

Anomalous Small-angle X-ray Scattering Investigation of Thermal Densification of Heavy Lanthanide Ion-loaded Diposil

J.V. Beitz,¹ S. Skanthakumar,¹ S. Seifert,² L. Fan,³ P. Thiyagarajan³

¹Chemistry Division, ²Advanced Photon Source (APS), and ³Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory (ANL), Argonne, IL, USA

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 contained ions of a heavy lanthanide element that had been sorbed into a chemically functionalized, highly porous silica, termed Diposil [1]. Diposil uses diphosphonic acid groups to strongly sorb heavy metal ions, such as lanthanides or actinides, in an ion-exchange process. Diposil is the basis of a Nuclear Energy Research Initiative project that seeks to establish a single material approach for reducing nuclear waste volume. These materials also are being investigated for their unusual photophysical properties.

Past work at ANL showed that heating these materials in air oxidizes their organic content and leaves behind phosphoric acid. The acid reacts with the sorbed metal ions to form metal phosphates or with the silica substrate to form silicophosphate phases [2]. Continued heating results in pore collapse (in a process termed thermal densification) and the formation of heavy-element phosphate nanophasess, as shown in our past studies on lighter lanthanide ions [3]. The purpose of our present work was to characterize the nature of such nanophasess and the influence of the metal ion's properties on important factors, such as the size of the produced nanophasess.

Methods and Materials

Samples were prepared as recently described [2]. In this process, Diposil, as a 60-100 mesh powder, was fully loaded with a given trivalent lanthanide ion from a 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. Then it was heated at 1K per minute to the end-point temperature, which was held for 1 hour. The samples then were rapidly cooled by turning off the power to the furnace. End-point temperatures of 973, 1073, 1173, 1273, 1373, and 1473K were used. 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 a temperature of 1173K or lower retained the larger particle size and sharper edges typical of as-received Diposil. 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.

The SAXS instrument on BESSRC beamline 12-ID at the APS has been described [4]. A mosaic charge-coupled device (CCD) detector array was used to record scattering patterns. Samples were held at ambient temperature during data acquisition. A given scattering pattern typically was collected by using a 1-second exposure of the sample to the monochromatic x-ray beam. Anomalous small-angle x-ray scattering (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

Both SAXS and ASAXS studies were carried out on sample materials that had been heated to 1173K or higher. The onset of pore collapse was observed in sample materials that had been heated to 1273K. In all cases, an ASAXS effect [3] was observed only from samples that had been heated to 1373K or higher. An example of such data is shown in Fig. 1 for the case of Gd-loaded Diposil that had been heated to 1373K. The data are presented as scattered intensity $I(Q)$ versus momentum transfer Q , where $Q = 4\pi\sin\theta/\lambda$, 2θ is the scattering angle, and λ is the x-ray wavelength. The energy of the incident x-rays

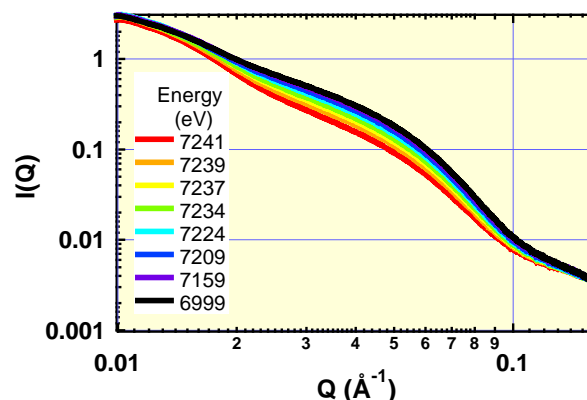


FIG. 1. Scattered x-ray intensity $I(Q)$ versus Q for Gd-loaded Diposil that had been heated to 1373K, as function of the incident x-ray energy.

was varied from near coincidence with the Gd L_3 edge to more than 200 eV below that edge, as shown.

The large reduction in $I(Q)$, which reached a maximum near $Q = 0.04 \text{ \AA}^{-1}$ as the incident x-ray energy approached the Gd L_3 edge at 7243 eV, is the hallmark of the anomalous scattering effect. The fact that the observed anomalous scattering effect occurred over a particular range of Q values is definitive evidence for the formation of Gd-containing nanophases. Only in the case of Lu-loaded Diphosil was the ASAXS effect reduced to a little larger than the statistical reproducibility of the SAXS pattern.

Radius of gyration R_g values were determined by Guinier analysis of SAXS data that had been recorded 200 eV or more below the L_3 edge of the lanthanide contained in the sample material. The observed R_g values for heavy lanthanide ion-loaded Diphosil that had been heated to 1373K are shown in Fig 2. In the case of Lu-loaded Diphosil, x-ray powder diffraction (XRD) studies showed a pattern that did not match that of any Lu-containing phase in the ICDD database. The heavy metal phase identified by XRD in all other cases studied was a lanthanide orthophosphate. Because the chemistry of the lanthanide elements is so similar and because the lanthanide loading of our samples was nearly identical, our observation of lanthanide nanophases whose size varied by more than a factor of three across the series of heavy lanthanides was unexpected.

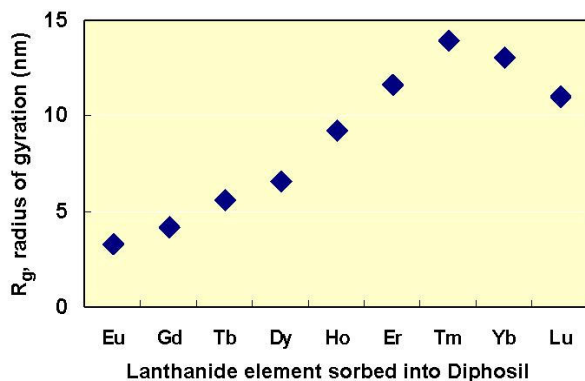


FIG. 2. Observed radius of gyration R_g of lanthanide phosphate nanophases that formed in lanthanide ion-loaded Diphosil that had been heated to 1373K.

On the basis of the assumption that the produced lanthanide nanophases are spherical, analysis of the SAXS data was carried out by using a Schultz polydisperse sphere model [5]. The trend in the resulting fit mean sphere radii was the same as the trend in R_g data that is shown in Fig 2. In addition, the fit width of the size distribution increased from Eu to Tm and then decreased slightly. These results show that the assumption of spherical nanophases is consistent with the observed data.

Discussion

Our work has shown that heavy metal phosphate nanophases form when metal ion-loaded Diphosil is heated to the pore collapse point. Observation of the ASAXS effect near the L_3 x-ray edges of lanthanide ions for samples heated to 1373K or higher provides definitive evidence that the observed nanophases contain heavy metal ions. The large variation in nanophase size with the atomic number of the contained lanthanide element in Fig. 2 is unexpected. It seems likely that variation in the interaction of lanthanide phosphates with silicophosphate accounts for much of this behavior. On the basis of chemical analysis and solid-state nuclear magnetic resonance (NMR) studies, about 75% of the initial phosphorus content of Diphosil is converted into silicophosphate during thermal oxidation of the organic content of Diphosil, while the remainder of the phosphorus is incorporated into lanthanide phosphate phases.

At high temperature, silicophosphate can act as a flux to promote the mobility of metal ion species. Two mechanisms that would account for the trend exhibited by Eu- through Tm-loaded Diphosil in Fig. 2 are (1) the initial formation of small metal-phosphate nanophases that become mobile and aggregate to form larger nanophases and (2) the variation in the solubility of lanthanide phosphates with the lanthanide's increasing atomic number. In either case, it is the interaction between lanthanide phosphates and the host phase as a function of the atomic number of the lanthanide that evidently is the dominant factor that contributes to the observed trend in nanophase size. Variation in the ionic radius of the lanthanide ions (see Fig. 3) and the dominant role of electrostatic attraction in the strength of lanthanide ion complexes contribute to this interaction. Distinguishing between the proposed mechanisms likely will require time-resolved high-temperature SAXS and

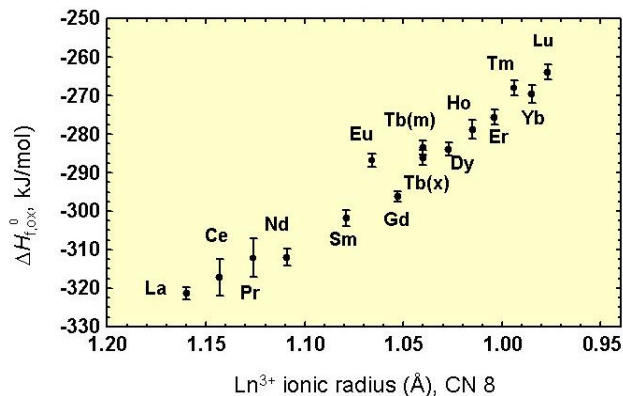


FIG. 3. Reported enthalpy of formation of lanthanide orthophosphates [6] as a function of the ionic radius of a trivalent lanthanide ion when its coordination number (CN) is 8 [7].

ASAXS studies of the growth kinetics of phase size and distributions of phase size.

For samples heated to 1373K, our observation that phase size peaks for Tm-loaded Diphosil suggests the onset of phase decomposition as a size-limiting factor. As shown in Fig. 3, the enthalpy of formation of lanthanide orthophosphates [6] exhibits a general, but irregular, trend toward decreased stability (less negative enthalpy of formation) with an increasing lanthanide atomic number. Although 1373K is far below the chemical decomposition temperature or melting point of lanthanide orthophosphates as bulk phases, it is known that nanophases exhibit significantly lower melting points and are less stable thermodynamically than are their corresponding bulk phases. Phase decomposition as a size-limiting factor is consistent with the lack of any observable Lu orthophosphate XRD peaks and a diminished ASAXS effect in Lu-loaded Diphosil that has been heated to 1373K.

Unexpectedly, the SAXS patterns that we observed for heavy lanthanide ion-loaded Diphosil heated to 1373K or higher were a function of the lanthanide ion initially sorbed into Diphosil. This is evidence that the nature of the heavy metal ion sorbed into Diphosil influences thermal densification. We plan to investigate Diphosil loaded with lanthanides having a lower atomic number to further probe the influence of metal ion properties on the thermal densification of Diphosil as well as the influence of a higher densification temperature on the formation of compact metal-containing phases.

Our present and past work has shown that thermal densification of heavy metal 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 encapsulates those ions 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, *Solvent Extr. Ion Exch.* **14**, 1077-1100 (1996).
- [2] J.V. Beitz and C.W. Williams, *Solvent Extr. Ion Exch.* **19**, 699-723 (2001).
- [3] J.V. Beitz, S. Skanthakumar, S. Seifert, L. Fan, and P. Thiyagarajan, *Advanced Photon Source Activity Report 2001*, ANL-02/06 (Argonne National Laboratory, Argonne, IL, December 2002).
- [4] S. Seifert, R.E. Winans, D.M. Tiede, and P. Thiyagarajan, *J. Appl. Crystallogr.* **33**, 782-784 (2000).
- [5] T. Reiker, A. Hanprasopwattana, A. Datye, and P. Hubbard, *Langmuir* **15**, 638-641 (1999).
- [6] S.V. Ushakov, K.B. Helean, A. Navrotsky, and L.A. Boatner, *J. Mater. Res.* **16**, 2623-2633 (2001).
- [7] R.D. Shannon, *Acta Crystallogr. A* **32**, 751-767 (1976).