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Nucleation in xerogels of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO-Cr}_2\text{O}_3$ system studied by EXAFS spectroscopy

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Abstract.

During nucleation and crystallisation processes from xerogels of the system studied, crystallites $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$ are formed. Analysis by EXAFS spectroscopy at the Zn K-edge of gels with different Cr concentration and thermal treatments compared to that of reference compounds ZnAl_2O_4 and ZnCr_2O_4 allow to identify the nature of the nucleating precursors and the phases formed in the crystallization steps. The formation of ZnCr_2O_4 nanocrystallites during the first steps of nucleation cannot be confirmed, while for high temperature treatments, the x value close to 0 as previously obtained is verified.

1- INTRODUCTION.

In the titled system, the sol->gel->glass->glass-ceramic transitions from low to high temperature have been yet investigated by classical techniques (X-Ray diffraction, SAXS, TEM, ESR) (1,2,3,4). A first conclusion is that chromium is a nucleating agent. Nanocrystallites of general formula $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$ are involved during the nucleation and crystallization processes, but x, sensitive to the initial concentration of Cr_2O_3 and to the thermal treatments is not clearly identified by classical techniques. A first series of EXAFS spectroscopy experiments at the Zn K-edge has been performed on two gels with different initial chromium composition and thermal treatments, and the results are compared to those obtained on reference compounds ZnAl_2O_4 , ZnCr_2O_4 (of spinel type), and ZnO .

2 - SUMMARY OF PRINCIPAL RESULTS.

Electron diffraction experiments (1,3) suggested that at the beginning of the nucleation the nanocrystallites contain $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$ with x values close to 1, whereas for high temperature, nanocrystallites are described as Cr^{3+} doped ZnAl_2O_4 (x values close to 0) overlapping the previous ones. Both are spinel type (Zn in tetrahedral site, and Al or Cr in octahedral site), and the two extreme members can be identified and finely differentiated by EXAFS spectroscopy at the Zn K-edge because the backscattering amplitude functions corresponding to the atomic pairs of Zn with its possible neighbours (O, Al, Cr) are quite different in the energy range concerned.

We have used the theoretical phase and amplitude functions from Mc Kale and Al (5), and calibrated the damping parameters on the reference compounds ZnCr_2O_4 and ZnO . We were particularly interested in the fits of the first and second peaks extracted from the RDF's of ZnAl_2O_4 . The first peak corresponds to the regular tetrahedron ZnO_4 . The second peak is correctly described taking into account the contribution of four atomic shells around Zn atoms: Al in octahedral site, Zn in tetrahedral site and two O atoms at different distances, confirming the crystallographical data. (Table 1)

TABLE 1: Zn (Tetrahedral site) surrounding in ZnAl₂O₄. Fit and cristallographical values.

	Neighbouring atom	N (fit value)	d(Å) (fit value)	N (cristallogr.)	d(Å) (cristallogr.)
1st shell	O	3.9(0.2)	1.96(0.02)	4	1.96
2d shell	Al	12	3.36(0.02)	12	3.35
	O	12	3.37(0.03)	12	3.39
	Zn	4	3.55(0.03)	4	3.50
	O	12	4.32(0.03)	12	4.27

During our EXAFS study, two samples with different initial chromium concentration have been investigated at the Zn K-edge:

- * Gel8 (0.15mol% Cr₂O₃) at 400°C (Gel8 LT) and 1000°C (Gel8 HT)
- * KCr2 (0.5 mol% Cr₂O₃) at 800°C.

2-1-1 Gel8 LT

In figure 1, we compare the Gel8 LT RDF with reference compounds: at this temperature much lower than the nucleation one, only short order appears. Comparison of the EXAFS spectra filtered from the first peak of the RDF of the Gel8 LT and reference compounds (Fig 2 a and b) shows that at this stage, the organization of O atoms around Zn differs strongly from the tetrahedra ZnO₄ encountered in the reference phases. It has been impossible to get a convenient modelization of the gel spectra with one or two oxygen shells, however it appears that the Zn atoms are roughly in a tetrahedral coordination with a Zn-O mean distance near to 2.0Å.

At this thermal stage, the absence of a middle or long range order, and the impossibility to identify a characteristic organized coordination Zn-O, prevents to describe a precursor of nucleation.

Fig1: Comparison of the RDF of Gel8 LT, ZnAl₂O₄ and ZnCr₂O₄

Fig 2a.EXAFS spectra corresponding to the 1st shell of O atoms around Zn, for Gel8 LT and ZnO reference.

Fig 2b.EXAFS spectra corresponding to the 1st shell of O atoms around Zn, for Gel8 LT, ZnAl₂O₄, ZnCr₂O₄.

2-1-2 Gel8 HT

In figure 3 are compared the RDF of Gel8 HT, ZnAl_2O_4 , ZnCr_2O_4 . It clearly confirms the formation of a long range order of spinel type up to 10 Å. The fits of the first and second peaks extracted from the gel8 HT describe the Zn surrounding as in ZnAl_2O_4 crystallites. (Table II)

TABLE II . Zn (tetrahedral site) surrounding in Gel8HT.

	Neighbouring atom.	N	d (Å)
1st shell	O	3.8 (0.3)	1.96 (0.02)
2d shell	Al	12	3.34 (0.02)
	O	12	3.37 (0.02)
	Zn	4	3.59 (0.03)
	O	12	4.11 (0.02)

Fig 3: Comparison of the RDF of Gel HT, ZnAl_2O_4 and ZnCr_2O_4 .

2-2 Results on KCR2 gel (0.5% Cr_2O_3 , thermal treatment at 800°C)

Previous results (1,3) supposed that at this stage, nuclei of composition near ZnCr_2O_4 are formed. We have tried to check this assumption.

1) The RDF shown on figure 4 evidences the absence of long range ordering up to 4 Å, at the opposite of what was presented on figure 3 concerning the Gel8 HT. The second peak at about 3 Å has a lower amplitude than the equivalent ones in reference compounds and Gel8 HT. For $R > 4$ Å, the peaks are weak and their distribution is closer to ZnAl_2O_4 than to ZnCr_2O_4 .

2) The EXAFS spectra filtered from the first peak of the KCR2 RDF (Fig 5) corresponds to the first shell of O atoms around Zn. It cannot be interpreted as a Zn-O₄ tetrahedron, corresponding exclusively to ZnAl_2O_4 .

Fig 4 : Comparison of the RDF of KCR2 Gel, ZnAl_2O_4 , ZnCr_2O_4 .

Fig 5 : EXAFS spectra corresponding to the 1st shell of O atoms around Zn, for KCR2 Gel, ZnAl_2O_4 , ZnCr_2O_4 .

3) Figure 6 represents the imaginary part of the Fourier Transform (FT) of the normalized EXAFS signal for KCR2 gel and ZnAl_2O_4 . This function is more sensitive to the inter-atomic distance than the moduli part. We remark a relatively good agreement between these curves. At the opposite, there is a real discrepancy between the KCR2 gel and ZnCr_2O_4 curves. (Figure 7)

As a conclusion, our EXAFS analysis does not confirm the existence of ZnCr_2O_4 nuclei. It would more suggest a crystalline phase precursor close to ZnAl_2O_4 type. As an explanation of such different observations, we can remember that EXAFS technique informs about average structure and may be insensitive to the existence of ten nanometre ZnCr_2O_4 nuclei.

Fig 6 : Imaginary part of FT of KCR2 Gel and ZnAl_2O_4 .

Fig 7 : Imaginary part of FT of KCR2 Gel and ZnCr_2O_4 .

3 - CONCLUSION.

These EXAFS results give an information on the x order value of $\text{Zn}(\text{Al}_{1-x}\text{Cr}_x)_2\text{O}_4$ nuclei and crystallites formed at the different stages of the transformations. But the measures performed at the Zn K-edge are not sufficient to precise the localization of Cr^{3+} ions in the different phases encountered. A second series of EXAFS analysis is in progress, but the low concentration of chromium in the samples studied introduces some difficulties in the data collection.

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REFERENCES.

- (1) Nie, W., Boulon, G., Mai, C., Esnouf, C., Xu, R., Zarzycki, J., J. Non-Cryst. Solids, 121 (1990) 282.
- (2) Nie, W., Boulon, G., Mai, C., Esnouf, C., Xu, R., Zarzycki, J., Mat. Chem. Phys., 25 (1990) 105-126.
- (3) Nie, W., Boulon, G., Mai, C., Esnouf, C., Xu, R., Zarzycki, J., J. Chem. Mat., 4 (1992) 216-222.
- (4) Nie, W., Boulon, G., "Nucleation and crystallisation in xerogel induced and probed by Cr" . European Workshop on Glasses and Gels, Montpellier 29-31 January 1992; Colloque C2, supplement au J; de Physique III, vol 2 (les Editions de Physique, 1992) pp 141-144..
- (5) McKale, A. G., Veal, B. W., Paulikas, A. P., Chan, S.K., Knapp, G.S., J. Am. Chem. Soc. 110, (1988) 3763