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The effect of γ-radiation in Li_4SiO_4 ceramic breeder blankets

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HIGHLIGHTS

- Li_4SiO_4 is γ-irradiated with different doses (5, 10 and 13 MGy) and its electrical bulk conductivity measured by EIS.
- The electrical measurements are compared with SiO_2 confirming the charge carrier role of Li^+ under thermal activation.
- The recombination effect of temperature during irradiation has been observed.

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ABSTRACT

Lithium orthosilicate (Li_4SiO_4) is considered one of the best candidates for the solid breeder blanket system (BBs) of future thermonuclear reactors. During reactor operation it will be bombarded by neutrons and gamma radiation which may alter its composition and properties, affecting its shielding role. The electrochemical impedance spectroscopy (EIS) is here used as a non-destructive tool for monitoring the electrical bulk conductivity of Li_4SiO_4 ceramic after different ionizing damaging treatments. The compound fabricated in our laboratories, was irradiated by a ^{60}Co in the Nayade-facility (CIEMAT-Spain). Several studies with slight experimental variations were realized and here presented to understand the dynamic of the charge carriers' movement and the role of intrinsic and extrinsic defects on the electrical properties of this candidate ceramic.

1. Introduction

The main objective of the EU test strategy related to test blanket modules (TBMs) in ITER is to provide the necessary information for the design and fabrication of breeding blanket system (BBs) in a future DEMO reactor [1]. The 8 MPa helium-cooled pebble-bed (HCPB) with lithium ceramic pebbles as breeder, an inlet temperature of 300 °C, outlet up to 500 °C and beryllium pebbles as neutron multiplier, is one of the modules that will be tested in ITER during TBM experimental campaign. [2]. Although to the date several lithium ceramics have been investigated, at present the official candidate as breeder in pebble-bed form are the orthosilicate (OSi–Li_4SiO_4) and the metatitanate (MTi–Li_2TiO_3) ceramics [3] plus a new EU pebble concept combining the advantages of OSi and MTi introduced as a secondary phase [4].

During reactor operation the pebbles will be exposed to neutrons and gamma radiation, thus electrical and changing magnetic field in the blanket zone may cause modifications in this insulator material leading to important changes in its electrical behaviour.

Gamma-irradiation presents three modes of physical interaction with the matter: (a) photoelectric effect—from 0.01 to about 0.5 MeV, (b) Compton scattering—from about 0.3 MeV to 8 MeV, and (c) pair formation (electron/positron), 5 MeV to 100 MeV [5]. Ionization is a secondary effect which results to be quite important in the case of insulators: when ceramics are subjected to gamma-rays, the electronic defects created involve changes in the valence states. Among the degradation mechanisms observed during the study of radiation effects in nuclear ceramics, the radiation induced conductivity is undoubtedly one of the most important [6]. If the blanket zone varies its insulating behaviour, the creation of an electrical and magnetic field may cause a closed electrical circuit, thus affecting the shielding role of the TBM.

The electrical measurements represent therefore, a useful tool for monitoring the degradation and the processes occurring after exposing the ceramic compound to a ionizing radiation damage [7,8]. The electrochemical impedance spectroscopy (EIS) is chosen

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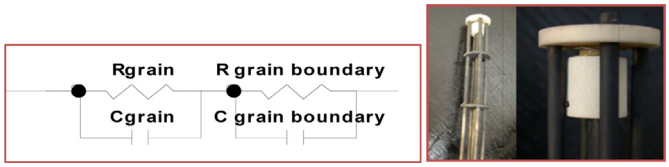

Fig. 1. The equivalent circuit (left) indicating resistive and capacitive terms controlling charge carriers movement through ceramics breeder blanket materials. In the right part, the picture of the experimental sample holder used for EIS measurements.

as a non-destructive tool to elucidate transfer mechanisms and dynamics of the Li^+ presumed to be the principal charge carrier [9,10], although the other ions (like O) may be mobile to a certain extent.

Li_4SiO_4 ceramic is considered a potential good candidate because of its compatibility with structural materials, release performance of bred tritium and high melting point [11]. In order to identify the microstructural modifications and provide reliable data on the variation of electrical properties, this paper conducts a detailed analysis on the changes induced after γ-irradiation at different doses and varying experimental conditions.

2. Fabrication and experimental measurements

Li_4SiO_4 powder was fabricated in the Materials department of LNF-CIEMAT, starting from SiO_2 gel (suspension of Ludox-TMA colloidal silica 34%) and lithium citrate (Aldrich hydrated $Li_3C_6H_5O_7$, 99%) as raw materials, reacting as:

$$4Li_3C_6H_5O_7 + 3SiO_2 + 18O_2 \rightarrow 3Li_4SiO_4 + 10H_2O + 24CO_2 \quad (1)$$

This method was selected as the best one for reaching a highly crystalline orthosilicate phase [12]. The multicomponent composition was manually mixed and then calcined at 250 °C during 12 h in an open oven for the organic residual elimination.

The composition was ball milled, mixed with ethanol and dried in a rotatory evaporator. The firing sequence was repeated several times plus an intermediate grinding stage at the end of each step, till a final heating at 950 °C during 10 h. The powders were then isostatically pressed at 200 MPa as cylinders of about 10 mm in diameter, cut as 2 mm thickness pellets and sintered at 950 °C/2 h in air. The density of the body measured by Hg-porosimetry was of 1.64 g/cm^3 (about the 80% of the theoretical value), as required to simulate the solid breeder pebble bed packing factor [13].

The samples were γ-irradiated by a ^{60}Co source in the Nayade pool irradiation facility at CIEMAT (Madrid, Spain), from 5 MGy up to 15 MGy. The irradiation treatments were performed at room temperature (25 °C ± 2 °C) in a sample holder immersed in dry nitrogen or, only in one case, at 250 °C using a thermocouple controlled oven.

Crystallographic phases were monitored by XRD, using a Philips diffractometer X-Pert-MPD with a CuK_α-radiation source and a Si monochromator. The impurities due to the fabrication process were detected by XPS and SIMS measurements. The XPS analyses were performed using a Perkin–Elmer PHI 5400 model equipped with an excitation source ($h\nu$ = 1253.6 eV), a Mg-$K\alpha$ anode and a beam size of 1 mm diameter. The Hiden SIMS Workstation operating under MASsoft7-Professional for ppb analysis, was used with a 6 kV oxygen ion gun. The surface composition and morphology of as-sintered and irradiated samples was studied by a SEM (scanning electron microscope), Hitachi S-2500 at 25 kV.

The electrical impedance spectroscopy method provides the overall conductivity of the sample, a combination of the ionic and the electronic contribution. The measurements were carried out using a frequency analyser (model Solartron 1255B) with platinum as blocking electrodes (see the sample holder in Fig. 1, right), all inserted in a tubular oven varying the temperature between 26 °C and 800 °C, over a frequency range from 40 Hz to 10^8 Hz. The silver electrodes were provided by a high conductivity paste (chosen as the best option for those highly porous and rough samples), dried in air at 130 °C during 15 min to eliminate the paste organic residuals.

The spectra were acquired using the "EQUIVCRT" (Equivalent Circuit Programme [14]) software.

According to Bauerle [15], it is possible to distinguish two main electrical contributions in a polycrystalline material: one related to the movement of the charge carriers along the grain, the other relative to its movement along the grain boundary (corresponding to two arcs in the Nyquist diagram). The measurement can thus be compared to an equivalent circuit as the one shown in Fig. 1(left), consisting of a series connection of two parallel combination of resistor R and capacitance C.

Considering the conductivity as:

$$\sigma T = \sigma_o \exp\left(-\frac{E_A}{k_B T}\right), \quad (1)$$

it was then possible to obtain the activation energy E_A of the conduction processes [16] from the relation:

$$\ln\sigma = -\left(\frac{E_A}{k_B T} + \ln\sigma_o\right), \quad (2)$$

as the slope of the curve of the Arrhenius plot, with k_B the Boltzman constant, T the temperature in Kelvin and σ_o a pre-exponential factor.

3. Results

The XRD patterns of the sintered sample before irradiation (Fig. 3a), matched with the monoclinic structure of space group $P21/m$ and crystal parameters a = 5.140 Å; b = 6.094 Å; c = 5.293 Å and β = 90° indicated by Baur [17]. It corresponds to a tetrahedral anion (SiO^{4-}) structure surrounded by different Li atoms floating around it, presenting one type of Si atom, three types of O atoms and six types of Li atoms (Fig. 2 right).

The chemical analysis made by XPS and SIMS (Fig. 3) on the as prepared material, reveals the presence of impurities. Since the purity of the raw material is about 99.95%, some trace metals (as aluminium) can be detected in the final bodies, while others can derive from the sample handling (as Na, P or Cl atoms).

The main grain size can be compared through SEM images captured on the surface (Fig. 4, left) and along the fresh fractured (Fig. 4, right) of Li_4SiO_4. The microstructure observed in the mirror-like polished surface (Fig. 4, left) demonstrates that the material is formed by the incomplete coalescence of the grains, which present a mean size of 5–8 μm, the surface looks quite porous and rough. In the case of the fresh fracture images (Fig. 4, right), it can be observed that the cracking occurs mainly intra-granularly and that closed porosity is present. Grain boundaries, clearly visible, represent the site for the impurities detected in the material, as confirmed by the SEM image with the highest magnification (Fig. 4, centre, white circle).

3.1. Ionic conductivity

The samples irradiated at different doses in a range included between 5 and 15 MGy are subjected to a thermal ramp between 26 and 800 °C with a step for each measurement of 50 °C for the bulk conductivity measuring.

A good fit between experimental data and theoretical arcs, confirms the suitability of the proposed equivalent circuit (see Fig. 5).

The bulk conductivity at 26 °C in as-prepared conditions is of 3.16×10^{-8} S/cm and it slightly increases with irradiation damage (i.e.: 2.24×10^{-7} S/cm for 13 MGy of irradiation-doses, see Table 1).