Fe\(^{3+}\) Ions in Amorphous Solids: EPR on Mechanically and Chemically Amorphized Al\(_2\)O\(_3\)

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Abstract. Stepwise amorphization of a low-level doped \(\alpha\)-Al\(_2\)O\(_3\) single crystal yielded powders without changes of the concentration and chemical nature of the dopants. Kind and degree of disturbances could be unambiguously monitored by the allowed and forbidden transitions of the Fe\(^{3+}\)-cw-EPR in X-band using a Bruker bimodal cavity. Based on simulations diagonalizing the spin Hamiltonian for \(S = 5/2\) it was possible to discriminate between regions as well as samples of structural order and disorder. The spectral pattern of the allowed and forbidden transitions of Fe\(^{3+}\) ions together with the field-position-dependent saturation behaviour (4.2 K) allowed us to differentiate between crystalline and amorphous components or regions of a sample.

1. Introduction

The knowledge concerning Fe\(^{3+}\) ions in crystalline compounds appears to be rather deep in comparison to that available for amorphous solids. The crystalline systems are commonly characterized by more or less complete spin Hamiltonians and by models describing the spin-relaxation behaviour [1]. Inspecting the literature on amorphous solids there is a lack of knowledge concerning systems produced as intermediates in solid-state chemical reactions or as materials with special properties (like doped glasses, devitrified glasses and ceramics, or even biological systems).

Although a large number of investigations has been done in the field of Fe\(^{3+}\) EPR [1–3], even today many phenomena cannot be interpreted consistently. New insights will be given here especially taking into account the influence of amorphous matrices of different physical and chemical natures on the EPR response of the incorporated Fe\(^{3+}\) ions.

The concept of the present contribution is the following: starting from very low Fe\(^{3+}\)-doped and sufficiently perfect \(\alpha\)-Al\(_2\)O\(_3\) single crystals, powders of different grades of distortion and amorphization were produced from one and the
same crystal by physical and chemical means. Finally, glassy samples represented by oxide glasses [4, 5] as well as by frozen solutions of Fe$^{3+}$ in inorganic acids were investigated. The latter ones were used to suppress the aggregation of the Fe$^{3+}$ species at the formation of a glassy phase. To compare the properties of the powdered α-Al$_2$O$_3$ single crystal with very low-doped α-Al$_2$O$_3$ powders, commercial ones with the purity of 99.99% and 99.9999% were taken into account.

Fe$^{3+}$ ions, incorporated into solids, are interesting probes for the structure and dynamics of the host. But they are also of influence on the physical and chemical properties of the actual matrix. In general, Fe$^{3+}$ ions yield good observable ESR signals from very different types of crystalline and amorphous solids. This is true, as long as the zero-field splitting is not too large ($|D| \leq \nu_{MW}$) and the interactions between the individual ions are not too strong. But in many cases – more than generally expected – combined effects of aggregation of the 3d$^5$-ions, of the strain from the glassy or disturbed crystalline matrix and the value and nature of the zero-field splitting can yield very complex ESR spectra. Even these spectra bear valuable information concerning the actual solid. This information can be extracted introducing stepwise selected physical and chemical perturbations and applying suitable models for the reproduction of the experimental spectra by simulation. Spectroscopic aspects directly lead to unresolved problems of Fe$^{3+}$ species in biochemistry [6a]. Examples for complex Fe$^{3+}$ spectra of biochemically relevant species like enzymes of the lipoxygenase-type are given in [6b]. It appears that a deeper understanding of these and related Fe spectra requires the application of methods and models developed and treated in this contribution. Focussed on spectral and diagnostic aspects, systematic changes of samples were brought about by physical and chemical means like milling with different depth of impacts, by complexing agents (deferoxamine mesitylate), or reactions of Al$_2$O$_3$ with alkaline and alkaline-earth oxides and with water, respectively. Furthermore, the cw EPR was applied in X-band in combination with a bimodal cavity and low temperature (4.2 K). Low temperatures were needed to improve the sensitivity of the ESR of very low-doped samples, to restrict the magnetic interactions between the Fe species and to discriminate between different EPR responses by characteristic saturation behaviour.

It is the aim of the present paper to find a consistent interpretation of the complex ESR spectra of amorphous and partially ordered systems containing Fe$^{3+}$ ions in different local environments and different states of aggregation. It will be shown how the constraints of a mechanically and chemically disturbed Al$_2$O$_3$ matrix on the incorporated Fe$^{3+}$ ions are reflected by the EPR spectra of these ions. Furthermore, evidence will be given that the detection of forbidden transitions using the bimodal cavity is a powerful and sensitive tool to discriminate between amorphous and crystalline regions of a sample. Moreover, the results should serve as test of models allowing the interpretation of the local structure and dynamics of Fe centres in biologically relevant systems.