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ScienceDirect
Materials Research Bulletin 41 (2006) 1825–1834
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Crystal structure of Sr-akermanite glass–ceramics

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Received 12 August 2005; received in revised form 18 February 2006; accepted 13 March 2006
Available online 4 April 2006

Abstract

A glass–ceramic of Sr-akermanite ($Sr_2MgSi_2O_7$, SG: $P\bar{4}2_1m$) was prepared by crystallization of a glass with composition of 2SrO–MgO–$3SiO_2$. Parameters of the crystal structure were refined by Rietveld method. The analysis of the experimental results showed the following: the unit cell of Sr-akermanite in the glass–ceramic is larger than in single crystal. The thermal expansion coefficients of Sr-akermanite, calculated from the lattice constants obtained from X-ray diffractograms at high temperatures, were $\alpha_a = 3.663 \times 10^{-6}\ K^{-1}$ and $\alpha_c = 6.666 \times 10^{-6}\ K^{-1}$. It is suggested that the atomic displacements from the atomic coordination in single crystal depend on the stress developed during the crystallization process and the thermal contraction stress developed during cooling. Both types of stresses are related to the presence of residual glass and should be responsible for the expansion of the crystal lattice.

Keywords: A. Glasses; C. X-ray diffraction; D. Crystal structure; D. Thermal expansion

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1. Introduction

Akermanite ($Ca_2MgSi_2O_7$), a member of the melilite group, is crystallized in tetragonal lattice system with space group $P\bar{4}2_1m$ and forms a layer compound. The sheets, composed of Mg–O tetrahedral and Si_2O_7 double pyramids, are held together by Ca–O bonds. Sr completely substituted akermanite for Ca ($Sr_2MgSi_2O_7$) was prepared using the Czochralski technique, described by Liebertz and Stahr in 1982 [1]. The crystal structure was reported by Kimata in 1983 [2]. $Sr_2MgSi_2O_7$ activated by rare earth elements have received much attention for their fluorescence [3]. $Sr_2MgSi_2O_7$ is expected to act as a fluorescence host material. $Sr_2MgSi_2O_7$:$Eu^{2+}Dy^{3+}$ is a material with high potential for long-lasting phosphors. For example, Xaio [4] has developed a blue-emitting material. The radiation is about 10 times higher than that of ordinary materials. The crystal structure is the most important factor for luminescence.

In addition, since a fluorescence glass–ceramic prepared by crystallizing of a parent glass has been described, many investigations have been done to improve the method of preparation [5]. However, as development advances, the lack of information about the crystal structure of glass–ceramics is stressed.

Glass–ceramics are produced by a controlled crystallization of glass. Crystallites in glass–ceramics undergo high tensile or compression stresses from the residual glass, resulting in distortion of the crystallites. Mastelaro and Zanotto [6] studied the residual stresses developed during the crystallization of Li_2O–SiO_2 glass–ceramics. Miura et al. [7] studied the crystallization-induced stresses of an amorphous silicon thin film. They showed that the silicon film shrinks, and a large tensile stress occurs in the film during the crystallization process.

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doi:10.1016/j.materresbull.2006.03.010

Coordination structures in transition metal ions are of the most important factors influencing the physical properties of fluorescent materials. The fluorescence property is structure-sensitive, and depends mainly on crystal distortion. Therefore, it is expected that there will be a correlation between fluorescence, thermal stresses, crystallization-induced stresses, and distortion in glass–ceramics. However, the crystallographic data, needed to consider quantitatively the relationship between crystal distortion and fluorescence in glass–ceramics, are still not available. A crystallographic study of the glass–ceramic, including the strain energy, is important. The present study is addressed in the crystal strain developed during the fabrication of Sr-akermanite glass–ceramic.

Generally, the traditional method of crystal structure refinement is used effectively with 0.10 mm or above in the size of the single crystal, but the method is not adequate to refine the crystal structure parameters of the smaller crystals in the glass–ceramic. Consequently, the crystal structure should be refined by a Rietveld method [8], which is effective in the analysis of powder crystal structure. This article presents the results of crystal structure refinement and the structural features of the Sr-akermanite glass–ceramic. The results are discussed under the consideration of the thermal stresses and the crystallization-induced stresses.

2. Materials and experimental procedure

2.1. Parent glass and crystallization

The composition of the parent glass was 2SrO–MgO–3SiO_2, which is a slight modification of the stoichiometric composition of Sr-akermanite, with regards to SiO_2 excess. The glass was prepared by a conventional melt-quenching method. The raw materials were of reagent grade. Fine powders of SiO_2, MgO and $SrCO_3$ were mixed with an agate mortar and pestle, and then melted at 1500 °C for 3 h in a platinum crucible. The melt was poured onto an iron plate. In order to remove the strain, the cast glass was annealed at 650 °C for 12 h. The glass–ceramic was prepared by heat treatment of the parent glass at 1100 °C for 12 h. The crystallization of the same parent glass at 850 °C has been described earlier by Fu [5].

Orientated crystallization of fresnoite glass–ceramic has been found in samples obtained with a temperature gradient heat treatment [9]. The orientated crystals make the refinement of the crystal structure factors too complex. In this study, to exclude any influence of orientated crystals in the crystal structure analysis, the glass–ceramic was ground using an agate mortar and pestle and the obtained powder was subjected to X-ray diffraction (XRD) analysis.

2.2. Thermal expansion coefficient

To estimate the linear coefficient of thermal expansion (CTE) of Sr-akermanite, which, to the knowledge of the author has not been reported, a mixture of the raw materials, which corresponds to the stoichiometric composition of $Sr_2MgSi_2O_7$, was heated at 1250 °C for 14 h in a platinum crucible. This mixture was not melted. The powder was ground using an agate mortar and pestle. XRD patterns of the powder were obtained at 30, 200 and 1000 °C using the RINT 1000 system equipped with a high-temperature furnace (Rigaku Corporation). The lattice parameters at each temperature were calculated by the least squares method, using the diffraction peak angles and a Miller index in the #22-0513 in JCPDS [10]. The CTE of Sr-akermanite was calculated from the changes of the lattice constant with temperature.

2.3. X-ray analysis and refinement with Rietveld method

X-ray diffraction powder patterns for the crystal structure of the glass–ceramic were recorded with a Philips powder diffractometer (X'pert) equipped with a curved graphite monochromator, using Cu Kα radiation. Four thousand five hundred and one data were collected between 10.0 and 100.0 in 2θ by a step-scan method with a step interval of 0.020. Calibration was carried out with an internal standard of high-purity alumina (SRM1976) from the National Institute of Standards and Technology (USA).

The lattice parameters of the glass–ceramic were calculated by the least squares method that was used in Section 2.2. The crystal structure parameters of the fresnoite glass–ceramic were refined by the Rietveld program PFLS, developed by Toraya and Marumo [11]. The reliability factor, R_p, is defined by the fitting parameter