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Nucleation and crystallisation in xerogel induced and probed by Cr

W. NIE ⁽¹⁾ and G. BOULON

Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Lyon I, URA au CNRS n° 442, Bâtiment 205, 69622 Villeurbanne Cedex, France

Abstract Nucleation and crystallization from xerogels of the system $\text{SiO}_2\text{-ZnO-Al}_2\text{O}_3$ are induced and probed by Cr. Besides the traditional techniques, such as X-ray diffraction, SAXS and TEM, ESR and optical techniques especially laser spectroscopy are employed for the investigation of the structural evolution during thermal treatments of these xerogels. Cr is served not only as a structure probe but also a nucleating agent. The devitrification of the system is found to be essentially initiated by the presence of traces of chromium.

Introduction

Nucleation and crystallization behaviours in glasses of the systems of $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-ZnO-Al}_2\text{O}_3$ doped with Cr_2O_3 have been studied in the laboratory for many years(1,2,3). Apart from the classical techniques used for these kinds of studies, such as X-ray diffraction, SAXS, TEM, ESR and optical techniques especially laser spectroscopy are employed in the current investigation concerning sol->gel->glass->glass-ceramic transitions in the $\text{SiO}_2\text{-ZnO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system. Some results have been published in three different journals(4,5,6). A parallel study was also carried out on the spectroscopic properties of Cr^{3+} -doped gahnite ZnAl_2O_4 which serves as a reference to follow the nucleation and crystallization processes(7,8). In contrary, the spectroscopic evolution of chromium during the nucleation and crystallization processes traces back the physical origins of the three most important Cr^{3+} fluorescent centres in ZnAl_2O_4 crystals(7,8).

In the current paper, we would like to summarize this work from a totally different point of view. Chromium is regarded as essentially a structure probe in the previous publications(1-6). After a brief of the role of chromium to the structural evolution in the systems, some general aspects of utilizing a probe to study structural evolutions are discussed.

⁽¹⁾ *Current address: LSM/CRT, Kodak-Pathé, 71102 Chalon sur Saône, France*

The preparation of samples have been described in references 5. Apart from the relative molar ratios between $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{ZnO}$, essential results reveal the dominant role played by traces of chromium to the structural evolution.

Summary of principal results

X-ray diffraction patterns shows the presence of Cr^{3+} -doped ZnAl_2O_4 crystallites only in the samples thermally treated at high temperatures ($>800^\circ\text{C}$). The sol->gel->glass transitions and the first stage of nucleation process can not be evidenced by this classical technique. The final crystalline phases in different samples are gahnite, mullite, quartz and willemite depending on initial compositions(5).

TEM micrographs shows the appearance of crystallites in the samples both in the beginning of nucleation and the end of crystallisation(6). From electron diffraction micrographs, on measuring the diameters of diffraction circles calibrated by an Al reference sample, lattice constants of crystallites as a function of heating temperatures for two samples Gel8 and KCR2 are obtained(Fig. 1). This figure clearly shows that the nucleation and crystallisation processes are initiated by Cr^{3+} aggregations. The initial concentration of chromium(0.3 mol% for Gel8 and 1 mol% for KCR2) determines the number of nuclei in the beginning of nucleation(at 800°C) and the final chemical composition of the crystallites at the end of crystallisation(at 1000°C).

Fig. 1 Lattices constants of crystallites obtained from electron diffraction.

Optical absorption and ESR spectra confirm the presence of Cr^{6+} and the formation of cluster radicals around Cr^{6+} . The $\text{Cr}^{3+} \leftrightarrow \text{Cr}^{6+}$ oxido-reduction occurs at the gel->glass transition stage till the beginning of nucleation(5). Fig. 2 shows the absorption spectra of Gel8 and KCR2 heat-treated at 1000°C . Cr^{3+} -doped ZnAl_2O_4 and ZnCr_2O_4 crystals are served as references. The different peak positions of Gel8 and KCR2 are directly related to their initial chromium concentrations.

Fig. 2 Absorption spectra of Gel8 and KCR2 heated at 1000°C referenced with that of $\text{Cr}^{3+}:\text{ZnAl}_2\text{O}_4$ and ZnCr_2O_4 .

In summary, the crystallites in the studied system can be described with a general formula $\text{Zn}(\text{Al}_{1-X}\text{Cr}_X)_2\text{O}_4$ with X near to one at the beginning of nucleation and near to zero(for Gel8) or between one and zero(for KCR2) depending on the initial chromium concentrations. Chromium ion is the nucleating agent.

Discussion and conclusion

Optical probes are widely used for the study of structural evolutions. Organic dyes and fluorescent ions are among the main kinds(9,10). We would like to discuss the validity of a probe and some general rules that should be followed concerning the choice of a structure probe.

There are two important aspects of an optically active structure probe: its validity and its sensitivity. The best probe would be the compromise of sensitivity/validity.

There are two kinds of probes. i) Natural: probes are components of the systems studied. In this case, it has near 100% validity; ii) Purposeful: probes are intentionally added to the studied system. Structure evolutions are inferred from changes of optical properties of probes that directly related to their local environments. The best probes are those which bring the lowest perturbation to the system and are sensitive enough to detect minute local structure changes. The probe is also preferred to be located in appropriate sites. The worse probes are those which gives the highest perturbation resulting in structure changes or those insensitive to environment changes. In this case, the probes loose their credibility to the study.

In reality, people seek often probes with high optical sensitivity on sacrificing validity. In the current study, as a probe, Cr^{3+} gives important informations on nucleation and crystallization processes since not only it locates both in nuclei and final crystallites but also its optical and paramagnetical properties are very sensitive to local environment changes. If looked as a natural probe, Cr^{3+} has high environmental sensitivity and 100% validity. Cr^{3+} plays at the same time the role of a nucleating agent and a structure probe.

In conclusion, the sol-gel->glass->glass-ceramic transitions of the system $\text{SiO}_2\text{-ZnO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ are probed by Cr^{3+} through ESR, optical absorption and laser spectroscopy as complementary techniques of X-ray diffraction, SAXS and TEM. The devitrification of the system is found to be initiated by the aggregation of Cr^{3+} . The chemical composition of crystallites can be described by a general formula $\text{Zn}(\text{Al}_{1-X}\text{Cr}_X)_2\text{O}_4$ with X near to one in the nuclei and near to zero in the crystallisation stage.

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