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SITE OCCUPANCY AND BINDING OF Eu$^{2+}$ IN THE SOLID ELECTROLYTE SODIUM β ALUMINA

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Résumé. — Nous avons dopé avec des ions Eu$^{2+}$ de l'alumine β au sodium et étudié par spectroscopie Mössbauer de 151Eu le déplacement isomérique, l'éclatement hyperfin et la variation du facteur de Debye-Waller en fonction de la température. Les ions Eu peuvent occuper 2 sites, dont l'un a une température de Debye et une densité électronique au noyau anormalement faibles.

Abstract. — We have doped sodium β alumina with Eu$^{2+}$ ions and studied the isomer shift, hfs, and temperature dependence of the Debye-Waller factor, using Mössbauer spectroscopy of the Eu$^{151}$ species. The Eu ions can be put into 2 sites, one of which has an anomalously low Debye temperature and electronic density at the nucleus.

Many New Technology storage battery systems for energy storage for vehicle use have been proposed. The electrode system 2 Na$^+$.3 S → Na$_2$S$_3$ has been intensively studied [1], since it has a high energy capacity per kilogram, is made of inexpensive materials which are widely available, and has been demonstrated to be long-lived and reliable in laboratory scale tests.

Sodium-sulfur storage batteries use some modification of sodium β alumina as a solid electrolyte. In this application, the alumina acts as an electronic insulator, preventing electrons from flowing between the (melted) sulfur and (molten) sodium electrodes, and as an ionic conductor, allowing Na$^+$ ions to diffuse from the sodium source to the reaction region, where Na$_2$S$_3$ is formed. Thus, the ionic conductivity in the sodium β alumina, as high as 30 Ωcm at room temperature, is a critical determinant of the internal resistance of the sodium-sulfur cell. In fact, the necessity for keeping the battery at high temperatures (200-300 °C) to obtain adequate diffusivity of the Na ions in the β alumina structure is a severe restriction on the wide application of this type of cell. Thus, extensive research [2] has been carried out to study the diffusivity of ions in this material, and the effects of structure and stoichiometry on the diffusivity [3].

Sodium β alumina forms in an extremely complex layer structure [4], with the idealized formula Na$_3$O.11 Al$_2$O$_3$. Actual crystals are far off stoichiometry, and the defects arising from this may contribute to the high ion diffusivity and conductivity. The structure can be described as consisting of layers of spinel blocks, about 9 Å thick, separated by Al-O-Al bridges. The planes (perpendicular to the c axis) through the oxygens of the Al-O-Al bridges are extremely open, and the Na ions reside on and diffuse in these planes. The open structure permits the substitution of many other mono- and divalent ions for the Na$^+$, and we have doped β alumina with Eu$^{2+}$ and

![Fig. 1. Eu$^{151}$ spectra of: (top) sample containing only B sites (300 K); (middle) sample containing A and B sites (300 K); (bottom), same sample but at 940 K, where the low f of the B sites allows the A site spectrum to be seen.](image-url)
observed the binding of these ions via Mössbauer spectroscopy.

Our samples were prepared by first making small crystals of β alumina and then doping them with Eu²⁺ by means of ion exchange in an electrolyte. Samples have been prepared with a wide range of Eu doping, with evidence that a substantial fraction of Na ions can be replaced by Eu.

Mössbauer spectra (Fig. 1) show that essentially all the Eu ions are divalent, and that two sites, which we henceforth « A » and « B », can be distinguished. Although the lines from the two sites overlap, it is possible to distinguish them, using constrained least-squares fits, by the different variations of the recoil-free fractions with temperature (Fig. 2) and the very different linewidths. The relative proportion of A and B site occupation is determined by the thermal history of the sample, with slow cooling after doping favoring B site population. The assignments, isomer shifts, and f(T) (Fig. 3) have been confirmed using samples doped with different relative populations in A and B sites. We find markedly different effective Debye temperatures and line-widths, and substantially different isomer shifts, for the two sites:

<table>
<thead>
<tr>
<th>Site</th>
<th>θD (K)</th>
<th>FWHM (mm/s)</th>
<th>I. S. (vs. EuF₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>310</td>
<td>3.5</td>
<td>-13.1</td>
</tr>
<tr>
<td>B</td>
<td>170</td>
<td>7.8</td>
<td>-14.6</td>
</tr>
</tbody>
</table>

Samples which contain only a small (≈ 1 %) Eu²⁺ doping exhibit a somewhat broader B site line.

The differences between values for the two sites present a unified and consistent picture. The A site, which is straightforward to understand, has an isomer shift appropriate for Eu²⁺ in an oxygen environment, θD similar to that of EuO, and a linewidth (from unresolved quadrupole splitting) similar to that observed in other Eu compounds. The B site has the lowest isomer shift ever reported [5] for Eu²⁺, corresponding to an unusually low electron density at the Eu nucleus. This would be expected for an Eu ion in a roomy site, where the 5s wave functions can expand somewhat. The very low θD is also symptomatic of a loosely bound site.

References


