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Observation of Anisotropic Oxygen Diffusion in Hexaaluminate

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Isotopic exchange of oxygen between a single crystal of Mn-substituted hexaaluminate and $^{18}O_2$-enriched gas was analyzed with secondary ion mass spectroscopy (SIMS). Observed concentration profiles of ^{18}O showed that the diffusion rate was higher along [110] as compared to along [001]. This implies that the pseudolayer structure of hexaaluminate influences the atomic diffusion, i.e., the loosely packed intermediate monolayer between closely packed spinel blocks, which spreads parallel to the (001) plane, is a preferential diffusion route of O^{2-} ions. © 1991 Academic Press, Inc.

Introduction

The hexaaluminate-related compound is one of the important functional inorganic materials which have been extensively studied in wide application fields, such as superionic conductors (*1*), host crystals for fluorescence (*2*), laser (*3*), and nuclear waste disposal (*4*). We have studied the catalytic properties of this structural compound and developed a hexaaluminate catalyst for high-temperature catalytic processes (*5–7*). Their excellent thermal stability, which could not been attained by conventional solid catalysts, is quite useful in retaining the large surface area necessary for catalytic reaction. In a series of studies, we noticed the anisotropic crystal growth and resultant thin planar morphology are effective in retaining a large specific surface area (*8*). Such an anisotropy in crystal morphology and in crystal growth was pointed out not only for hexaaluminate (*9*) but also for other isomorphous compounds, e.g., hexaferrites or hexagalletes, by several researchers (*10, 11*). It appears to be closely related to the unique crystal structure consisting of an alternative stacking of spinel blocks and intermediate monolayers with large mono-, di-, or trivalent cations in the [001] direction. For the basic interpretation of the relationship between this pseudolayer crystal structure and crystal growth, we noted that atomic diffusion presented an interesting approach.

This study was directed toward the eluci-

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TABLE I

DIFFUSION-ANNEALING CONDITIONS

Composition of sample[a]	Temperature (°C)	Diffusion time (min)	O_2 pressure (10^3 Pa)	$^{18}O_2/(^{18}O_2 + {}^{16}O_2)$ after annealing
$Ba_{0.75}Mn_{0.47}Al_{11.23}O_{18.3}$	800	120	1.97	0.95
$Ba_{0.75}Mn_{0.47}Al_{11.23}O_{18.3}$	900	120	1.97	0.95

[a] Valence of Mn is supposed to be 3.0.

dation of the structural effect on the O^{2-} diffusion in single crystals of Mn-substituted barium hexaaluminate. The SIMS analysis employed in this study is believed to provide the most useful information on the evaluation of isotopic diffusion along different crystal axes.

Experimental

The material used for ^{18}O diffusion-annealing and subsequent SIMS analysis was single crystal Mn-substituted hexaaluminate. For the single crystal growth of Mn-substituted barium hexaaluminate, a sintered rod was prepared from corresponding oxide/carbonate mixtures by heating at 1450°C. The chemical composition of these starting samples was adjusted to $BaMnAl_{11}O_{19}$. The single crystal was grown by a floating zone apparatus (Nichiden Kikai Co.) equipped with a Xe arc lamp. The crystal growth was operated at a constant rate (3 mm/hr) in air. The single crystals as grown were a rod-like shape ca. 5 mm in diameter. They were confirmed to be a single hexaaluminate phase with no impurity phase from powder X-ray diffraction of the crushed crystals. The chemical composition of the crystal was Ba : Mn : Al = 0.75 : 0.47 : 11.23 as revealed by energy-dispersive X-ray analysis. Since the crystal contained many cracks, several clear parts were cut to a suitable size in order to expose (001) and (110) planes, which were checked by the back reflection Laue method. The crystal surface was polished with a diamond paste.

Diffusion annealing in an $^{18}O_2/^{16}O_2$ mixture was done in an electrical furnace. Detailed experimental conditions were summarized in Table I. The $^{16}O/^{18}O$ ratios in the diffusion-annealed sample are analyzed with an ion microanalyzer (Hitachi, IMA-2A) under the following typical conditions: primary ions, $^{40}Ar^+$; primary ion energy, 10 keV; primary ion beam current, 2.0 μA; primary ion beam size, 180–250 μm. The secondary ion beam was detected from the whole area of a flat-bottomed crater which was obtained by focusing the primary ion beam above the sample surface. Intensities of negative secondary ions of mass/charge ratio 16 and 18 were recorded. To suppress the charge buildup on the sample surface, the electron beam was irradiated during measurement.

Results and Discussion

Figure 1 shows the concentration profiles of ^{18}O ions in the [001] and [110] directions of Mn-substituted sample diffusion-annealed at 800 and 900°C. Under the present annealing conditions, the ^{18}O penetration depth is too small (<1.0 μm) to quantify exactly. Thus, the profiles are plotted as a function of sputtering time in this figure. Although some scattering was found in these concentration profiles, it is not attributable to the fluctuation of the current density of the secondary ion beam.

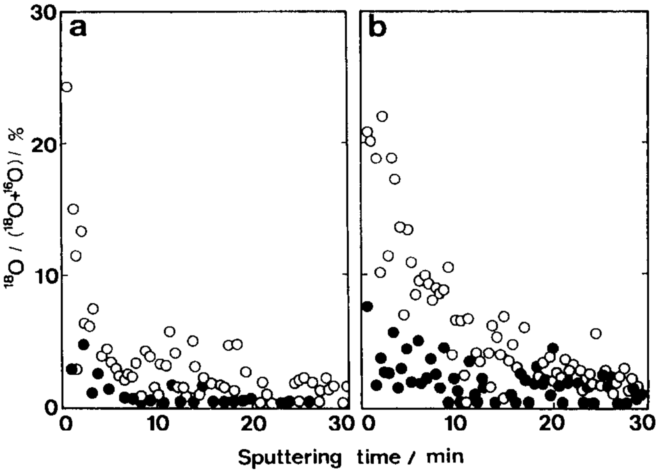

FIG. 1. Concentration profiles of ^{18}O in Mn-substituted barium hexaaluminate in [001] (●) and [110] (○) directions. Diffusion annealing at (a) 800°C, (b) 900°C.

It is apparent that ^{18}O penetration along [110] was more significant than along [001]. The extent of penetration in both directions increased with an increase in annealing temperature. The surface concentration of ^{18}O was smaller than the concentration in the gas phase. This means that the ^{18}O transfer from gas phase to hexaaluminate single crystal was controlled not only by bulk diffusion but also by an isotopic exchange reaction at each surface. The (110) surface shows a catalytic activity for the isotopic exchange reaction higher than that of the (001) surface. When the surface exchange reaction is assumed to be of first order, the roughly estimated diffusion constant along [110] is an order of magnitude larger than that along [001].

The SIMS result indicates the anisotropic oxygen diffusion in the hexaaluminate. From simple analogy with the Na^+ conduction in β-alumina compounds, the relation between the anisotropic oxygen diffusion and the pseudolayer structure of hexaaluminates can be theorized as follows. Manganese-substituted hexaaluminate, in which Mn species play a key role in catalytic oxidation due to the reduction–oxidation cycle (Mn^{2+}–Mn^{3+}) in the lattice (*6*), is considered to have a pseudolayer structure similar to that of β-alumina type $Ba_{0.75}Al_{11}O_{17.25}$ (*12–14*). As shown in Fig. 2, the crystal structure of β-alumina consists of alternative stacking of spinel blocks and the intermediate monolayer along [001]. Since the ionic arrangement in spinel blocks is the close-packing of O^{2-} ions, oxygen diffusion is expected to be isotropic. In fact, aniso-

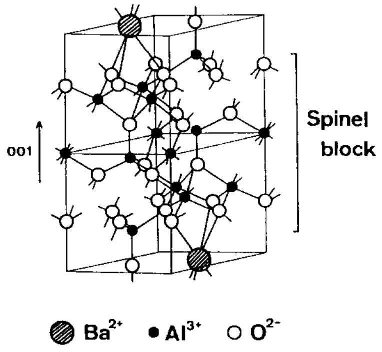

FIG. 2. Crystal structure of ideal β-alumina.

tropic O^{2-} diffusion was not reported for these spinel oxides, such as $MgAl_2O_4$. On the other hand, Ba^{2+} and O^{2-} ions are loosely packed in the monolayer. Several researchers reported that there are some intermediate sites available for O^{2-} ions to occupy (*1*). The monolayer playing the role of a preferential diffusion route for oxygen ions is consistent with the anisotropic diffusion observed in the hexaaluminate structure.

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