Nucleation and growth processes leading to new glass-ceramics in the bismuth borotellurite system: evidences for a chemical demixtion phenomenon

Marine Cholin[1,2], *Cécile Genevois*[3], *Maggy Colas*[1], *Julie Cornette*[1], *Pierre Carles*[1], *Franck Fayon*[3], *Sébastien Chenu*[1,4], *Mathieu Allix*[3], *Yann Launay*[1], *Gaëlle Delaizir*[1], *Philippe Thomas*[1], *Vincent Couderc*[2], *Jean-René Duclère*[1,*]

[1] Institut de Recherche sur les Céramiques, UMR 7315 CNRS, Université de Limoges,

Centre Européen de la Céramique, Limoges, France

[2] Institut XLIM, UMR 7252 CNRS, Université de Limoges, France

[3] Conditions Extrêmes et Matériaux : Haute Température et Irradiation, UPR 3079 CNRS,

Orléans, France

[4] Institut des Sciences Chimiques de Rennes, UMR CNRS 6226 - Université de Rennes 1,

35042 Rennes, France

Abstract

In this work, the molar composition $30TeO_2$-$40B_2O_3$-$30Bi_2O_3$ doped with $0.5Er_2O_3$ was specifically investigated. Thanks to a two-step heat-treatment, which combines both nucleation and growth processes, new glass-ceramics containing $Bi_2Te_2O_7$ crystals were successfully fabricated. Nucleation parameters (*i.e*. an optimal temperature of 405°C maintained for a duration of 2h) were determined via a DSC study. The growth temperature was fixed at 450°C and a minimum time of 45 min at that temperature was necessary to evidence the first signs of crystallization, as testified by X-ray diffraction data. Mechanisms of crystallization were also deeply explored. Through nanoscale observations by Transmission Electron Microscopy, as well as local chemical analysis coupled with Electron Energy Loss Spectroscopy (EELS) analysis, the impact of the growth process was understood. Starting from a homogeneous nucleated glass, the latter provoked a chemical demixtion characterized by the spatial separation of tellurium enriched areas which will further give birth to the crystallization of boron-free

$Bi_2Te_2O_7$ polycrystals, dispersed within a boron-rich residual amorphous matrix. Besides, such nanoscopic investigations were comforted by the macroscopic Scanning Electron Microscopy data, where it was clearly observed that both the density and size of the polycrystalline entities dispersed in the glassy matrix increase with the time of the growth heat treatment. In addition, Raman spectroscopy data revealed that drastic spectral modifications occur for boron oxide structural units during partial crystallization. Such transformations reflect the strong evolution of the coordination number of boron atoms, which switches from ~ 3.1 in the case of the nucleated glass to a value close to 3.9 for the glass-ceramic sample obtained after a heat treatment of 2h at the growth temperature of 450°C. Raman maps were as well recorded on this series of samples (both glass and glass-ceramics), and a Principal Component Analysis conducted on such maps allowed to statistically confirm the local EELS results, *i.e.* the occurrence of the phase separation with the growth process. Boron Nuclear Magnetic Resonance spectroscopy experiments are now planned on the same samples in order to access the same local modifications occurring around boron atoms during partial crystallization, but thanks to another structural probe. Optical transmission measurements showed that transparency quickly drops after 1h of heat treatment, in agreement with the size of polycrystalline entities found larger than 500 nm. Finally, photoluminescence properties of Er^{3+}-doped samples unambiguously indicated that consequential spectral and temporal modifications occur beyond 45 min to 1h of heat treatment, demonstrating the important changes of the rare-earth ions environment with the crystallization, thus in perfect agreement with all the aforementioned data.

Keywords: borotellurites ; glass-ceramics ; phase separation ; chemical demixtion

*Corresponding author: Jean René DUCLERE

Email: jean-rene.duclere@unilim.fr