Transparent glass-ceramic materials synthesized by Spark Plasma Sintering (SPS) for photonic applications

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ABSTRACT

1 Introduction

Transparent glass-ceramic materials combine thermal stability and good optical properties compared to single crystals, high mechanical properties and low manufacturing costs [1]. Spark Plasma Sintering (SPS) is an alternative processing method to prepare transparent glass-ceramic materials. SPS combines uniaxial pressure and heating based on the Joule effect, and offers the possibility of sintering powders up to full density [2]. However, various extrinsic and intrinsic factors affect transparency of glass-ceramics. Some extrinsic factors are the processing parameters such as particle size of the glass powder, temperature, time and pressure. Intrinsic factors are carbon contamination, pores and secondary phases.

Glass-ceramics of the $Li_2O–Al_2O_3–SiO_2$ (LAS) system [3] with very low thermal expansion have been successfully obtained by SPS. Delaizir et al. [4] used SPS for the preparation of $62.5GeS_2–12.5Sb_2S_3–25CsCl$ glass-ceramics in order to reduce the sintering time compared with conventional sintering. Laure et al. [5] reported sintered soda-lime glass microspheres by SPS. In all these works, the SPS experiments had to be carefully optimized with respect to temperature, time and pressure.

The main objectives of this paper is the preparation of transparent GCs containing low phonon fluoride phases such as $KLaF_4$ & $NaLaF_4$ by controlling the processing parameters, namely particle size of the glass powder, pressure, temperature and holding time. Carbon contamination was avoided by using platinum foil. Final materials with low porosity, nanometer-sized crystals dispersed within the glassy matrix and high transparency have been prepared.

2 Experimental

Glasses with compositions $70SiO_2–7Al_2O_3–16K_2O-7LaF_3$ (mol%) and $70SiO_2–7Al_2O_3–8Na_2O–8K_2O-7LaF_3$ (mol%) doped with different concentrations of NdF_3 (0.1 and 0.5 mol%) and TmF_3 (0.1, 0.5 and 1.0 mol%), respectively, were prepared by melt-quenching method at temperatures between 1600-1650°C. The glasses were milled and the glass powders sieved to obtain fractions <40 µm, <63 µm, and 63-100 µm. Pellets were prepared applying a pressure of 2000KPa and sintered under vacuum, using optimized SPS processing parameters such as temperature, pressure and holding time in a DR. SINTER SPS-510CE. Pulsed direct current (pulses of 12 ms on/2 ms off) was applied. The temperature was measured by an optical pyrometer focused on a hole in the graphite die.

3 Results and Discussion

The SPS optimum processing parameters were found to be: temperature- 700°C, pressure- 22MPa, holding time-10 to 20 min. Carbon contamination originating from the graphite dies employed in the SPS experiments was observed. Contamination could be eliminated by using platinum foil to cover the samples inside the die.

The prepared oxyfluoride GCs exhibited high stability and transparency. Similarly, $NaLaF_4$: Tm^{3+} 0.1, 0.5 and 1.0 mol% doped transparent GCs were obtained by SPS. Fig. 1 shows the XRD patterns for the $KLaF_4$ (α and β) glass-ceramics. The size of the crystals being in the range ~19-23 nm for α-$KLaF_4$, using the Scherrer equation [2]. Transparency decreases with decreasing particle size of the used glass powder, as confirmed by the measurement of optical spectra in transmission mode.

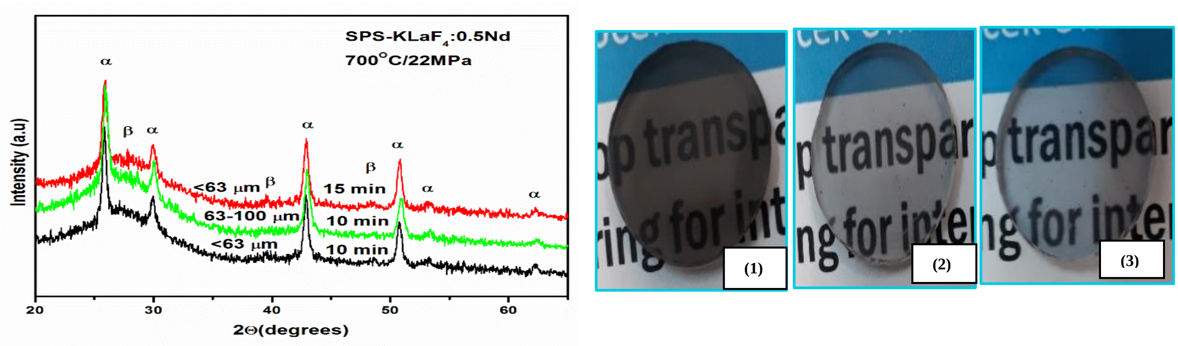

Fig. 1. XRD profile and appearance of $KLaF_4$ glass-ceramics: 0.5 mol% Nd doped TGCs from powders of different particle sizes (1) <40 µm (2) <63 µm (3) 63-100 µm

4 Conclusion

Transparent oxyfluoride TGCs were successfully prepared by SPS. $KLaF_4$ and $NaLaF_4$ nanocrystals containing GCs were obtained by the optimized SPS process. The sintered samples were transparent in the visible wavelength range. The use of platinum foil, to cover pellets during SPS, effectively reduced carbon contamination.

Keywords: Spark Plasma Sintering; Transparent Glass-ceramics; $KLaF_4$; $NaLaF_4$; Photonics.

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