An Anomalous Small-angle X-ray Scattering Investigation of Thermally Densified, Heavy-metal-ion-loaded Diphosil

J. V. Beitz,[1] S. Skanthakumar,[1] S. Seifert,[1] L. Fan,[2] P. Thiyagarajan[2]
[1]Chemistry Division and [2]Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Conventional and anomalous small-angle x-ray scattering (SAXS) studies were carried out on a series of primarily vitreous silica materials that had been loaded with heavy metal ions. These materials are based on a chemically functionalized, highly porous silica termed Diphosil [1]. Diphosil uses diphosphonic acid groups to nearly irreversibly sorb heavy metal ions, such as lanthanides or actinides, in an ion exchange process. Diphosil is the basis of a Nuclear Energy Research Initiative project that seeks to establish a single material approach for reducing nuclear waste volume. The materials are also being investigated for their unusual photophysical properties.

Past work at Argonne National Laboratory showed that heating these materials in air burns out their organic content and leaves behind phosphoric acid, which reacts with the sorbed metal ions to form metal phosphates or with the silica substrate [2]. That work also provided preliminary evidence that further heating leads to pore collapse and aggregation in a process that has been termed thermal densification. Our present work is being done to identify the factors that influence thermal densification of heavy-metal-ion-loaded Diphosil.

Methods and Materials

Samples were prepared as recently described [2]. In this process, Diphosil, as a 60-100 mesh powder, was fully loaded with a given lanthanide ion from dilute nitric acid solution. The resulting material was rinsed briefly with deionized water. This material was held at 378K for a few hours to dry and then was heated at 1K/min to the end-point temperature, which was held for 1 h. The samples were then rapidly cooled by turning off the power to the furnace. Trivalent Eu, Gd, Tb, and Lu ions were loaded into Diphosil. End-point temperatures of 973, 1073, 1173, 1273, 1373, and 1473K were used, resulting in 24 distinct sample materials as well as an additional six samples that contained Diphosil with no heavy metal loading that had been heated to the same end-point temperatures. Material heated to 1273K or higher consisted of particles that were irregularly shaped, striated, roughly rectangular slabs with rounded edges that typically were a few hundred micrometers in length. Material heated to 1173K or lower temperatures retained the larger particle size and sharper edges typical of as-received Diphosil. For SAXS studies, a single layer of particles of a given sample material was held between two pieces of adhesive-backed 25-µm-thick polyimide tape that spanned a 6-mm-diameter hole in a 75-µm-thick brass sheet.

The BESSRC SAXS instrument on 12-ID-C at the APS has been described [3]. A mosaic charged coupled device (CCD) detector array was used to record scattering patterns. A National Institute of Standards and Technology (NIST)-traceable sample of silver-filled bentonite clay was used to calibrate the SAXS instrument. Samples were held at ambient temperature during data acquisition. The x-ray beam diameter at the sample was 0.3 mm. A given scattering pattern was collected by exposing the sample for 0.1 to 1 s to the monochromatic x-ray beam. Anomalous SAXS (ASAXS) data were recorded from just above the L_3 edge of the lanthanide ion of interest and proceeding through a series of successively longer x-ray wavelengths to approximately 200 eV below the L_3 edge.

Results

Examples of the recorded SAXS data for Diphosil with no heavy metal ion loading as well as fully Eu-, Gd-, Tb-, and Lu-loaded Diphosil are shown in Fig. 1 as scattered intensity I vs. Q, the momentum transfer. ($Q = 4\pi\sin\theta/\lambda$, where 2θ = the scattering angle and λ = the x-ray wavelength.) In each case, the sample material had been heated to 1373K. It is clear that the presence of metal ion loading influenced the observed SAXS intensity as a function of Q, as did the particular metal ion that was loaded into Diphosil. The data shown in Fig. 1 were recorded 200 eV below the L_3 edge of the lanthanide ion that had been loaded into Diphosil.

Analysis of the SAXS data for Tb-loaded Diphosil that had been heated to 1373K, by using a unified fit with constant background, gave a fit radius of gyration (R_g) value of 6.1659 ± 0.0005 nm. We had investigated this same material previously by using small-angle neutron scattering (SANS) at the Intense Pulsed Neutron Source at Argonne with run times of typically 1 to 2 h per sample. Immersion in 58% D_2O + 42% H_2O contrast-matched the silica content of this material in SANS and resulted in a fit R_g value of 6.14 ± 0.12 nm, in good agreement with the value found by using SAXS. The SANS data also provided evidence that particles of Tb-loaded Diphosil that had been heated to 1373K were impenetrable by water, a condition that is consistent with a loss of open porosity. The sample volume interrogated by the neutron

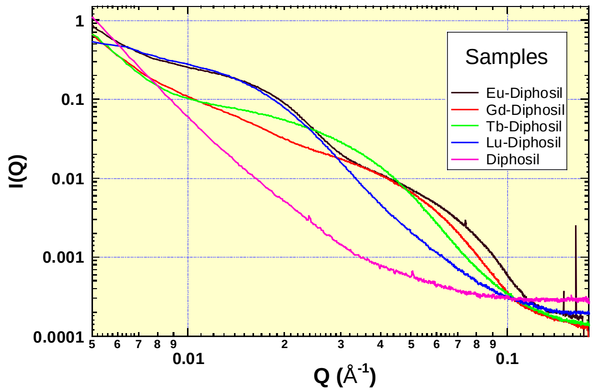

FIG. 1. SAXS observed from Diphosil and Eu-, Gd-, Tb-, and Lu-loaded Diphosil that had been heated to 1373K.

beam was 0.11 cm^3 in our SANS studies, whereas the interrogated volume for our SAXS work was 5.3×10^{-6} cm^3.

An example of our recorded ASAXS data is shown in Fig. 2 for the case of Tb-loaded Diphosil that had been heated to 1373K. It is evident that a significant anomalous scattering effect was observed only over a limited range of Q values as the x-ray energy approached the L_3 edge of Tb at 7513 eV. This is definitive evidence that the nanophases in this material, whose size was measured by using SANS and SAXS methodologies, do, in fact, contain Tb. Our conventional x-ray powder diffraction studies identified the presence of $TbPO_4$ in thermally densified Tb-loaded Diphosil. In addition, laser-induced fluorescence studies on Tb^{3+} ions in this material have provided evidence of facile ion-ion energy transfer, which is consistent with Tb^{3+} ions that are in close proximity to each other.

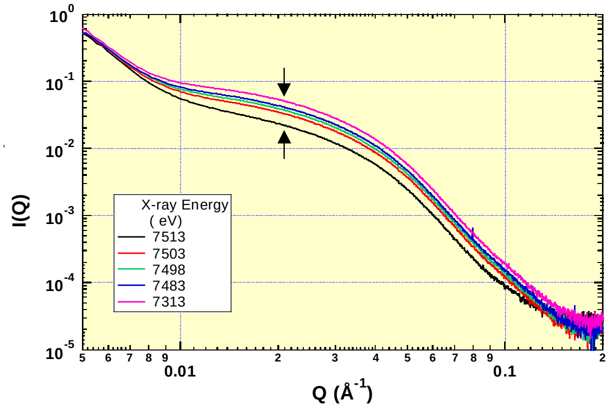

FIG. 2. The ASAXS effect observed in Tb-loaded Diphosil that had been heated to 1373K is evidence of Tb-containing nanophases in this material.

Discussion

Our work has shown that SANS and SAXS studies provide valuable complementary insight into the sintering and aggregation that lead to pore collapse and formation of compact metal phosphate nanophases during thermal densification of heavy-metal-ion-loaded Diphosil. For example, contrast-matching by using immersion in 58% D_2O + 42% H_2O provides a means of suppressing scattering from the silica content of our materials in SANS, whereas ASAXS can provide definitive evidence as to the presence heavy metal ions in the compact nanophases that are produced by thermal densification of metal-ion-loaded Diphosil.

The SAXS patterns that we observed for metal-ion-loaded Diphosil heated to a given temperature were unexpectedly a function of the lanthanide ion initially sorbed into Diphosil. This is evidence that the nature of the heavy metal ion that is sorbed into Diphosil influences the thermal densification of Diphosil. In addition, ASAXS studies on Lu-loaded Diphosil suggest that no compact Lu-containing phase formed at the highest temperature (1473K) used for thermal densification. We plan to investigate Diphosil loaded with lanthanides with atomic weights intermediate between Tb and Lu (e.g., Dy, Ho, Er, Tm, or Yb) to further probe the influence of metal ion properties on thermal densification of Diphosil as well as the influence of higher densification temperatures on the formation of compact metal-containing phases in the case of the heaviest lanthanide ions.

With the exception of Lu-loaded Diphosil, our present work, together with our past studies, shows that thermal densification of lanthanide-ion-loaded Diphosil results in the formation of metal phosphate nanophases that chemically fix the metal ions that had been sorbed from aqueous solution and encapsulate them in nanophases that are embedded in vitreous silica. Vitreous or glassy silica is one of the most radiation-resistant glasses known and is noted for its broad optical transmission range.

Acknowledgments

Use of the Actinide Facility, the APS, and the Basic Energy Sciences Synchrotron Radiation Center (BESSRC) was supported by the U. S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), under Contract No. W-31-109-ENG-38. This work was carried out under the auspices of the DOE BES and the DOE Office of Nuclear Energy, Science, and Technology under Contract No. W-31-109-ENG-38.

References

[1] R. Chiarizia, E. P. Horwitz, K. A. D'Arcy, S. D. Alexandratos, and A. W. Trochimczuk, Solv. Extr. Ion Exch. **14**, 1077-1100 (1996).

[2] J. V. Beitz and C. W. Williams, Solv. Extr. Ion Exch. **19**, 699-723 (2001).

[3] S. Seifert, R. E. Winans, D. M. Tiede, and P. Thiyagarajan, J. Appl. Cryst. **33**, 782-784 (2000).