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Feature article

Synthesis of the biphasic mixture of Li_2TiO_3-Li_4SiO_4 and its irradiation performance

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ABSTRACT

Triphasic Li_2TiO_3-Li_2SiO_3-Li_4SiO_4 powders were synthesized by the ultrasonic-assisted solution combustion method. The triphasic Li_2TiO_3-Li_2SiO_3-Li_4SiO_4 composites can be further transformed into biphasic Li_2TiO_3-Li_4SiO_4 ceramics via the phase transformation of Li_2SiO_3 into Li_4SiO_4 at a temperature of 900 °C for 2 h in air. The phase, microstructure, and irradiation behavior of biphasic composites were investigated. The average ceramic grain size is about 0.4 μm. Irradiation defects in the biphasic Li_2TiO_3-Li_4SiO_4 ceramics were calculated by SRIM software package. The largest displacement damage is 47.14 dpa under 100 keV Ar ion implantation. Observation of the surface and cross-section morphologies reveals that crystallinity of composite ceramics decreases after irradiated. However, the elements compositions are not affected by Ar ion implantation.

1. Introduction

Lithium orthosilicate (Li_4SiO_4) and lithium metatitanate (Li_2TiO_3) are considered as the most favored tritium breeder materials in test blanket module (TBM) of ITER due to their favorable thermal mechanical stability, low activation levels, and sufficiently high lithium density [1–4]. However, single phase tritium breeder materials have some insufficients. For example, Li_2TiO_3 shows superior mechanical properties compared to Li_4SiO_4, but Li_4SiO_4 offers a slightly better tritium release at lower temperatures and a higher lithium density [5–8]. Thus, the combination of these two kinds of materials is expected to gain a breeder material with improved mechanical properties and good tritium release [9,10].

Some recent studies have fabricated the synthesis of biphasic Li_2TiO_3-Li_4SiO_4 (or Li_2SiO_3) materials and their mechanical properties [10–13]. Knitter [10] fabricated Li_2TiO_3-Li_4SiO_4 pebbles by a melt-spraying method and showed that the biphasic mixtures of Li_4SiO_4 and Li_2TiO_3 exhibit improved mechanical properties relative to the single phase materials. The crush load of Li_4SiO_4 pebbles with 20 mol% Li_2TiO_3 is up to 15 N. Hanaor [11] investigated the phase stability in the quasi-binary Li_2TiO_3-Li_4SiO_4 system and pointed out that such two-phase compositions are attainable through solution based methods with appropriate processing parameters. Ogawa [12] prepared Li_2SiO_3-Li_2TiO_3 pellets through a solid state reaction and found that the 30% Li_2TiO_3 phase can effectively inhibit the Li vaporization from Li_2SiO_3 phase. Zhang [13] prepared the Li_2TiO_3-Li_4SiO_4 core-shell ceramic pebbles by the solid state reaction and graphite bed process. The average crush load of 50% Li_2TiO_3-50% Li_4SiO_4 pebbles sintered at 1100 °C for 5 h is up to 104.79 N. Although the Li_2TiO_3-Li_4SiO_4-/Li_2SiO_3 composites were prepared by these studies, most of the biphasic materials were synthesized by conventional solid state processing. Hence, searching a facile, low-cost and efficient synthesis process is one of the main concerns for further research of Li_2TiO_3-Li_4SiO_4 material.

Solution combustion synthesis (SCS) requiring shorter time periods and using less amount of external energy is an attractive technique for the synthesis of homogeneous, high-purity, and crystalline oxide powders at significantly lower temperatures than the conventional synthesis methods [14]. However, the control over the shape of the obtained nano-structured materials is yet to be considered as a challenge in SCS [15]. Recently, ultrasound has been used for processing advance materials [16]. Ultrasonic-processing of materials is fundamentally different from the conventional processing due to its cavitation [17]. During cavitation, bubble collapse produces intense local heating (>5000 K), high pressures (>20 MPa), and very short lifetimes. Cavitation also results in generation of local turbulence and liquid micro-circulation (acoustic streaming) in the reactor enhancing the rates of the transport processes. These extreme conditions and mechanical effects of cavitation can drive a variety of chemical reactions and tailor the crystal size and shape of nanomaterials. So far, ultrasound is gaining increasing popularity in all of the soft chemistry strategies for the preparation

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of inorganic nanoparticles. However, an investigation of preparing nano-structured materials via the ultrasonic-assisted SCS method has not been performed thus far.

It is known that in an operating fusion reactor, the radiation damage in tritium breeder materials will be produced by fast neutrons, energetic tritons (2.7 MeV) and helium ions (2.1 MeV) generated by $^{6}Li(n,\alpha)^{3}H$ reaction [18]. The damage caused by radiation may result in the microstructure changes and hence have an impact on the tritium release behavior, and on the thermal and mechanical properties of materials. Thus, the study of microstructure changes in pebbles is essential to evaluate its irradiation performance. Many studies have investigated the behavior of Li_4SiO_4 and Li_2SiO_3 under irradiation. However, laboratory work with samples during or after neutron irradiation is cumbersome, particularly owing to the induced activity of the samples [19]. The cycle of neutron irradiation is generally as long as 2 years. Thus, it is reasonable to irradiate the samples with high energy ions which could simulate the effects of fast neutron without making the sample radioactive. E. Carella [20] investigated the electrical properties of Li_4SiO_4 ceramic after γ-radiation treatments at different dose. It is concluded that the γ-radiation effects on the dielectric properties of ceramic depend strongly not only on the γ-dose but also on the prior history of the material. Nakazawa [21] studied the structural change of Li_2TiO_3 irradiated with high energy ion (160 MeV Xe, 80 MeV O), and found the disordering in the surface layer of Li_2TiO_3 irradiated. However, the composite Li_2TiO_3-Li_4SiO_4 materials are not studied with respect to their behavior under irradiation and the microstructure changes.

In the present study, triphasic mixtures of Li_2TiO_3, Li_2SiO_3 and Li_4SiO_4 were firstly fabricated by an ultrasonic-assisted solution combustion. And the Li_2TiO_3-Li_4SiO_4 composite ceramic was further obtained via Li_2SiO_3 transformation into the monoclinic phase of Li_4SiO_4 at a sintering process. The crystal structure, microstructure, and radiation effects of the composite were investigated.

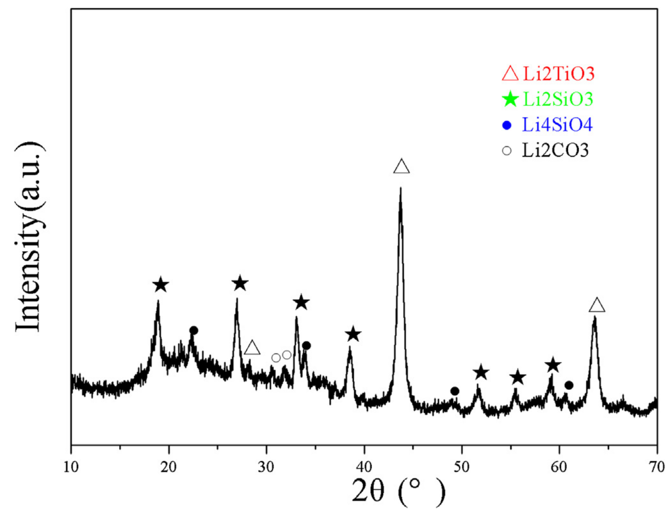

Fig 1. XRD pattern of the as-combusted powder.

2. Experimental procedure

2.1. Synthesis

Lithium nitrate ($LiNO_3$, AR), tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS, AR), tetrabutyl titanate ($Ti(OC_4H_9)_4$, TBOT, AR) and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, AR) were used as raw materials. TEOS, TBOT and $LiNO_3$ were used as oxidizers, citric acid as a reductant

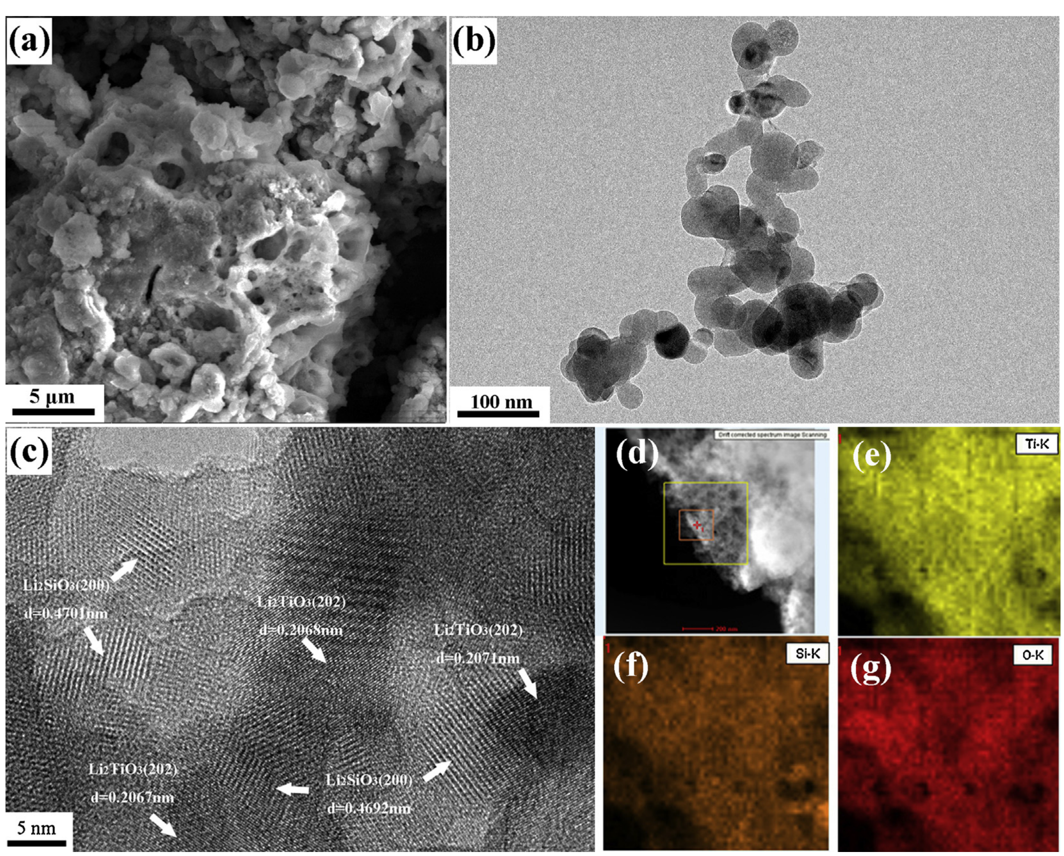

Fig. 2. FE-SEM and TEM image of the as-combusted powder. (a) FE-SEM; (b) TEM; (c) HRTEM; (d)–(g) Elemental mapping analysis of Si, Ti and O in powder by TEM.

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