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The Hydration Process of La_2O_3 Studied by the Electron Spin Resonance of Gd^{3+} and Mn^{2+} Ions

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The hydration of single-crystal La_2O_3 samples was studied following the evolution versus time of ESR spectra of Gd^{3+} and Mn^{2+} ions which enter the lattice substitutionally at lanthanum sites. Our results, which confirm those obtained previously on the macroscopic scale, permit a better understanding of the hydration process on the atomic scale.

Introduction

The hexagonal modification of lanthanide oxides A-Ln_2O_3 belongs to the space group $P\bar{3}m1$ (D^3_{3d}). The character of such a structure is that the metallic atom, La in our case, is sevenfold coordinated, with C_{3v} symmetry along the crystalline c-axis. However, there are two types of oxygen atoms in this arrangement. One is inside a tetrahedron of lanthanum atoms, the other is six-coordinated and is further from the metallic atoms than the former (about 2.70 Å versus 2.40 Å).

Along the c-axis the structure is formed of a succession of slabs of a "complex cation" $(LaO)^{n+}_n$ consisting of OLa_4 tetrahedra edge-linked in a manner derived from the CaF_2 structure, separated by planes of oxygen anions (*1*). This model implies a certain amount of covalent bonding inside the "complex cation" $(LaO)^{n+}_n$. Our previous ESR work on Mn^{2+}-doped single-crystal La_2O_3 (*2*), which emphasized the existence of two types of bonds in La_2O_3, was a confirmation of Caro's structural principle.

Many papers have been devoted to the hydration process of lanthanum oxide. We shall refer here to the works (weight increase experiments and X-ray diffraction studies) of Foex (*3*) and Touret and Queyroux (*4*), the conclusions of which are:

(a) La_2O_3 melted and ground is more sensitive to hydration than a single-crystal sample.

(b) Penetration of water takes place between the "complex cations" $(LaO)^{n+}_n$ and the oxygen planes.

(c) The thickness of a single-crystal specimen increases along the c-axis.

(d) The reaction spreads out inside the sample between unaltered lamellas of oxide.

(e) From La_2O_3 the reaction leads directly to $La(OH)_3$ which has the UCl_3 type hexagonal structure (*5*) and the c-axis of which is perpendicular to that of La_2O_3.

Experiments and Results

La_2O_3 single-crystals doped with either Gd^{3+} or Mn^{2+} (~1000 ppm) were obtained with a solar furnace of the Laboratoire des

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Ultraréfractaires at Odeillo (France) using a slow cooling procedure, as described in (*2*). They were conserved in quartz tubes sealed under vacuum.

In the ESR experiments, the sample is set at the center of the rectangular TE_{102} resonant cavity of a conventional X-band ($\lambda = 3$ cm) spectrometer. The sample holder is a Perspex rod cut longitudinally into two parts lightly bounded by two India rubber bands. This avoids the destruction of the specimen but nevertheless allows its expansion along the crystalline *c*-axis.

The Gd^{3+} ion has an electronic configuration $4f^7$ with a ground state $^8S_{7/2}$. When such an ion is put in a crystal field, it is well known that the spin degeneracy is split under the combined action of the crystal field and spin–orbit interaction. Due to the axial symmetry of the substitutional site in La_2O_3, the ground level is split into four Kramers doublets. The distance between the two extremes, which is known as the zero-field splitting, is equal to about 1.6 cm^{-1} (*6*, *7*). If we except some trigonal charge-compensated Gd^{3+} centers in CaF_2 (*8*, *9*), this value is the largest ever reported for this ion. Consequently, the X-band resonance pattern is not the seven-line one usually obtained. With the maximum field value available ($H \sim 7500$ G) the $Gd^{3+}:La_2O_3$ spectrum obtained with $\mathbf{H} \parallel c$, consists of five lines which exhibit their extremum position.

During the hydration of the sample, which is left in ambient air at room temperature, the intensity of these lines decreases continuously. About 12 hr after the beginning of the experiment an extra line appears in the $g = 2$ region ($H \sim 3400$ G). It belongs to the $Gd^{3+}:La(OH)_3$ spectrum, a study of which was previously made by Scott (*10*). Figure 1 represents three steps in the evolution of the $g = 2$ region of the spectra. In Fig. 1a, we see the $m_S = -\frac{1}{2} \rightarrow \frac{1}{2}$ fine structure line of the $Gd^{3+}:La_2O_3$ spectrum. Twenty-seven hours later, three lines of the $Gd^{3+}:La(OH)_3$ spectrum are already well resolved (Fig. 1b). At the end of the experiment ($t = 88$ hr), the $Gd^{3+}:La_2O_3$ spectrum has completely disappeared, but five of the seven lines of the $Gd^{3+}:La(OH)_3$ spectrum are easily observable (Fig. 1c). In this case, the static field is perpendicular to the $La(OH)_3$ *c*-axis and the experimental line positions are

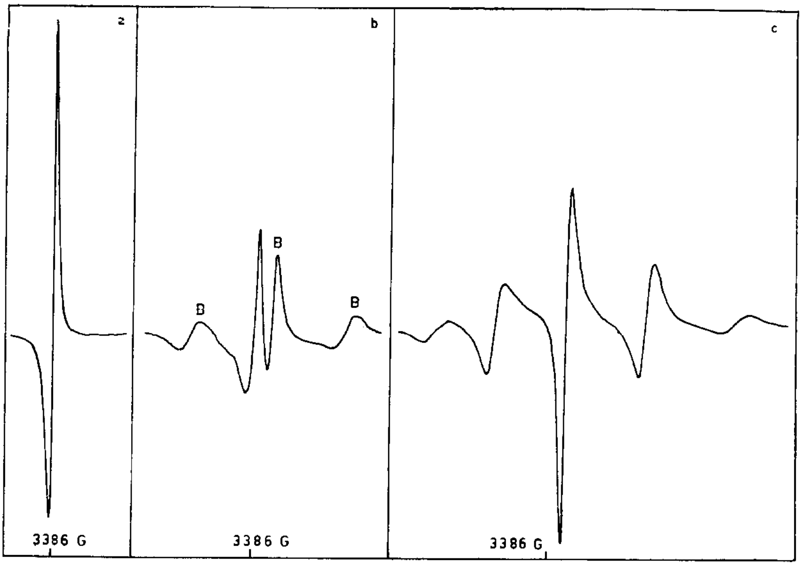

FIG. 1. Evolution of the ESR spectra ($g = 2$ region) during the sample hydration. (a) $t = 0$: $m_S = -\frac{1}{2} \rightarrow \frac{1}{2}$ line of $Gd^{3+}:La_2O_3$ spectrum with $H \parallel$ to the La_2O_3 trigonal axis. (b) $t = 27$ hr: The B lines belong to the $Gd^{3+}:La(OH)_3$ spectrum. (c) $t = 88$ hr: $Gd^{3+}:La(OH)_3$ spectrum with $H \perp$ to the $La(OH)_3$ *c*-axis; the two extreme lines are missing.

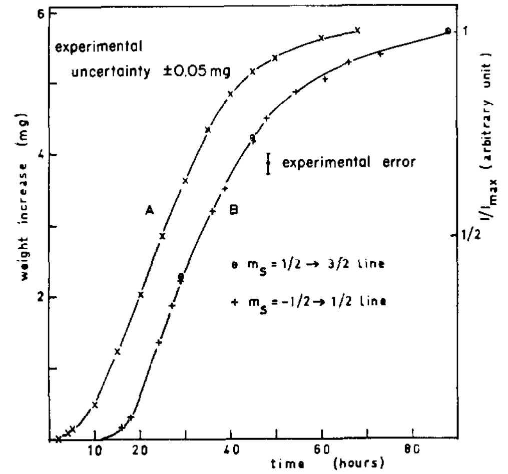

FIG. 2. Comparison between the weight increase curve (A) and the intensity increase of some lines of the $Gd^{3+}:La(OH)_3$ spectrum (B). Two different samples from the same batch were used.

in good agreement with the theoretical ones deduced from Scott's spin-Hamiltonian parameters.

In Fig. 2 we have plotted the intensity increase of some lines of the $Gd^{3+}:La(OH)_3$ spectrum versus time and compared it to the weight increase curve of another La_2O_3 single-crystal sample from the same batch.[1] Although these two curves are slightly shifted in time, we notice that they have the same shape. Such a shift can be easily explained knowing that there is a difference of sensitivity between the two experimental setups.

These observations (continuous decrease of the $Gd^{3+}:La_2O_3$ spectrum associated with a regular increase of the $Gd^{3+}:La(OH)_3$ spectrum) support the conclusion that the hydration of La_2O_3 leads directly to $La(OH)_3$.

Further information about what happens inside the sample during the hydration process can be obtained from the evolution of the $Mn^{2+}:La_2O_3$ spectrum. The electronic configuration of the Mn^{2+} ion is $3d^5$ with a ground state $^6S_{5/2}$, which is an orbital singlet. The axial crystal field removes the degeneracy completely. The existence of a nuclear spin $I = \frac{5}{2}$ leads to a hyperfine interaction between the nuclear and electron spins. Consequently, for each type of defect present in the crystal, the spectrum must be compounded of 30 "allowed" lines only when the static field is parallel or perpendicular to the symmetry axis of the paramagnetic center. Due to the valence state of Mn^{2+} some lattice imperfections (probably one O^{2-} vacancy for two divalent ions) are needed to preserve the charge balance, and the existence of different types of Mn^{2+} centers is expected. Our previous work on this subject (*2*) has shown that the charge compensation did not take place in the immediate neighborhood of the manganese ion as we recorded a unique ESR pattern whatever the orientation of the sample in the dc field. In the spin-Hamiltonian describing the spectra, the hyperfine coupling tensor has two components: $A_{\parallel} = -70.81 \times 10^{-4}\ \mathrm{cm}^{-1}$ and $A_{\perp} = -67.63 \times 10^{-4}\ \mathrm{cm}^{-1}$ (*2*). In first order the $A_{\parallel}$ value gives the hyperfine splitting between two successive lines of the central pattern ($m_S = -\frac{1}{2} \to \frac{1}{2}$ fine structure transition) when the magnetic field is aligned with the crystalline *c*-axis. In a previous paper (*2*), by reference to the work of Šimanek and Müller (*11*) we were able to show that the Mn^{2+} coordination in the (MnO_x) cluster is not equal to 7. There exists covalent bonding with the three or four ligands that are the nearest neighbors located in the "complex cation" $(LaO)_n^{n+}$. This situation also holds true for the rare-earth atoms as what the Mn^{2+} "sees" is a picture of the situation in the host lattice.

As for Gd^{3+} the intensity of the $m_S = -\frac{1}{2} \to \frac{1}{2}$ transition (in fact the six corresponding hyperfine lines), a transition which is insensitive to the weak random perturbations of the local crystal field, decreases regularly (Fig. 3), thus indicating that the amount of La_2O_3 in the sample is lower and lower. But, from the beginning to the end of the experiment the value of the hyperfine splitting *does not change*. This means that in the surviving La_2O_3 domains, the "complex cations" $(LaO)_n^{n+}$ have not yet been attacked. With time, more and more such layers are destroyed by combination with water molecules, thus explaining the

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[1] Identical weight-increase curves were obtained with samples either left in ambient air or put in an atmosphere saturated with H_2O vapor but free from CO_2.

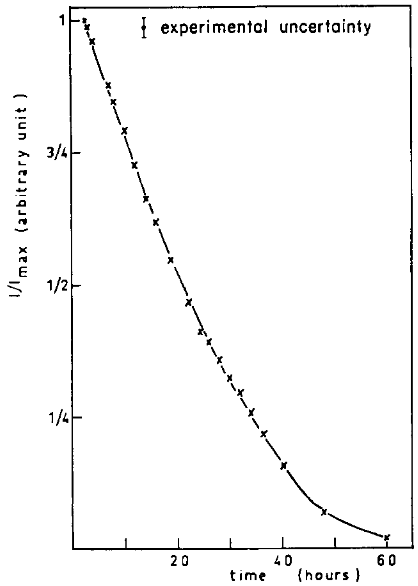

FIG. 3. $Mn^{2+}:La_2O_3$ spectrum with $H \| c$: decrease of the $m_S = -\frac{1}{2} \rightarrow \frac{1}{2}$ line intensity versus time.

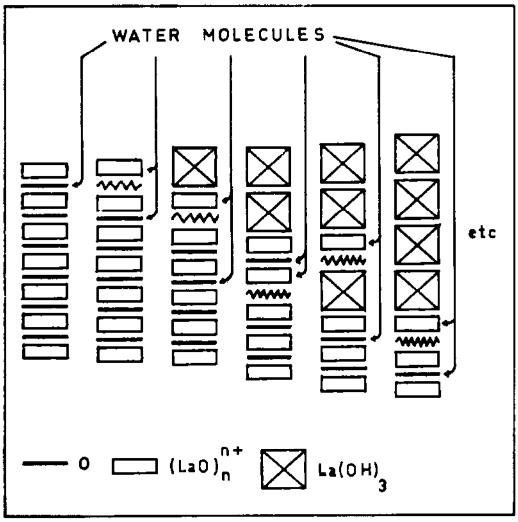

FIG. 4. Schematic representation of the hydration process of La_2O_3. Penetration of water takes place between "complex cations" and oxygen planes (——— O leads to ∿∿∿). The amount of water is such that the composition $La(OH)_3$ is reached (□ leads to ☒ $La(OH)_3$).

decrease in the ESR signal intensity. On the other hand, it is worthwhile to underline the nonexistence of a $Mn^{2+}:La(OH)_3$ pattern. This is quite surprising as one would expect to see at least the $m_S = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition in the case of a distribution of Mn^{2+} symmetries. A possible explanation could be that the Mn^{2+} ions are associated and hence interact significantly with one another, but the reason why such a process would arise is not clear at all.

Figure 4 gives a schematic representation of the hydration process from the above results.

Conclusion

Our observations are in good agreement with those in the literature concerning the hydration process of La_2O_3 on the macroscopic scale (points a, c, and e of the introduction). Although, unfortunately, they are not able to give any information about the rearrangement of lanthanum atoms during the transformation $La_2O_3 \rightarrow La(OH)_3$, we nevertheless think that they permit us to take a small step forward in the understanding of this process on the atomic scale. This can be seen considering the precisions they bring to points b and d of the introduction.

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