High-energy X-ray Scattering Study of Rare Earth Ultraphosphate Laser Glasses

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Introduction

Rare earth (R) phosphate glasses, or REPGs, exhibit interesting luminescent and magnetic properties that are utilized in a variety of optical, optoelectronic, and optomagnetic applications. For example, R_2O_3-doped phosphate glasses are a preferred material for use in high-energy and high-peak-power laser systems.

Naturally, structural features of REPGs play key roles in determining their optical properties. For example, the coordination environments of the rare earth ions affect the optical gain of an amplifier glass. Electric dipole coupling between neighboring excited ions leads to concentration quenching by a cooperative upconversion process that results in the loss of an excited ion. Nonradiative de-excitation can occur if one of the excited ions is coupled with an -OH impurity. Thus, detailed information about the local structural environment around R^{3+} ions is important for understanding the photoluminescent behavior of REP glasses.

Depending on the O/P ratio, phosphate glasses are classified as polyphosphates (O/P is >3), metaphosphates (O/P is ~2.5), and ultraphosphates (O/P is <2.5). The clear majority of REPGs currently used in optical applications are rare earth-meta/polyphosphates. Consequently, the relationships between the atomic structures and optical properties of rare earth-meta/polyphosphate glasses have been well documented. Recent preliminary studies of rare earth-ultraphosphate glasses (REUPGs) have indicated that they, too, may be developed for various optical/optomagnetic applications. Mainly because of preparation difficulties, however, atomic structure-optical/magnetic property relationships of REUPGs have been relatively unexplored. By using a sealed ampoule melting technique, the investigators are now able to prepare anhydrous REUPGs ($0.05 < x < 0.25$) at will. At the time this experiment was performed, K. Marasinghe and R. Brow were in the process of writing a National Science Foundation (NSF) proposal titled, "Structure-Property Relationships of Novel Rare Earth-Ultraphosphate Glasses," seeking funds to conduct a comprehensive investigation of the atomic structure-property relationships of REUPGs. This proposal called for investigating the atomic structure of REUPGs by using a multitude of techniques, including neutron and high energy x-ray diffraction (HEXRD), x-ray absorption spectroscopy, ir and Raman spectroscopy, and x-ray photoelectron spectroscopy.

This high energy x-ray diffraction study was an exploratory investigation designed to collect preliminary data needed for the above-described NSF proposal.

Methods and Materials

Several rare earth ultraphosphate glasses of batch composition $xR_2O_3(1\text{-}x)P_2O_5$ (R = Nd or Er and $0.05 < x < 0.30$) were prepared by using the sealed ampule technique. The exact chemical composition of these glasses was determined by using the inductively coupled plasma (ICP) technique. Other important properties, such as glass transition temperature, refractive indices, and luminescence characteristics, were also measured.

High-resolution pair-distribution functions were measured from high-energy scattering experiments at beamline 11-ID-C at the APS. High energy (114 keV) combined with small angles of scatter (up to 30°) could cover a large momentum transfer Q range of 0.5 to 30 $Å^{-1}$. A preliminary analysis of data was conducted by using the software package ISOMERX developed by C. Benmore's group at ANL.

Results

A preliminary analysis of data showed that successful HEXRD experiments could be conducted in spite of handling difficulties resulting from the hygroscopic nature of the samples. As mentioned above, the main purpose of this study was to collect preliminary data for a planned NSF proposal. This three-year proposal (July 2003 to June 2006, principal investigators K. Marasinghe and R. Brow) was funded (NSF Award Nos. 305199 and 305202), and the investigators have already secured future beam time at the APS to conduct detailed HEXRD studies on samples related to this NSF-sponsored project.

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