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# Competing redox reactions in Fe-containing AlO(OH) and Al<sub>2</sub>O<sub>3</sub> matrices: A combined investigation by Mössbauer, ESR spectroscopy and thermal analysis

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**Abstract.** The investigation of iron-doped AlO(OH)/Al<sub>2</sub>O<sub>3</sub> systems revealed that the combined employment of Mössbauer and ESR spectroscopies together with thermal analysis yields meaningful data with complementary information. This mutual complementarity is based on the coexistence of Fe point defects with the corresponding aggregated FeO<sub>x</sub> species which has been observed even for very low Fe concentrations. Competing redox processes between the dopant, the AlO<sub>x</sub> matrix, and the gas atmosphere during the thermal treatment enable the generation of solid phases exhibiting specific chemical properties. The entire reaction process is influenced by a specific mechanical and thermal pre-treatment that affects predominantly oxydative processes in the matrix. A protecting influence of the matrix preventing further reductive attack of the Fe<sup>3+</sup> and Fe<sup>2+</sup> ions by hydrogen has been established.

## 1. Introduction

Crystalline and amorphous hydroxylic (AlOOH) and oxidic (Al<sub>2</sub>O<sub>3</sub>) precursors of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> have been doped with iron species for various reasons: (i) to reduce the temperature of the phase transition yielding  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> when forming corundum protective layers, and (ii) to yield particular mechanical properties of the polycrystalline product phases via an enhanced grain boundary concentration of FeO<sub>x</sub> or (Fe<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>. These processes are strongly influenced by mechanical activation both of the educts and the precursors for the Fe doping.

Both the mechanical activation and the thermal transformation to give  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> have been investigated by employing the title methods. The activation depends on the kind of Fe compounds used for the doping and the gas atmosphere during the thermal analysis (TA) heating run. The competing redox processes occurring during the TA runs deliver unique information about the active role of the AlO<sub>x</sub> matrix for the solid state reactions. Furthermore, they allow directly to influence certain properties of the resulting materials.

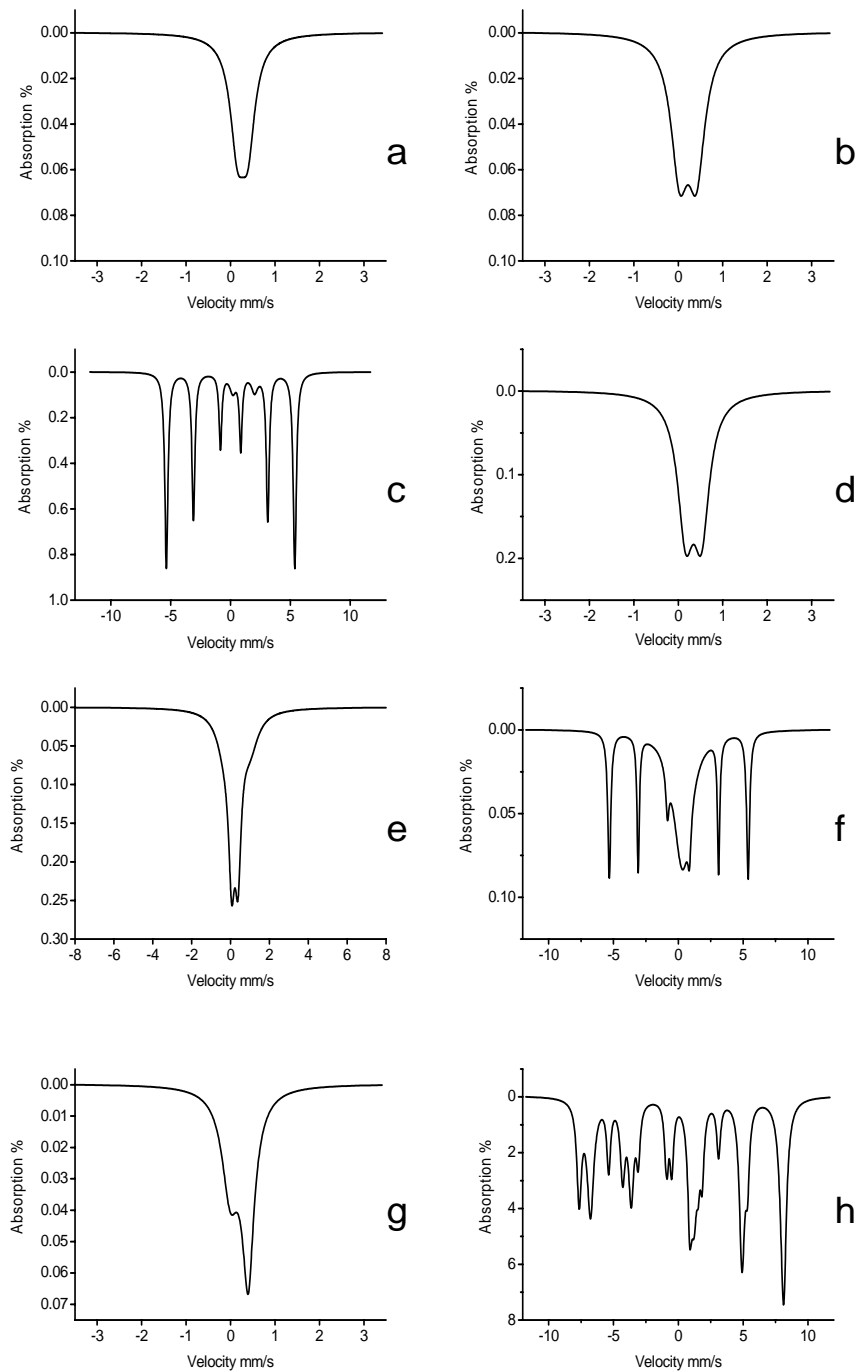
## 2. Results and Discussion

For the present study, the Fe concentration given as  $\text{Fe}_2\text{O}_3$  was limited by the range  $c \leq 0.1\text{mol}\%$ . Under these conditions, the combination of Mössbauer, ESR, and TA measurements yields complementary information. As an example, a sample of  $\alpha\text{-Al}_2\text{O}_3$  calcined at  $1500\text{ }^\circ\text{C}$  can be regarded (Figure 1g). It contains only very few iron impurities and exhibits the typical ESR spectrum for the system  $\{\alpha\text{-Al}_2\text{O}_3:\text{Fe}^{3+}\}$ . The position of the fine-structure transitions is undoubtedly governed by the symmetry of the matrix [1] (Figure 2a). Shape and intensity of the transitions depend on the mode of the  $\text{Fe}^{3+}$  insertion into the matrix and, therefore, on the given structural perfectness of the  $\alpha\text{-Al}_2\text{O}_3$  lattice. Under these conditions, the concentration of the  $\text{Fe}^{3+}$  species placed on  $\text{Al}^{3+}$  positions is sufficient to yield a meaningful ESR spectrum such as displayed in Figure 2a. The integral of the spectrum, however, shows that these  $\text{Fe}^{3+}$  point defects affect only a comparably small part of the total ESR intensity (Figure 2b). The latter is predominantly located at  $g \sim 2$  and originates from phase precursors of the approximative formula  $(\text{Fe}_x\text{Al}_{1-x})_2\text{O}_3$  [2] which yields the Mössbauer spectrum according to Figure 1g. Taking into account the above mentioned aspect of the present study to obtain complementary information from different analytical methods, this result can be regarded as a first approach: the Mössbauer data primarily correspond to the aggregated species being in coexistence or even in equilibrium with the point defects.

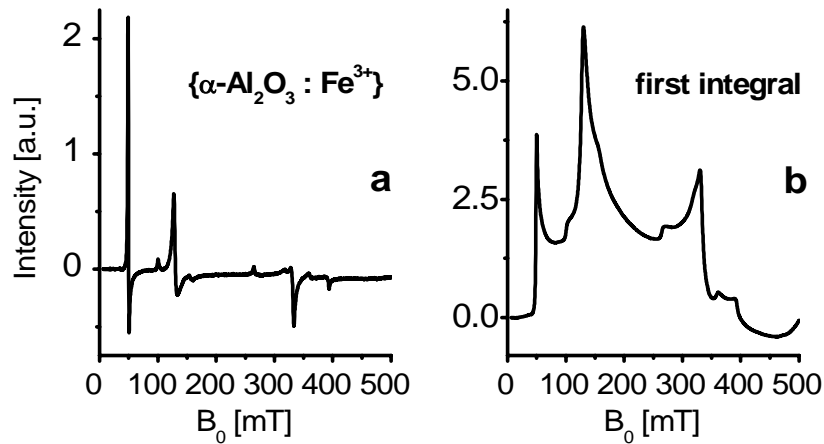
Comparable effects could be observed for the common educt of the  $\alpha\text{-Al}_2\text{O}_3$  formation, i.e. the crystalline  $\text{AlO}(\text{OH})$  which already contains iron impurities. Here, we are dealing with the weakly aggregated and rhombohedrally distorted Fe-O species which cause ESR signals at  $g \sim 4.3$  whereas the aggregated species are indicated by broad lines at  $g \sim 2$ . In this case as well, the Mössbauer data correspond to aggregated species and yield the parameters  $\delta = 0.27\text{ mm/s}$ ,  $\Delta = 0.23\text{ mm/s}$  and  $\Gamma = 0.39\text{ mm/s}$  (Figure 1a). After strong mechanical activation by 50 hours milling (cf. Figure 3) the Mössbauer parameters change as follows:  $\delta = 0.22\text{ mm/s}$ ,  $\Delta = 0.38\text{ mm/s}$  and  $\Gamma = 0.47\text{ mm/s}$ . This means that the mechanochemical reaction which is accompanied by a water release [3], shifts the value of  $\delta$  down to a 4 to 5 coordination of the  $\text{Fe}^{3+}$  ions, whereas the values of  $\Delta$  and  $\Gamma$  increase due to the mechanically induced broader statistical distribution of the bond angles in the  $\{\text{FeO}_x\}$  polyhedra. These findings can be related to the properties of a nominally undoped sample being prepared via a sol-gel route and showing a low Fe concentration [ $c(\text{Fe}_2\text{O}_3) \sim 0,01\text{ mol}\%$ ] (Figure 1d). The corresponding Mössbauer parameter at  $293\text{ K}$  are as follows:  $\delta = 0.24\text{ mm/s}$ ,  $\Delta = 0.29\text{ mm/s}$  and  $\Gamma = 0.37\text{ mm/s}$  and, respectively, at  $78\text{ K}$ :  $\delta = 0.34\text{ mm/s}$ ,  $\Delta = 0.36\text{ mm/s}$  and  $\Gamma = 0.44\text{ mm/s}$ . The increasing values for  $\Delta$  and  $\Gamma$  can be explained by the stronger distortion of the matrix at the low temperature. In general, the values represent the typical ones for  $\text{Fe}^{3+}$  ions in  $\{\text{FeO}_x\}$  polyhedra with  $x = 4 \dots 6$ .

After co-milling of the originally crystalline  $\text{AlO}(\text{OH})$  with  $1\text{ wt}\%$   $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and a subsequent TA heating run under  $\text{N}_2/10\%\text{H}_2$  (Pt) (Figure 3) one obtains a doublet ( $\delta = 1.10\text{ mm/s}$ ,  $\Delta = 1.82\text{ mm/s}$ ,  $\Gamma = 0.64\text{ mm/s}$ ) in coexistence with a sextet ( $\delta = 0.01\text{ mm/s}$ ,  $\Delta = 0.01\text{ mm/s}$ ,  $\Gamma = 0.27\text{ mm/s}$ ,  $hf = -33.34\text{ T}$ ) with  $\sim 8.2\%$  and  $91.8\%$  relative intensity, respectively (Figure 1c). These parameters unambiguously represent  $\text{Fe}^{(0)}$  being formed by reduction. Interestingly enough, the doublet of  $\sim 8\%$  represents  $\text{Fe}^{2+}$  ions, which were not reducible due to a stabilization via reactive implementation into the matrix.

This idea is supported regarding a further sample doped by adding  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in a sol-gel process. The sample contains  $0.13\text{ mol}\%$   $\text{Fe}_2\text{O}_3$  and, after TA under  $\text{N}_2$ , yields a part of the total intensity of  $\sim 60\%$  indicating  $\text{Fe}^{3+}$  ions ( $\delta = 0.26\text{ mm/s}$  and  $\Delta = -0.02\text{ mm/s}$ ), and  $\sim 39\%$  of a second phase with  $\delta = 0.14\text{ mm/s}$ ,  $\Delta = -0.66\text{ mm/s}$ ,  $hf = -33.35\text{ T}$ . It may represent  $\text{Fe}^{(0)}$  or  $\text{Fe}_x\text{N}$  [4]. Preferably, however, the second phase is assigned to be  $\text{Fe}_x\text{N}$  due to an isomer shift larger than zero.  $\text{Fe}_x\text{N}$  should be not only a product of a reduction (e.g. by organic residues), but also of an internal nitridation of  $\text{Fe}^{(0)}$  via intermedially formed  $\text{NH}_3$ . This would explain that the  $T_p$  decrease ends up at  $\sim 1110\text{ }^\circ\text{C}$ , i.e. the number of appropriate  $\text{FeO}_x$  seeds [5] is not sufficient.

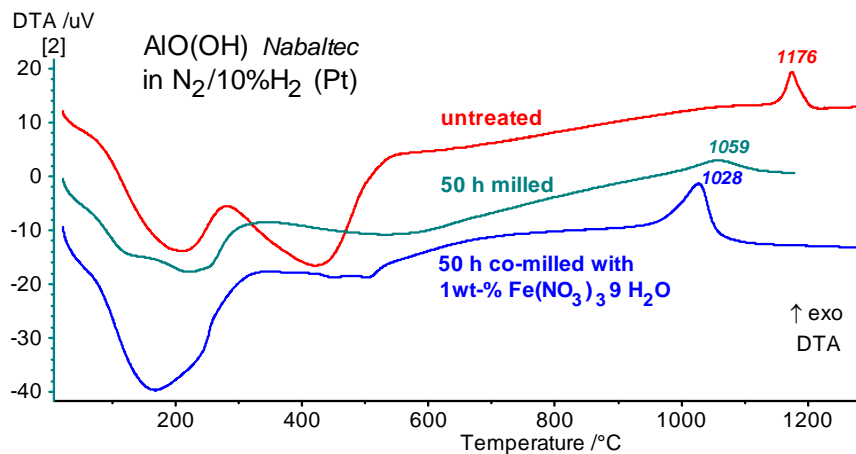


**Figure 1.** Mössbauer spectra of differently treated compounds:  
(a) AlO(OH) crystalline (commercial, Nabaltec);  
(b) as (a), 50 h milled, after TA under  $N_2/10\%H_2$  (1200 °C);  
(c) as (a), 8h co-milled with 1 wt-%  $Fe(NO_3)_3 \cdot 9H_2O$ ,  
after TA under  $N_2/10\%H_2$  (1200 °C);  
(d) AlO(OH) xerogel, undoped, measured at 78 K;  
(e) AlO(OH) xerogel,  $Fe(NO_3)_3 \cdot 9H_2O$  (0.52 mol-%  $Fe_2O_3$ ) added to the sol;  
(f) as (e) after TA under  $N_2/10\%H_2$  (1200 °C);  
(g)  $\alpha-Al_2O_3$  (commercial, VEB Laborchemie Apolda), calcined at 1500 °C;  
(h)  $Fe(NO_3)_3 \cdot 9H_2O$  after TA under  $N_2/10\%H_2$  (1200 °C);



**Figure 2.** ESR spectra of  $\{\alpha\text{-Al}_2\text{O}_3:\text{Fe}^{3+}\}$  powder measured at 78 K (a) and its first integral (b)

If the external reductive force is enhanced (e.g. by heating under  $\text{N}_2/10\%\text{H}_2$ ) an unexpected result is obtained. The sample yields a Mössbauer spectrum with a  $\text{Fe}^{3+}$  doublet ( $\delta = 0.21$  and  $\Delta = -0.002$  mm/s). Quite surprisingly, it amounts to  $\sim 50\%$  of the total intensity, whereas the remaining 50% are caused by  $\text{Fe}^{(0)}$ . Despite of the reductive conditions, a large part of  $\text{Fe}^{3+}$  is



**Figure 3.** DTA curves of  $\text{AlO}(\text{OH})$  in  $\text{N}_2/10\%\text{H}_2$  (Pt crucibles) for different sample pre-treatments

formed by chemical reaction with the matrix being under formation and structural reorganization. As a consequence, further reductive attack is prevented.

Competing redox processes *without* the participation of a matrix can be observed in the case of pure  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  being subjected to a TA heating run under  $\text{N}_2/10\%\text{H}_2$ .

The characterization of the residue of the TA treatment by Mössbauer spectroscopy (Figure 1h) led to the following composition:

- 13.0%  $\text{Fe}^{2+}$  ( $\delta = 1.08$  mm/s,  $\Delta = 0.31$  mm/s and  $\Gamma = 0.49$  mm/s);
- 15.6%  $\text{Fe}^{(0)}$  ( $\delta = 0.006$  mm/s,  $\Delta = -0.02$  mm/s and  $h_f = 33.27$  T);
- 27.5% Magnetite A-sites  $\delta = 0.27$  mm/s,  $\Delta = -0.03$  mm/s and  $h_f = 49.10$  T;
- 43.7% Magnetite B-sites  $\delta = 0.65$  mm/s,  $\Delta = -0.02$  mm/s and  $h_f = 46.09$  T.

It is noteworthy that only 15.6% Fe<sup>(0)</sup> and a considerable amount of magnetite are formed. The oxydative atmosphere, formed during the thermal decomposition of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, effectively competes with the hydrogen of the carrier gas in the TA run. However, at higher temperatures (TA up to 1200 °C) the fraction of reduced Fe species in the product mixture increases.

Finally, another interesting way to obtain Fe-doped α-Al<sub>2</sub>O<sub>3</sub> should be mentioned here. It concerns the formation of alumina in an O<sub>2</sub>/H<sub>2</sub> flame starting from a Fe-doped AlN precursor yielding a strongly distorted system ( $g' \sim 4.3$  in the ESR [6], not shown here). There is a coexistence of weakly aggregated point defects with precursors of (Fe<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>. This system is characterized by two doublets in the Mössbauer spectrum:

$\delta_1 = 0.23$  mm/s,  $\Delta_1 = 0.82$  mm/s and  $\Gamma_1 = 0.78$  mm/s (Fe<sup>3+</sup> ions representing ~80 % of the spectral intensity);

$\delta_2 = 0.84$  mm/s,  $\Delta_2 = 1.77$  mm/s and  $\Gamma_2 = 0.78$  mm (Fe<sup>2+</sup> ions in the aggregated part, ~20 %).

Obviously, this kind of a “pulse-like” pyrolysis of AlN, which yields hollow balls of α-Al<sub>2</sub>O<sub>3</sub>, creates a partly reductive atmosphere thus explaining the formation of Fe<sup>2+</sup> species. A further reduction, however, which would lead to Fe<sup>(0)</sup>, or even to a nitridation of iron could not be observed here. The applied temperature-time regime, obviously, prevents the reductive action.

### 3. Conclusions

For concentrations of c(Fe<sub>2</sub>O<sub>3</sub>) ≤ 0,01 mol-% already, a distribution of Fe species could be established both in polycrystalline and amorphized systems: (i) as point defects in the matrix lattice which can be followed by ESR spectroscopy, and (ii) as aggregated species acting as precursors of phases like (Fe<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sup>(0)</sup> which can be successfully studied by Mössbauer spectroscopy. The actual phase composition together with the possible formation of further species such as FeAlO<sub>4</sub> precursors can be directed by redox processes of internal (residual carbon from the sol-gel process, NO<sub>3</sub><sup>-</sup> etc.) or external (H<sub>2</sub>; O<sub>2</sub>) reaction partners during or prior (!) to the thermal matrix transformation. A comprehensive inspection of the spectroscopical and thermoanalytical findings shows that

(i) the FeO<sub>x</sub> phases can significantly decrease the phase transformation temperature to yield α-Al<sub>2</sub>O<sub>3</sub> provided the FeO<sub>x</sub> phases exhibit both a suitable grain formation kinetics and particle size;

(ii) the transforming matrix does not exhibit only oxydative properties due to the *in situ* water release and the related formation of reactive surface sites, but is able as well to prevent the reduction of the matrix-incorporated Fe<sup>3+</sup> ions up to ~50 % of the total amount by the external hydrogen gas flow covering the temperature range up to 1200 °C.

### 4. References

- [1] Stösser R, Scholz G, Buzaré J Y, Silly G, Nofz M and Schultze D 2005, A magnetic resonance investigation of the process of corundum formation starting from sol-gel precursors, *J. Am. Ceram. Soc.* **88**, 2913-22
- [2] Scholz G, Stößer R, Krossner M and Klein J 2001, Modelling of multifrequency ESR spectra of Fe<sup>3+</sup> ions in crystalline and amorphous materials: A simplified approach to determine statistical distributions of spin-spin coupling parameters, *Appl. Magn. Res.* **21**, 105-23
- [3] Stößer R and Feist M 2008, Exothermal water release from Pseudoboehmite gels and their mechanically treated analoga caused by activated hydrogen, *J. Phys. Chem. C* **112**, 16438-444
- [4] Rissanen L, Neubauer M, Lieb K P and Schaaf P 1998, J The new cubic iron-nitride phase FeN prepared by reactive meagnetron sputtering, *J. Alloys Compounds* **274**, 74-82
- [5] Nofz M, Stößer R, Dörfel G and Schultze D 2005, The thermally induced transformation of pseudoboehmite gels - a comparison of the effects of corundum seeding and iron doping, *J. Europ. Ceram. Soc.* **25**, 1095-107
- [6] Brenneis R, personal communication.