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Crystallisation and microstructure of nepheline–forsterite glass-ceramics

M.I. Martín[a], F. Andreola[b], L. Barbieri[b], F. Bondioli[b], I. Lancellotti[b], J.Ma. Rincón[a], M. Romero[a,*]

[a]*Group of Glassy and Ceramic Materials, Department of Construction, Eduardo Torroja Institute for Construction Science (IETcc), CSIC, Serrano Galvache 4, 28033 Madrid, Spain*

[b]*Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università degli Studi di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena, Italy*

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Abstract

This work presents the results of a study focused on the development of forsterite–nepheline glass-ceramic with the use of rice husk ash (RHA) as a silica source. The glass-ceramics were produced by a sintering process of a glassy frit formulated in the MgO–Al_2O_3–SiO_2 base system with the addition of B_2O_3 and Na_2O to facilitate the melting and pouring processes. The crystallisation study was carried out by depicting the TTT curve (Time–Temperature–Transformation). The mineralogical characterisation of the glass-ceramic materials was carried out using the X-ray diffraction (XRD). The crystallisation activation energies were calculated by the Kissinger method. The results obtained show that devitrification of the RHA glass leads to a glass-ceramic material composed of nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and forsterite ($2MgO \cdot SiO_2$). A study of the microstructure by scanning electron microscopy (SEM) allowed to establish the morphological evolution in both the shape and spatial arrangement of the nepheline and forsterite crystals on heating.

Keywords: A. Sintering; B. Microstructure-final; D. Glass-ceramics

1. Introduction

Glass-ceramics are established materials that exhibit advantageous thermal, optical, chemical, mechanical and electrical properties [1]. The great variety of compositions and the potential for the development of special microstructures with specific technological properties have allowed glass-ceramic materials to be used in a wide range of applications, such as kitchen cooktops [2], prostheses for surgical implants [3], glazes for ceramic tiles [4], telescope mirrors, radomes [5], insulators [1] and electronic packaging [6]. Glass-ceramics are produced from a parent glass by a sequential thermal process that involves controlled crystallisation, which consists of the growth of one or more crystalline phases within the vitreous mass [7]. The earliest glass-ceramics were produced by a conventional glass route and subsequently crystallised, usually by heat treatment in two stages to produce nucleation, which was followed by crystal growth. In recent years, the sintering method has proven to be a technically viable route for the manufacture of glass-ceramics. This process usually involves milling a glass frit into fine particles, which are then shaped by conventional forming techniques and subsequently heat treated to provide sintering and crystallisation of the glass particles. A sintering process is normally used when the parent glass exhibits a strong tendency for surface crystallisation or when complex shapes are required [8]. Because the most important forming systems are based on silicate compositions, the key crystalline phases of glass-ceramics are principally silicates [1].

Forsterite (Mg_2SiO_4) is the magnesium rich end-member of the olivine solid solution series [9], and it is endowed with low electrical conductivity and a low dielectric constant, refractoriness and excellent insulation properties (even at high temperatures) and good biocompatibility. All of these favourable technological properties have led to the adoption of forsterite in many important technologies,

*Corresponding author. Tel.: +34 91 302 04 40; fax: +34 91 302 07 00.
E-mail address: mromero@ietcc.csic.es (M. Romero).

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including substrates for high-frequency electronics, ceramic-metal seals, the iron and steel industry, tunable lasers [10] and even as a bone implant material [11].

Forsterite has been synthesised by various techniques, including the conventional solid-state reaction of periclase (MgO) and silica (SiO_2) [12], the mechanical activation of a talc and magnesium carbonate powder mixture [13], the polymer precursor method [14] and the sol–gel method [15]. However, the sintering temperature of forsterite is approximately 1500 °C, which is too high and limits its use. Many efforts have been made to improve the workability of forsterite, including reduction of the firing temperature by the addition of alumina [16] or low melting point glasses [17]. Another possible way to produce forsterite materials at lower temperatures is through the glass-ceramic process. Indeed, several investigations report the devitrification of forsterite as a secondary crystalline phase in glass-ceramics belonging to different composition systems [18–22].

Nepheline ($NaAlSiO_4$) is a tectosilicate belonging to the also designated nepheline group $(Na,K)AlSiO_4$. The nepheline phase is characterised by high chemical mechanical strength and impact resistance. Nepheline-based glass-ceramics are demonstrated to be suitable for use in microwave ovens [23] and dental applications [24,25]. Nepheline glass-ceramics are usually prepared from glasses of the Na_2O–Al_2O_3–SiO_2 system and by the addition of different nucleating agents, such as TiO_2, Cr_2O_3, ZrO_2 or LiF to promote crystallisation [26,27].

Nepheline- and forsterite-containing glass-ceramics are normally prepared from high purity proportions of pure chemicals. They can also be prepared from cheaper raw materials such as wastes because the glass-ceramic process has been established as a suitable way to valorise mining and industrial wastes [5,28], including fly ash from incineration [29,30] and thermal power plants [4,31], wastes from hydrometallurgical processing plants [28], residual glass fibres from polyester matrix composites [32] and bagasse ashes [8], among others wastes. One residue that has experienced a significant increase in production in recent years is biomass ash, which originates from the combustion of biological material for energy purposes. It is clear that the current energy model in which more than 80% of energy production is based on fossil fuel consumption is not sustainable. For this reason, governments worldwide are implementing policies aimed at increasing the use of renewable energy resources. The use of biomass for energy purposes has multiple environmental benefits (i.e., reduction of CO_2 emissions, non-production of solid particles and sulphur and nitrogen pollutants, stimulation of economic growth in rural areas, reduction of dependence on external fuel supplies, and re-use of wastes generated by agricultural activities).

Rice husk ash (RHA) is a waste material that is produced by burning rice husks; in particular, it is produced when rice husks are used as fuel for kilns to produce bricks and other clay products or in rice mills to generate steam for the parboiling process. Rice husks contain approximately 75% organic volatile matter and the balance of 25% of the weight is converted into ash during the firing process. This ash, which is known as RHA, is a carbon neutral green product that contains approximately 85–90 (wt%) amorphous silica. Worldwide, approximately 120 Mt of rice husk are produced annually, which gives rise to a global production of 21 Mt/year of RHA [33]. In general, RHA is dumped as a waste [34,35]; however, because of its composition, it may be used as a source of silica in the steel industry [36] and as a pozzolanic material for the cement industry [37,38]. In the ceramic sector, several studies have been conducted in recent years to valorise RHA. In particular, the use of this ash has been investigated as a secondary raw material in the manufacture of whiteware products [39], pigments [34,40], glazes [35,41], brick compositions [42] and glass-ceramic materials in the SiO_2–Na_2O–CaO [43] and SiO_2–Al_2O_3–Li_2O [44] systems, as well as in cordierite-based glass-ceramics [45].

In a recent paper [33], the authors have demonstrated the feasibility of producing forsterite–nepheline-based glasses from a RHA mixture that incorporates B_2O_3 and Na_2O to facilitate the melting process. Significant environmental benefits are attained by using RHA as a source of silica: (a) avoided landfill disposal of the residue; (b) minimisation of the natural raw materials consumption. Besides, the RHA is a not hazardous residue, so the materials resulted do not cause further damage (environmental impact). These glasses could lead to glass-ceramics that combine the beneficial properties associated with both the forsterite (low electrical conductivity, low dielectric constant, refractoriness and excellent insulation properties) and nepheline (high mechanical strength and impact resistance) crystalline phases. The development of a material that combines these properties could find many applications, such as building material (ceramic tiles) in which these properties are required. It is known that the nature of the devitrified crystalline phases, as well as their shape, size and spatial arrangement, are the most important factors that affect the technical properties of glass-ceramics. Therefore, the aim of this work is to study the evolution of the crystalline phases and microstructures during the crystallisation process of a forsterite–nepheline-based glass produced from RHA as a silica source.

2. Materials and methods

A glass (hereafter designated RHA glass) in the SiO_2–Al_2O_3–MgO–Na_2O base system was formulated with rice husk ash from a plant producing semi-parboiled rice as a silica source (Garibaldi 1889, Colussi S.p.A., Milan, Italy). Prior to its use, the ash was sieved to a particle size < 250 μm. B_2O_3 and Na_2O (as Na_2CO_3) were added to the ash to facilitate the melting process. The chemical reagents used (all of A.R. quality) were Al_2O_3, MgO, B_2O_3 and Na_2CO_3. The components (46.52% ash, 13.84% Al_2O_3, 13.16% MgO, 22.17% Na_2CO_3 and 4.33% B_2O_3) were mixed for 30 min in a blender (TURBULA) to produce a