-change memory, Nat. Nanotechnol. 2011, 6 (8), 501−505.
(14) Cui, S.; Chahal, R.; Boussard-Plédel, C.; Nazabal, V.; Doualan, J. L.; Troles, J.; Lucas, J.; Bureau, B. From selenium- to tellurium-based glass optical fibers for infrared spectroscopies, Molecules 2013, 18 (5), 5373−5388.
(15) Houizot, P.; Boussard-Plédel, C.; Faber, a J.; Cheng, L. K.; Bureau, B.; Van Nijmatten, P. a.; Gieselen, W. L. M.; Pereira do Carmo, J. Lucas, J. Infrared single mode chalcogenide glass fiber for space., Opt. Express 2007, 15 (19), 12529−12538.
(16) Churbanov, M. F.; Shiryaev, V. S.; Suchkov, A. I.; Pushkin, A. A.; Gerasimenko, V. V.; Shaposhnikov, R. M.; Dianov, E. M.; Plotnichenko, V. G.; Koltashev, V. V.; Pyrkov, Y. N.; Lucas, J. Adam, J.-L. High-purity As-S-Se and As-Se-Te glasses and optical fibers, Inorg. Mater. 2007, 43 (4), 441−447.
(17) Ligero, R. a.; Vazquez, J.; Villares, P.; Jimenez-Garay, R. Crystallization kinetics in the As-Se-Te system, Thermochim. Acta 1990, 162, 427−434.
(18) Vermeulen, P. A.; Momand, J.; Kooi, B. J. Reversible amorphous-crystalline phase changes in a wide range of Se1-xTex alloys studied using ultrafast differential scanning calorimetry, J. Chem. Phys. 2014, No. 141, 024502.
(19) Xu, W.; Wang, L. M.; Nieman, r. a.; Angell, C. A. Ionic Liquids of Chelated Orthoborates as Model Ionic Glassformers, J. Phys. Chem. B 2003, 107 (42), 11749−11756.
(20) Bureau, B.; Boussard-Pledel, C.; Lucas, P.; Zhang, X.; Lucas, J. Forming glasses from Se and Te, Molecules 2009, 14 (11), 4337−50.
(21) Eifert, J. R.; Peretti, E. A. The Phase Diagram of the System Tellurium/Arsenic, J. Mater. Sci. 1968, 3, 293−296.
(22) Henderson, D.; Ast, D. Viscosity and crystallization kinetics of As 2 Se 3, J. Non-Cryst. Solids 1984, 64, 43−70.
(23) Svoboda, R.; Malek, J. Structural relaxation in Se-rich As-Se glasses, J. Non-Cryst. Solids 2013, 363, 89−95.
(24) Ghosh, G.; Sharma, R. C.; Li, D. T.; Chang, Y. a. The Se-Te (Selenium-Tellurium) system, J. Phase Equilib. 1994, 15 (2), 213−224.
(25) Porter, D. A.; Easterling, K. E. Phase Transformations in Metals and Alloys, second ed.; CRC Press, 2004.
(26) Callister, W. D.; Rethwisch, D. G. Materials Science and Engineering; Wiley, 2011.