	Experiment title: XRD study of nano glass ceramic powders	Experiment number: MA 644
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Report:

X-ray diffraction is a powerful tool to investigate the structure and size of nanoparticles which are created in glass ceramics upon thermal annealing. The focus of our work was on fluorozirconate (FZ) glasses which are additionally doped with chlorine to enable the growth of BaCl_2 nanocrystals in the glasses. The nominal composition of 5 mol% EuF_2 -doped fluorochlorozirconate (FCZ) glasses is $48\text{ZrF}_4\text{-}10\text{BaF}_2\text{-}10\text{BaCl}_2\text{-}20\text{NaCl-}3.5\text{LaF}_3\text{-}3\text{AlF}_3\text{-}0.5\text{InF}_3\text{-}5\text{EuF}_2$ (values in mole percent). The samples were subsequently

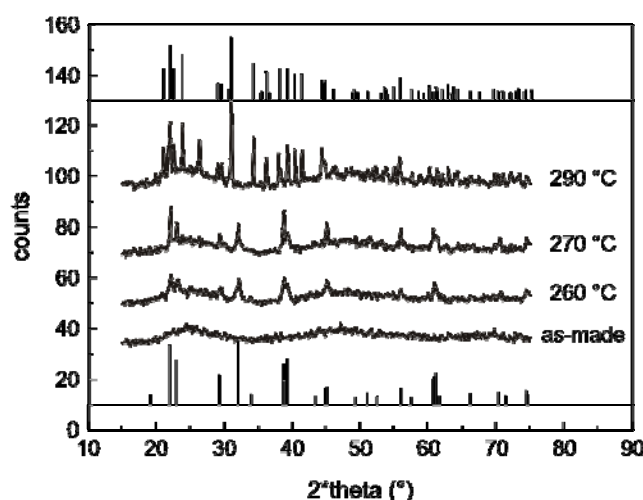


Figure 1: XRD data of 5 mol% EuF_2 doped glass ceramics: as made and annealed at 260, 270, and 290 °C. The curves are vertically displaced for clarity; the line pattern of hexagonal phase BaCl_2 (PDF #45-1313) and orthorhombic phase BaCl_2 (PDF #24-0094) are shown for comparison.

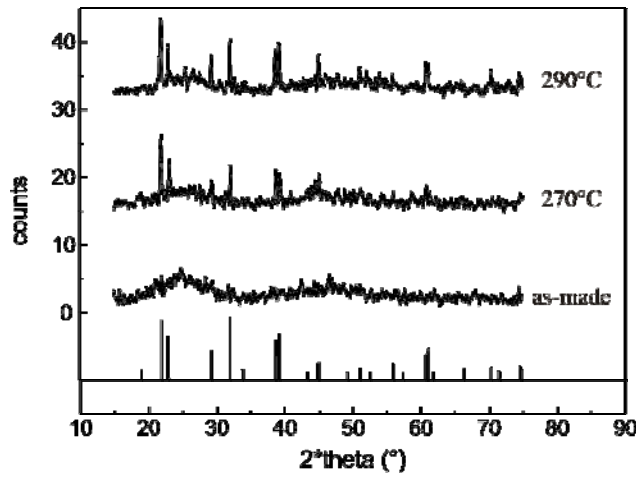


Figure 2: XRD data of 2 mol% EuCl_2 doped glass ceramics: as made and annealed at 270 and 290 °C. The curves are vertically displaced for clarity; the line pattern of hexagonal phase BaCl_2 (PDF #45-1313) is shown for comparison.

brought to temperatures above the glass transition temperature of approximately 210 °C and held there for 20 minutes. This thermal treatment was performed in an inert nitrogen atmosphere and in ambient atmosphere. The visible appearance of the as-made glass is almost clear, but after thermal processing there is evidence of crystallization in all of the glasses, i.e. the glasses become milky white. However, samples tempered in ambient atmosphere became milky white at lower annealing temperatures compared to the samples annealed in a nitrogen atmosphere. The corresponding XRD spectra after annealing in nitrogen are shown in Figure 1.

In the as-made glass no evidence of crystallization can be found, i.e. only the broad reflections due to the glassy background can be seen. For the samples annealed at 260 and 270 °C the XRD data comprise sharp peaks that we identify as arising from hexagonal BaCl_2 (space group P-62m (189), $a = 0.8066$ nm, $c = 0.4623$ nm). In the spectrum of the sample annealed at 290 °C several sharp peaks appear; these are associated with orthorhombic BaCl_2 (space group Pnam (62), $a = 0.7865$ nm, $b = 0.9421$ nm, $c = 0.4731$ nm). However, there are additional peaks from unknown phases. The XRD pattern for the main unknown phase can be fitted to a structure of hexagonal symmetry with lattice parameters $a = 0.390$ nm, $c = 0.407$ nm and a P6/mmm (191) space group. These peaks are marked with asterisks in Figure 1. We have been unable to determine the composition of this phase.

The same experiments were performed for samples annealed under ambient conditions. Despite the fact that these samples change their visible appearance at lower temperatures the XRD data are similar to those obtained for the samples annealed in nitrogen (within experimental error).

Furthermore, another series of Eu-doped FCZ glass ceramics was prepared. The nominal composition was $51\text{ZrF}_4\text{-}20\text{BaCl}_2\text{-}20\text{NaF-}3.5\text{LaF}_3\text{-}3\text{AlF}_3\text{-}0.5\text{InF}_3\text{-}2\text{EuCl}_2$ (values in mole percent). The corresponding XRD data are shown in Figure 2. Again in the as-made glass no evidence for crystallization was found. For the samples annealed at 270 and 290 °C several reflections can be found; these can be attributed to hexagonal phase BaCl_2 . No reflections from orthorhombic phase BaCl_2 can be found which is in contrast to the first sample set.