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XPS and DRIFTS Study of Cerium in Ce-Si-Al-O-N Glasses

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Abstract

Glasses belonging to the Ce-Si-Al-O-N system have been prepared by heating physical mixtures of CeO_2, AlN and SiO_2 under N_2. A sample in which AlN has been replaced by Al_2O_3 was also prepared for studying the influence of the nitrogen content in the oxidation state of cerium. X-ray Photoelectron Spectroscopy (XPS) and Diffuse Reflectance Fourier Transform Spectroscopy (DRIFTS) of the prepared glasses indicated that the amount of Ce^{4+} ions present in the glass matrix is very low, if any, in all samples. The presence of nitrogen in the glass network alters the electronic density of all the elements present in the glass, as demonstrated by XPS, but does not modify the coordination polyhedra of cerium that remains unchanged whatever the nitrogen content of the glass network.

Introduction

Preparation, structure and properties of glasses in the Ce-Si-Al-O system have been previously studied [1,2,3]. The glass domain, according to these authors, is encountered in the following molar compositional range: 15-30 % CeO_2/16-23% Al_2O_3/47-62% SiO_2.

On increasing cerium content the physical properties of the glasses are modified in such a way that the glass transition temperature decreases while the thermal expansion coefficient, density and hardness increase [3]. All these modifications are related to a decrease in the network connectivity produced by the insertion of cerium ions [2] that results in an increase in the amount of non-bridging oxygens in the [SiO_4] tetrahedra as well as in an increase of the Al^{IV}/Al^{VI} ratio [4]. On the other hand, nitrided glasses also show enhanced physical properties.

The oxidation state of cerium ions in these glasses has been studied by a wide variety of techniques. In every case, both Ce^{3+} and Ce^{4+} ions are present in the obtained glasses depending on the relative proportions of both oxidation states on the preparation method [5], cerium concentration [2] and basic character of the matrix [6]. Particularly, the relative proportion of Ce^{3+} ions increases if the glasses are obtained under N_2 atmosphere.

Lixiviation studies have shown that plutonium has an apparently high mobility in glassy matrices as a result of the +4 oxidation state [7]. Geochemical behaviour of ^{235}U fission products is similar to that shown for lanthanides [8]. The reducing character of nitride ions in glass media previously shown by us [9] leads us to study the influence of nitrogen on the oxidation state of cerium in SiAlON glasses as a way of modelling the behaviour of ^{235}U fission products in glass matrices.