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XANES- and EXAFS-Investigations on Chromium-Doped Mullite Precursors

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Abstract: Chromium-doped non-crystalline mullite precursors for ceramics were investigated with x-ray absorption spectroscopy at the Cr K edge. They were prepared using a sol-gel-route. 3 wt% Cr_2O_3 were added to partially substitute aluminium by chromium in the aluminosilicate network. The aim of the study was to characterize the development of the electronic and geometric structure of the precursor at different temperatures prior to its crystallization to mullite. The x-ray absorption spectra of the precursors and of several reference compounds were taken using monochromatized synchrotron radiation at the storage ring ELSA in Bonn, Germany. X-ray absorption near edge structure (XANES) measurements showed that the oxidation number of chromium shifts towards lower values with increasing temperature. Analogously, a transition from tetrahedral to octahedral coordination symmetry takes place. It was observed by extended x-ray absorption fine structure (EXAFS) measurements that interatomic distances concerning the first coordination shell increase with increasing temperature. Changes in the EXAFS amplitude and the appearance of a second coordination shell reveal a development of the short range ordered mullite towards a crystalline mullite.

1. INTRODUCTION

Mullite is an aluminosilicate which plays an increasing role as main constituent of advanced ceramics and composites [1]. The growing interest on mullite as technological material is due to its useful mechanical properties and chemical composition as well as its heat resistance. Transition metals can be incorporated to modify these properties. If the cation radius is similar to that of Al^{3+} , as it is the case for Cr^{3+} , they can give information on the different aluminium sites as well. The constitution of the non-crystalline precursor phases influences the microstructure and therefore the properties of the later ceramic material. As EXAFS and XANES provide information on the local structure around the excited atom [2-5], they do not require long-range order, and thus are especially useful for the investigation of such non-crystalline materials as they are given in this study.

2. EXPERIMENTAL

2.1 Sample synthesis

Appropriate amounts of tetraethoxysilane (TEOS) and aluminium-sec-butyrate (Al-O-Bu) were diluted with isopropanol and admixed with an ethanol solution of chromium(III)acetylacetonate to obtain the bulk composition 72% Al_2O_3 , 25% SiO_2 and 3 % Cr_2O_3 . Gelification was carried out by addition of distilled water with a pH adjusted to 1,5 with HCl. The gel was dried over several hours and thus a fine greenish precursor powder was obtained. The starting precursor powder was calcined at 450°, 600°, 800°, 900°, 1100° and 1750°C for 15 hours.

2.2 Measurements and data reduction

The spectra were taken at the beamline BN3 of the synchrotron radiation laboratory at the electron accelerator ELSA [6] operated in the storage ring mode with an electron energy of 2.3 GeV and an average current of about 50 mA. The synchrotron radiation was monochromatized at the Cr K edge by means of a Lemmonier type double crystal monochromator [7] equipped with two Ge (220)-crystals. All measurements were performed in transmission mode with two ionization chambers kept at 500 mbar air pressure.

The XANES spectra were obtained by scanning the energy region from 5940 to 6120 eV with steps of 0.2 eV and an integration time of 1 s per point. The absolute energy scale was fixed by the first inflection point of chromium in austenitic steel at 5989 eV. From the raw data, a linear background was subtracted. Spectra were normalized relative to the edge jump. The edge positions were determined according to Capeheart et al. [8].

EXAFS spectra cover an energy range between 5850 and 7000 eV. According to the spectral features, they were recorded with three different step widths with an integration time of 2 s per point. The EXAFS analysis was performed using a program package by Ertl et al. [9]. Due to problems in the final fitting procedure of the Fourier-analyzed data, here just the Fourier transformed of the k^3 -weighted EXAFS function $\chi(k)$ is discussed, as already this function provides the relevant information.

3. RESULTS AND DISCUSSION

As a basis for the interpretation of the Cr K XANES data, spectra of chromium compounds with different coordination and oxidation numbers were recorded [10]. All compounds with Cr in tetrahedral coordination have a characteristic pre-edge structure in common, resulting from a transition $1s - 3d$ which is forbidden for pure octahedral symmetry. Due to their lower ionic radii, only Cr^{4+} , Cr^{5+} and Cr^{6+} can occupy tetrahedral sites. To obtain the oxidation number of Cr, reference compounds with oxygen in the first coordination sphere are used. As a result, a direct correlation between the chemical shift of the rising edge and oxidation number can be derived: the edge shifts towards higher energies with increasing oxidation number as is shown in Fig. 1.

The pre-edge structure in the spectra of the precursors calcined between 450° and 800°C [Fig. 2] reveals the existence of tetrahedrally surrounded Cr. With the oxidation numbers determined by the correlation described above, the following conclusions concerning the chromium near-range order can be drawn: at 450°C , mainly tetrahedrally coordinated Cr^{6+} is present in the precursor. The interpretation of the 600°C -sample offers different possibilities: the assignment of pre-edge structure oxidation number to tetrahedral Cr^{6+} contradicts the results of other spectroscopic investigations [11]. More straightforward is the assumption of an admixture of tetrahedral Cr^{6+} and Cr^{5+} ions with some amount of Cr^{3+} , resulting in an "average" oxidation number of approximately four. The 800°C -sample spectrum is explained with Cr^{3+} in a distorted octahedral environment plus a minor amount of tetrahedrally surrounded $\text{Cr}^{3+}/\text{Cr}^{6+}$ ions. Between 800 - 1000°C , a general decrease in oxidation number towards +3 due to the occurrence of glass-like or crystalline bound Cr^{3+} [11] can be observed. The 1100°C spectrum resembles that of crystalline Cr^{3+} -doped mullite, which leads to the conclusion that the short-range order generally approaches that of crystalline mullite formed at temperatures above 1200°C .

Figure 1: Correlation of oxidation number and Cr K edge positions of reference compounds and mullite precursors

Figure 2: Cr K XANES spectra of mullite precursors heat-treated at different temperatures

The Fourier transformed of the k^3 -weighted EXAFS function show first maxima at $1.27 \text{ \AA}$ (450°C), $1.54 \text{ \AA}$ (800°C) and $1.60 \text{ \AA}$ (1100°C), representing the first coordination shell with oxygen atoms as nearest neighbours. Though these values cannot be taken as absolute distances as they are still uncorrected for phase shifts, the difference of approximately $0.3 \text{ \AA}$ corresponds to that between tetrahedral and octahedral coordinated Cr in crystalline chromium oxides [12,13] and thus confirms the results obtained by XANES. The appearance of a second peak at ca. $2.5 \text{ \AA}$ at higher temperatures is due to the distance between Cr and Al/Si in the second coordination shell [14]. The EXAFS amplitude, which increases by a factor 2 when going from 800° to 1100°C , reflects a general increasing ordering process [11], i.e. the transition from an amorphous state towards crystalline mullite.

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