Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 359 (2006) 132–138
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Structural aspects of barium borosilicate glasses containing thorium and uranium oxides

R.K. Mishra [a], V. Sudarsan [b], C.P. Kaushik [a], Kanwar Raj [a], S.K. Kulshreshtha [b], A.K. Tyagi [b,*]

[a] *Waste Management Division, Bhabha Atomic Research Centre, Mumbai 400085, India*
[b] *Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India*

Received 29 March 2006; accepted 15 August 2006

Abstract

Barium borosilicate glasses incorporated with 15.86 wt% ThO_2 and containing different amounts of uranium oxide were prepared by conventional melt quench method. Based on ^{29}Si and ^{11}B magic angle spinning nuclear magnetic resonance (MAS NMR) studies, it has been confirmed that uranium oxide incorporation is associated with distortion of borosilicate network as revealed by the increase in the relative concentration of Q^2 structural units of silicon as well as the increase in the quadrupolar coupling constant (C_q) of BO_3 structural units. The increased number of non-bridging oxygen atoms brought about by the increase in Q^2 structural units of silicon facilitates the incorporation of both uranium and thorium ions in the sites created by non-bridging oxygen atoms (network modifying positions) in the glass. Uranium oxide incorporation above 7.5 wt% resulted in the phase separation of ThO_2 as revealed by the X-ray diffraction studies. The present study focuses on the structural changes with the borosilicate network of barium borosilicate glasses brought about by the introduction of thorium and uranium ions.
© 2006 Elsevier B.V. All rights reserved.

PACS: 81.05.Kf; 28.41.Kw; 61.18.Fs; 82.56.0b

1. Introduction

Borosilicate glasses have potential application in nuclear industry as suitable matrix for the immobilization of high-level nuclear wastes [1,2]. India has vast thorium resources amounting to about 1/3rd of the world reserve for its energy security on a sustainable basis. Accordingly, India has an ambitious program to use thorium in the blanket zone of fast breeder reactors at an appropriate growth of installed nuclear power in the second stage of nuclear energy program, which will be followed by introduction of Advanced Heavy Water Reactors (AHWR) based on Th–$^{233}U^{mox}$ (mixed oxide) fuel in the third stage [3]. Thorium and uranium will be among the main components present in the waste along with fission products like ^{137}Cs, ^{90}Sr, ^{106}Ru etc., which will be left over after the reprocessing of the spent fuel from reactors based on

* Corresponding author. Tel.: +91 22 2559 5330; fax: +91 22 2550 5151.
E-mail address: aktyagi@barc.ernet.in (A.K. Tyagi).

0022-3115/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2006.08.006

Th–$^{233}U^{mox}$ fuels [4]. This needs to be immobilized in a suitable inert matrix before their long term disposal in repositories. Borosilicate glass is one of the suitable candidates for immobilization of high level nuclear wastes, containing thorium, uranium and other fission products. No studies have been reported on the structural aspects of borosilicate glasses containing both thorium and uranium oxides, even though there are some reports on the structural aspects of borosilicate/silicate glasses incorporated with either thorium oxide or uranium oxide [5–12]. Extended X-ray absorption fine structure (EXAFS) studies on thorium incorporated silicate glasses revealed that the coordination around Th^{4+} depends on the concentration of ThO_2 in the borosilicate glass [5]. Recently we have reported that barium borosilicate glasses have got improved extent of ThO_2 incorporation compared to borosilicate glasses without BaO [6]. Based on ^{29}Si and ^{11}B MAS NMR studies, it has been inferred that Th^{4+} occupy sites which are created by non-bridging oxygen atoms (network modifying positions) in the glass, leaving the borosilicate network unaffected. This is further supported by the relatively large concentration of non-bridging oxygen atoms present in barium borosilicate glasses as revealed by the ^{17}O NMR study reported by Zhao et al. [13]. Uranium in borosilicate/aluminosilicate glasses is known to exists as U(IV), U(V) and U(VI) species, and depending up on the oxidizing or reducing environment used for glass melting, either U(VI) or U(IV) predominates in the glass matrix [7,8]. Further, the presence of ions like Ce^{4+}, Cr^{3+}, Ti^{3+} etc. also changes the relative concentration of different U species [8–10]. UV–visible-infrared absorption technique has been extensively used to identify and estimate the relative concentration of different uranium species present in the glass samples. Glancing angle EXAFS studies on borosilicate glasses containing Fe^{3+} and U^{6+} revealed that U^{6+} occupies the sites created by non-bridging oxygen atoms (network modifying positions) in the glass along with Na^+ ions, leaving the borosilicate network unaffected [11]. Similar behaviour of uranium ions has also been reported in ferric phosphate glasses by Mesko et al. [14].

Depending upon the oxidation state of the uranium ions, it can have different coordination polyhedra around them and this is expected to have significant effect on the structure of the glass network as well as on the extent of ThO_2 incorporation in the glass. Hence it will be of interest to study the structural aspects of borosilicate glasses when both uranium and thorium oxides are incorporated in it. Solid state nuclear magnetic resonance using ^{29}Si and ^{11}B as the probe nuclei combined with X-ray diffraction technique can be very effectively used for understanding the structural aspects as well as extent of ThO_2 incorporation in these glasses. Such studies will be helpful for the development of new glass formulations for the immobilization of wastes from the proposed nuclear reactors based on Th–U^{mox} fuels. The present work is an attempt to understand the influence of simultaneous incorporation of thorium and uranium oxide, on the structural network of barium borosilicate glass. Keeping this in mind, we have prepared barium borosilicate glasses containing a fixed concentration of ThO_2 (15.86 wt%) and incorporated with different amounts of uranium oxide (UO_3) and studied their structural aspects using ^{29}Si and ^{11}B MAS NMR and XRD techniques. ThO_2 amount was kept at 15.86 wt% as it is close to the optimum ThO_2 concentration that can be incorporated into the barium borosilicate glass without any phase separation.

2. Experimental

Required amounts of analytical grade $Ba(NO_3)_2$, $NaNO_3$, SiO_2 and H_3BO_3 were taken so as to get the base glass with a composition $(SiO_2)_{0.39}(B_2O_3)_{0.25}(Na_2O)_{0.12}(BaO)_{0.24}$ and mixed with required amounts of $Th(NO_3)_4 \cdot 5H_2O$ and UO_3, ground well and heated at 1000 °C for 4 h in siliminite crucibles. The free flowing melt was quenched between two stainless steel plates. For all the glass samples, the ratio of Na_2O to BaO and SiO_2 to B_2O_3 were maintained constant, and are 0.5 and 1.56, respectively. Further the constituents of the glass formulations were proportionately changed in such a way that SiO_2/Na_2O, SiO_2/B_2O_3, SiO_2/BaO, B_2O_3/Na_2O and B_2O_3/BaO are same for all the samples with different amounts of ThO_2 and UO_3. X-ray diffraction patterns were recorded using a Philips PW1710 X-ray diffractometer with nickel filtered Cu-K_α radiation. ^{29}Si and ^{11}B MAS NMR patterns were recorded using a Bruker Avance DPX 300 machine with basic frequencies of 59.62 and 96.29 MHz, respectively. Typical 90° pulse durations employed for ^{29}Si and ^{11}B NMR experiments were 4 and 2 μs, respectively, with corresponding delay times 8 and 3 s. Powdered samples were packed inside zirconia rotors and subjected to a spinning speed of 5 kHz for MAS NMR experiments. ^{11}B static

Download English Version:

https://daneshyari.com/en/article/1569763

Download Persian Version:

https://daneshyari.com/article/1569763

Daneshyari.com