



	Experiment title: Crystallization study of tellurite-based glass-ceramics doped with erbium	Experiment number: 08-02-337
Beamline: BM08	Date of experiment: from: April 15 to: April 20	Date of report: July 2004
Shifts: 12	Local contact(s): Dr. Carlo MENEGHINI	<i>Received at ESRF:</i>
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Report:

**This work is described in the following article: “Influence of Er³⁺ on the early stages of crystallization of chloro-tellurite glasses studied by XRD and EXAFS”
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(Accepted for publication in Journal of Non-Crystalline Solids)**

The purpose of this work was to study in situ the crystalline phases segregated from the precursor oxyhalide glass matrix, by thermal treatments using time-resolved X-ray powder diffraction, recorded during the early stages of thermal transformation. The studied compositions were 40 TeO₂–20 ZnO–40 ZnCl₂ (hereafter designated by 424) and 60 TeO₂–20 ZnO–20 ZnCl₂ (hereafter designated by 622) (expressed in mol %), doped with an additional x mol% of erbium (x=1 to 10), hereafter designated by 622+x.

The X-ray diffraction data were collected at the diffraction hutch GILDA (BM08 line), under the supervision of Dr. Carlo Meneghini and Dr. Francesco D’Acapito, with $\lambda = 0.620 \text{ \AA}$, using image plate detection and an angular resolution of 0.01°.

The glass samples were ground and mounted in spinning silica glass capillaries ($\varnothing 0.5 \text{ mm}$), which can be heated up to 800 °C, by an air blower. Dynamic studies were performed from 240 °C to 500 °C, at heating rates from 1.3 °C/min to 4 °C/min.

Isothermal studies were also carried out at selected temperatures (table 1). Data analysis was carried out in a digitalized image plate with the FIT2D software, for image processing and the GSAS software, for powder diffraction analysis.

Figure 1 presents a digitalized image plate of the X-ray diffraction pattern from the 424+1 sample, for a dynamic study. The corresponding 3D X-ray diffraction pattern is shown in figure 2.

Figure 3a and 3b presents the XRD patterns obtained from dynamic measurements, for the 622 and 622+1 compositions, between 398 °C and 467 °C, showing the early stages of the crystallization process. At 398 °C, both patterns were typical of amorphous samples, but, at 411 °C, some crystallisation was detected. Using the GSAS software and the Inorganic Crystal Structure Database (ICSD), $Zn_2Te_3O_8$ (ICSD 16784) was found to be the first crystalline phase to appear for the 622 composition, at 411 °C, while α - TeO_2 (paratellurite, ICSD 202792) appeared at 423 °C, with no other major crystalline phase present, as seen from the residue (figure 4a.). The introduction of 1 mol% $ErCl_3$ substantially modified the crystallization patterns (Fig. 3b), completely inhibiting the formation of the α - TeO_2 phase. In fact, for the 622-1 composition, there was some crystallisation at 411 °C, but the phase(s) formed could not be identified with the GSAS software and the ICSD database. On the other hand, the $Zn_2Te_3O_8$ phase only appeared at 436 °C, becoming the major phase above this temperature, as seen from the residue of figure 4b. This result clearly demonstrates that erbium was a causative factor in the crystallisation of these glasses, for as little as 1 mol%. Larger amounts of erbium chloride prevented the formation of both the α - TeO_2 and $Zn_2Te_3O_8$ phases, with other unidentified phase(s) appearing between 2 and 10 mol% $ErCl_3$.

In the XRD patterns of the glass samples of Figure 3, we follow the changes of the crystallization process: for example, at 436 °C, the diffraction peak at $2\theta = 18.9^\circ$ (Fig. 3a), corresponding to α - TeO_2 (paratellurite), has a maximum amplitude and then decreases for higher temperatures. The formation of unknown phase(s) for 2 to 10 mol% $ErCl_3$, in the XRD patterns of the glasses studied showed that the presence of erbium chloride affected the crystallisation process. No phase could be identified by XRD, for either Er or Cl species. Crystallite sizes around 7 nm, were estimated using the Scherrer formula.

In conclusion, the combination of dynamic and isothermal XRD measurements allowed the monitoring of the crystallisation process in chloro-tellurite glasses. The erbium content affected the crystallisation process, since α -TeO₂ and Zn₂Te₃O₈ phases, present in heat treated compositions without erbium chloride, did not form in compositions with 2-10 mol% erbium, where new crystalline phases precipitated but could not be identified.

Table 1 – Compositions (mol%) and characteristic temperatures of glasses in the TeO₂-ZnO-ZnCl₂-ErCl₃ system and optimal heat treatment parameters, from dynamic and isothermal studies.

Composition (mol %)	Dynamic Test	T _{xd} (°C)	Isothermal Test	T _{xi} /t _{xi}
622c	240-480°C / 1h	400	350°C / 3h 400°C / 3h 500°C / 1h	400°C / 6 min
622c1c	240-480°C / 1h	410	400°C / 3h 450°C / 3h	400°C / 20 min 450°C / 6 min
622c2c	240-540°C / 1h	440	400°C / 2h	400°C / 80 min
622c3c	240-540°C / 1h	510	420°C / 3h 440°C / 3h	420°C / 80 min 440°C / 40 min
622c5c	240-480°C / 3h	440	420°C / 2h 450°C / 3h	420°C / 45 min 450°C / 14 min
622c10c	240-480°C / 3h	430	400°C / 2h 500°C / 2h	500°C / 6 min
424c	240-480°C / 1h	314	-	-
424c1c	240-480°C / 1h	373	320°C / 2h 350°C / 2h	350°C / 18 min
424c3c	240-480°C / 1h	383	350°C / 2h 375°C / 2h	375°C / 28 min
424c5c	240-480°C / 1h	400	350°C / 2h 375°C / 2h	375°C / 48 min
622f1f	240-540°C / 1h	383	400°C / 2h	-
622f3f	240-540°C / 1h	387	375°C / 2h	375°C / 60 min
622f5f	240-540°C / 1h	393	375°C / 2h	375°C / 8 min

T_{xd} is the crystallization temperature obtained in the dynamic test.

T_{xi} is the crystallization temperature obtained in the isothermal test.

Fig. 1-Digitalized image plate of the X-ray diffraction pattern from the 424+1 sample, for a dynamic study (increasing temperature with time). The light scale is linear with the intensity of diffraction.

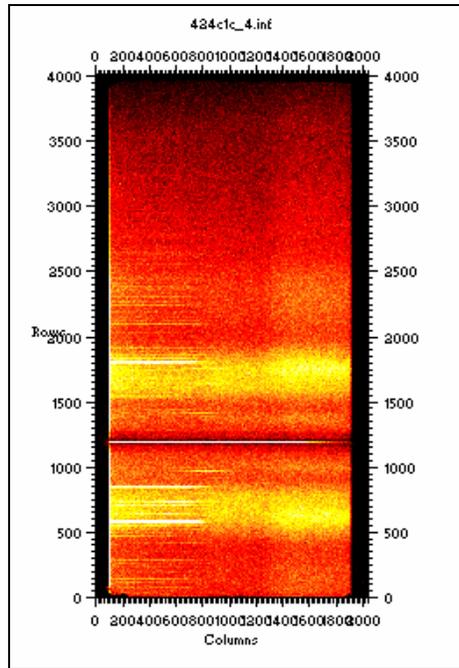


Fig. 2 – 3D representation of the X-ray diffraction pattern from figure 1. The grey scale is linear with the intensity of diffraction.

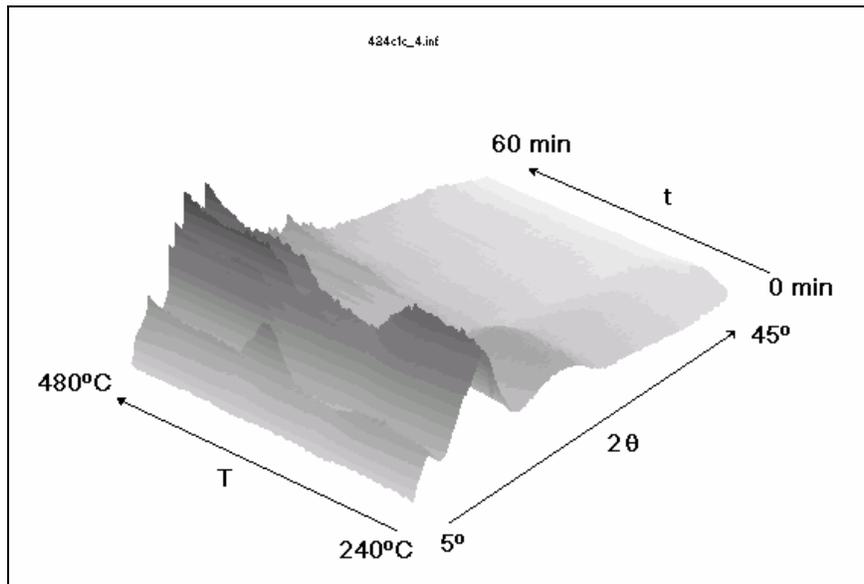


Fig 3a – XRD patterns of the 622 glass composition, with increasing temperatures of heat treatment (heating rate = 4 °C/min). Identified phases: α -TeO₂ (#) (ICSD 202792) and Zn₂Te₃O₈ (*) (ICSD 16784).

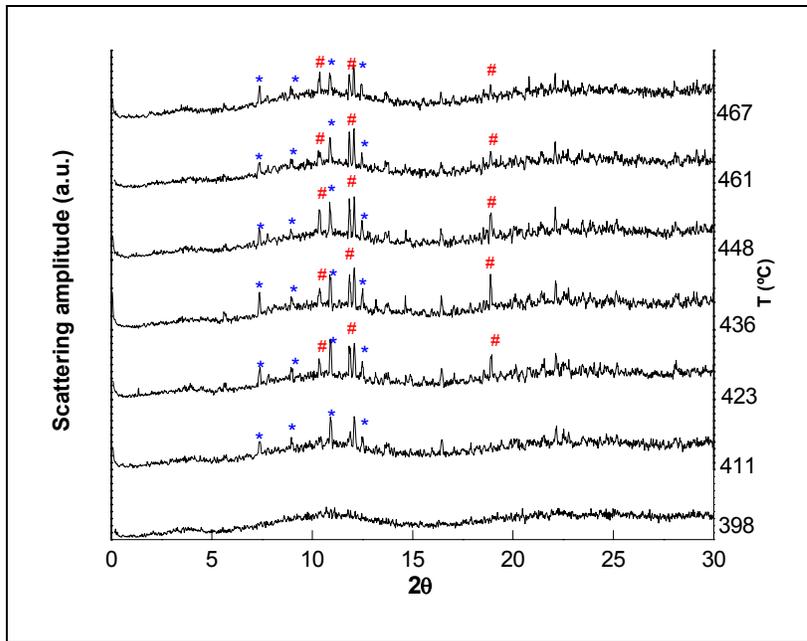


Fig 3b – XRD patterns of the 622+1 glass composition, with increasing temperatures of heat treatment (heating rate = 4 °C/min). Identified phases: α -TeO₂ (#) (ICSD 202792) and Zn₂Te₃O₈ (*) (ICSD 16784).

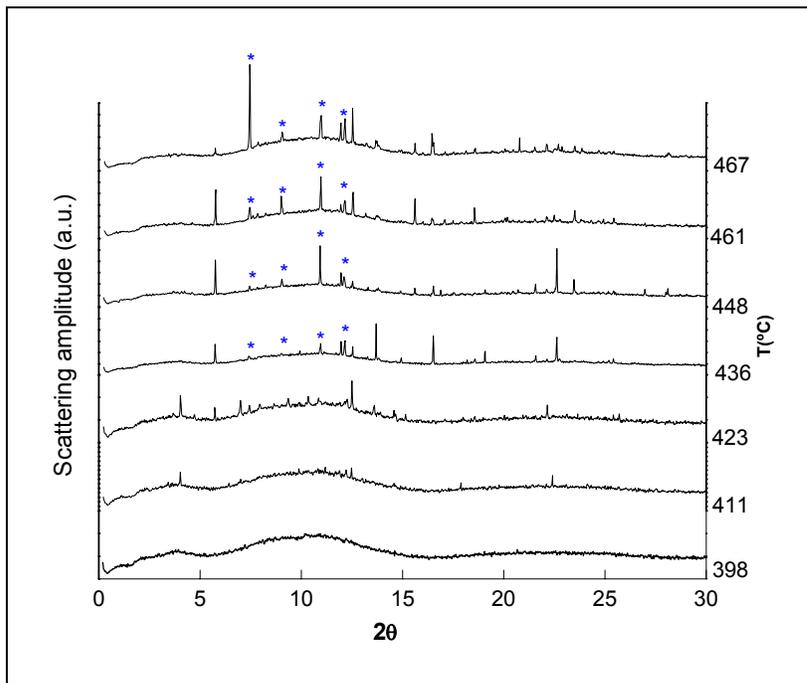


Fig 4a - XRD fittings, using GSAS software, for the 622 composition heat-treated at 450°C for 5 min. Identified phases: α -TeO₂ (ICSD 202792) and Zn₂Te₃O₈ (ICSD 16784).

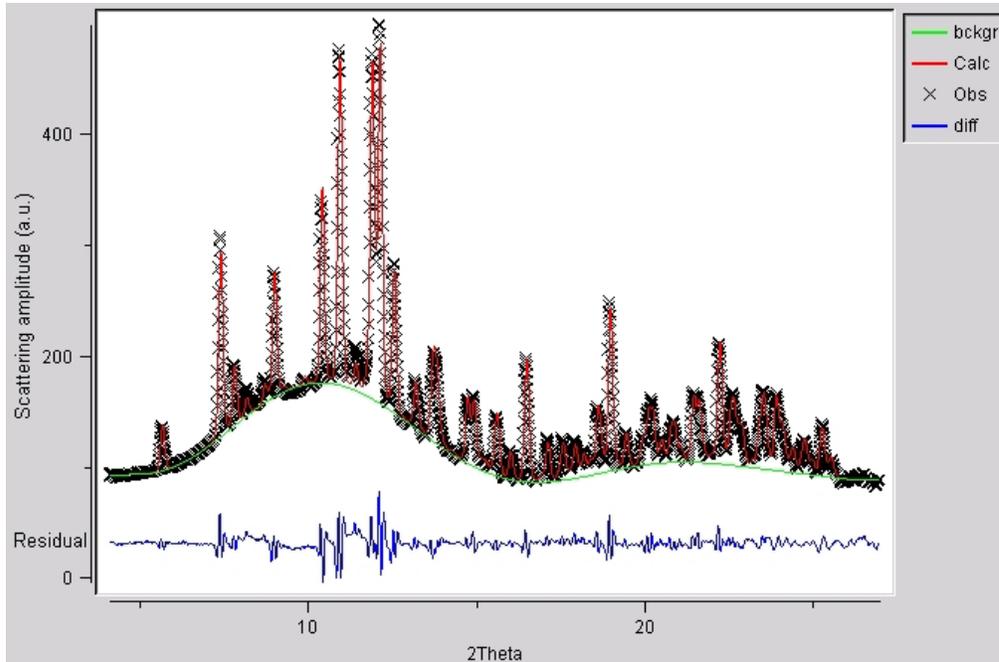


Fig. 4b - XRD fittings, using GSAS software, for the 622-1 composition heat-treated at 450°C for 180 minutes. Identified phase: Zn₂Te₃O₈ (ICSD 16784).

