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Eu–O Bonding and Spectroscopy of Eu(III) in β''-Alumina

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The trivalent β''-aluminas are the only crystalline solids yet reported in which trivalent cations are significantly mobile at moderate temperatures (≈400°C). The investigations described in this paper examined the factors that influence the Eu(III) ion distribution, bonding, and spectroscopy in a range of Na(I)–Eu(III) β''-alumina compositions. The low-temperature ion-exchange synthesis used to prepare these materials leads to unusual Eu(III)–O bonding in the structure. The trivalent ions are relatively free to move in β''-alumina at moderate temperatures because there appears to be no site in the conduction layers at which the trivalent ion–oxygen bonding is particularly strong. The site occupations and the optical properties of the Eu(III) ions in β''-alumina have been shown to be sensitive to the thermal history of the samples.

I. Introduction

In recent years, it has been found that the sodium ions in the fast ion conductor, β''-alumina (typically, $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$), can be replaced by a wide variety of multivalent ions through a process of ion exchange (*1*). Crystals of this material containing trivalent cations are a new family of solid electrolytes, principally interesting for their optical properties (*2*). A good example is Nd(III) β''-alumina, which lases efficiently in both pulsed and cw modes (*3*).

The structure of the β''-alumina framework (space group $R\bar{3}m$) is shown in Fig. 1 (*4*). Close-packed layers containing aluminum, magnesium, and oxygen ions separate more spacious conduction layers within which the mobile ions reside. The conduction layers contain widely spaced oxygen ions ("column oxygens"), which link the close-packed blocks to form a three-dimensional ionic framework. This framework is virtually unchanged by ion exchange, although it does undergo some distortion as different ions occupy the conduction layers.

There are two well-defined crystallographic sites for the mobile ions in the conduction layers. In Na(I) β''-alumina, the Na(I) ions primarily occupy the four-coordinate, Beevers–Ross-type (BR) site, which has C_{3v} symmetry (*5*). In Eu(III) β''-alumina, the Eu(III) ions predominantly occupy the eight-coordinate midoxygen (mO) sites (C_{2h} symmetry) (*6*). In some isomorphs, cations also are found between the mO and BR sites in intermediate $18h$ ($R\bar{3}m$ notation) sites of symmetry C_s (*7*).

The investigations described in this paper examined the factors which influence the Eu(III) ion distribution, bonding, and spectroscopy in a range of Na(I)–Eu(III) β''-alu-

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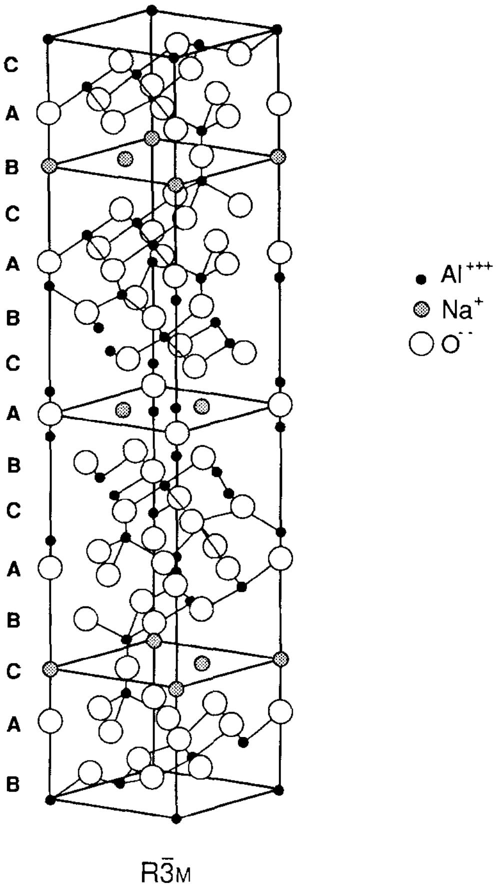

FIG. 1. The structure Na(I) β″-alumina.

mina compositions. Of particular interest was the effect of thermal history and Eu(III) concentration on the structural and optical properties of the material. The results reveal that the low-temperature ion-exchange synthesis used to prepare these materials leads to unusual Eu(III)–O bonding in the structure.

II. Experimental

Na(I) β″-alumina single crystals, the starting materials for the preparation of Na(I)–Eu(III) β″-alumina, were grown by the flux evaporation method (*8*). The crystals, typically 4 × 4 × 0.5 mm in size, were cut and polished by conventional methods. To monitor the extent of exchange, a ^{22}Na tracer was introduced into the samples by ion exchange in labeled $NaNO_3$ at 340°C. After annealing at 500°C for 24 hr to ensure homogenous tracer distribution, the samples were sealed with $EuCl_3$ (Cerac, 99.9%) in quartz ampoules under 200 Torr of dry oxygen.

Careful control of the conditions of ion exchange is quite important for obtaining good-quality samples. The principal challenge in the synthesis is to prevent the formation of Eu(II) ions, which diffuse into β″-alumina much faster than Eu(III). It appears that oxygen must be present during the reaction to maintain the Eu(III) oxidation state (*9*). In addition, trial-and-error revealed that pure Eu(III) samples were produced only when $EuCl_3$ was used as the exchanging salt. With other salts (e.g., $EuBr_3$), significant amounts of EU(II) were incorporated into the samples, even in the presence of oxygen. Chlorine gas would seem a logical alternative to oxygen, but when the reactions were run under chlorine gas, the crystals degraded severely. The reaction conditions used here, 650°C for about 24 hr, yielded clear, colorless crystals with >95% of the Na(I) replaced by Eu(III). Samples with lower concentrations of Eu(III) were prepared by exchanging at lower temperatures (typically 500°C) for shorter periods of time (e.g., 1–6 hr).

Fluorescence and excitation spectra from the samples were collected on a Perkin–Elmer MPF-66 spectrophotometer. This instrument has a maximum resolution of about 0.5 nm (20 cm^{-1} at 500 nm). An Oxford Instruments DN-1704 liquid nitrogen cryostat was used, which limited the effective range of the spectrophotometer to about 220–850 nm.

III. Results

Two distinct types of fluorescence spectra were identified for Eu(III) ions in >98%

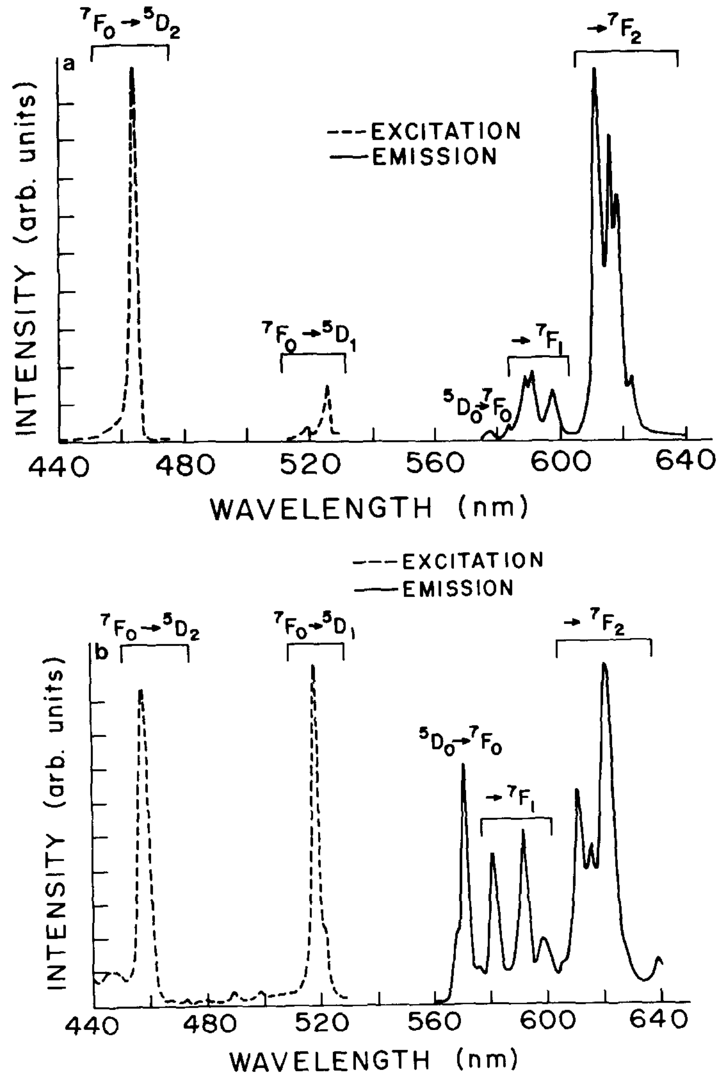

FIG. 2. Excitation and emission spectra of Eu(III) in 98% exchanged Eu(III) β''-alumina: (a) from Eu(III) ions in mO sites and (b) from Eu(III) ions in BR sites.

exchanged Eu(III) β''-alumina at 77 K. These are shown in Fig. 2, along with the associated excitation spectra. The emission peaks are due to transitions from the $^5D_0$ excited state down to the ground state ^7F_J multiplet. For simplicity, only the $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_2$ transitions are shown. The number of emission peaks in Figs. 2a and b indicates that several quite similar sites contribute to each of these spectra. Preliminary site-selective laser spectroscopy experiments at 10 K have verified that at least three distinct but very similar Eu(III) sites contribute to Fig. 2a and at least two sites contribute to Fig. 2b.

The fluorescence spectrum in Fig. 2a (I_{ex} = 464 nm) is characterized by a low intensity for the J-forbidden $^5D_0 \rightarrow {}^7F_0$ transition, indicating that it results from Eu(III) ions sitting in sites which have (or are very close to having) inversion symmetry. In the conduction layer of β''-alumina, the only site which has inversion symmetry is the mO site (C_{2h}). The $^5D_0 \rightarrow {}^7F_0$ transition in the emission spectrum in Fig. 2b (I_{ex} = 518 nm) is much more intense relative to the other transitions in the spectrum, indicating that it is derived from Eu(III) ions in sites lacking inversion symmetry. In fact, a single crystal X-ray diffraction study of the ion arrangement in Eu(III) β''-alumina has shown that Eu(III) ions occupy the BR and mO sites, but not the intermediate $C_s(18h)$ sites (*6*). Therefore, the Eu(III) ions lacking inversion symmetry are presumably those in BR sites. Naturally, it would be somewhat risky to assign the spectra based on symmetry considerations alone, in view of the unusual and complex structure of β''-alumina. Therefore, our assignments were made in a manner consistent with the X-ray diffraction results mentioned above and the effects of thermal history described in the following discussion.

Excitation and emission spectra of other compositions of Na(I)–Eu(III) β''-alumina are shown in Figs. 3 and 4. At all Eu(III) concentrations, two types of spectra are identified, corresponding to mO-type and BR-type sites. The splitting and relative intensities of the spectra vary somewhat with concentration, but the general features are quite similar to the spectra of the 97% exchanged sample. The presence of Na(I) ions in the samples appears to induce subtle changes in the crystal field that the Eu(III) ions experience, but does not greatly change the site occupations of the Eu(III) ions in the structure. The thermal history of the samples, however, does significantly affect the Eu(III) site occupations.

In order to examine the relative occupations of the mO and BR sites in Eu(III) β''-alumina, the excitation spectra for emission at 612 nm were collected. The excitation spectra of emission at this wavelength contain contributions from both the mO and the BR sites (see Figs. 2–4). The relative intensities of the excitation peaks due to mO-type and BR-type sites are thus qualitative measures of the relative occupations of the two types of sites. The $^7F_0 \rightarrow {}^5D_1$ excitation peaks for fluorescence at 612 nm of a 94% exchanged sample of Eu(III) β''-alumina after various thermal treatments are shown in Fig. 5. The peak at 518 nm corresponds to excitation of BR-type sites, while the peak at 525 nm is due to Eu(III) ions in mO-type sites.

In a sample that has been cooled quickly from 600°C, the intensity of the BR peak is relatively high, indicating that a significant percentage of the Eu(III) ions occupy BR sites. When the sample is subsequently annealed at 325°C, the intensity of the BR site peak decreases while the intensity of the mO site peak increases. The kinetics of the relaxation process are slow. As Fig. 5 shows, the system does not reach a steady state until it has been annealed for 4 days. The effects of quenching and annealing on the spectra are reversible, so long as no degradation of the samples occurs during the annealing and quenching process.

IV. Discussion

In this investigation, we have used optical spectroscopy, a probe of the energy level structure of an ion's valence shell, to study the site occupations and bonding of Eu(III) ions in β''-alumina and to gain a greater understanding of the reasons for the unusually rapid diffusion rate of trivalent cations in this structure. We also examined the role of thermal history in determining the Eu(III) site occupations, and thus the optical properties, of Eu(III) β''-alumina. The first topic addressed in this discussion concerns the nature of the Eu(III)–O bonds in β''-alumina.

When the bonds between the Eu(III) ions and its surrounding ligands are partially covalent, the excited states of the valence

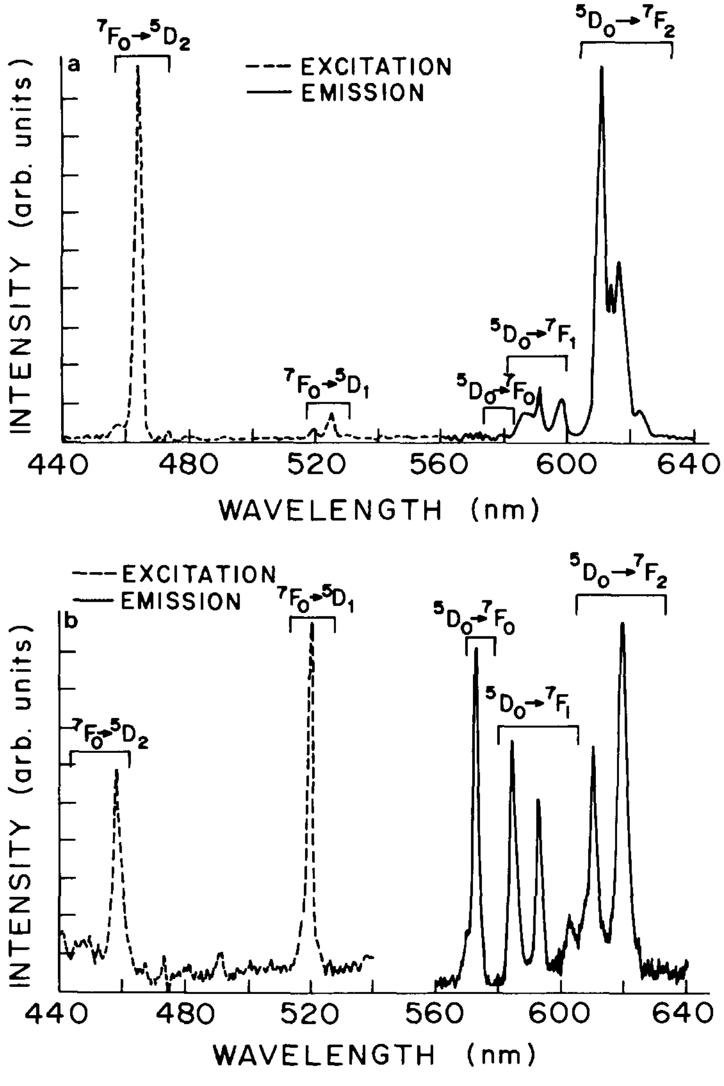

FIG. 3. Excitation and emission spectra of Eu(III) in 30% exchanged Na(I)–Eu(III) β''-alumina: (a) from Eu(III) ions in mO sites and (b) from Eu(III) ions in BR sites.

electrons are shifted to lower energies (*10*). The center of gravity of the excited states of Eu(III) can thus be taken as a measure of the strength of the bonding between Eu(III) and its surroundings. In analyzing the covalency of Eu(III)–ligand bonds, it is customary to look at the nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition, because neither of these energy levels is split in any crystal field, thus removing any uncertainty in the determination of the center of gravity of the excited state. Caro *et al.* (*11*) have reviewed the effect of covalency on the energy of the $^5D_0 \rightarrow {}^7F_0$ transition for Eu(III). For a wide variety of oxides and oxyhalides, the transition falls between 17,200 and 17,300 cm^{-1} (578.0–581.4 nm). Caro *et al.* report that the value for Eu_2O_3 is about 17,220 cm^{-1} (*11*).

From our spectra, the values of the $^5D_0$

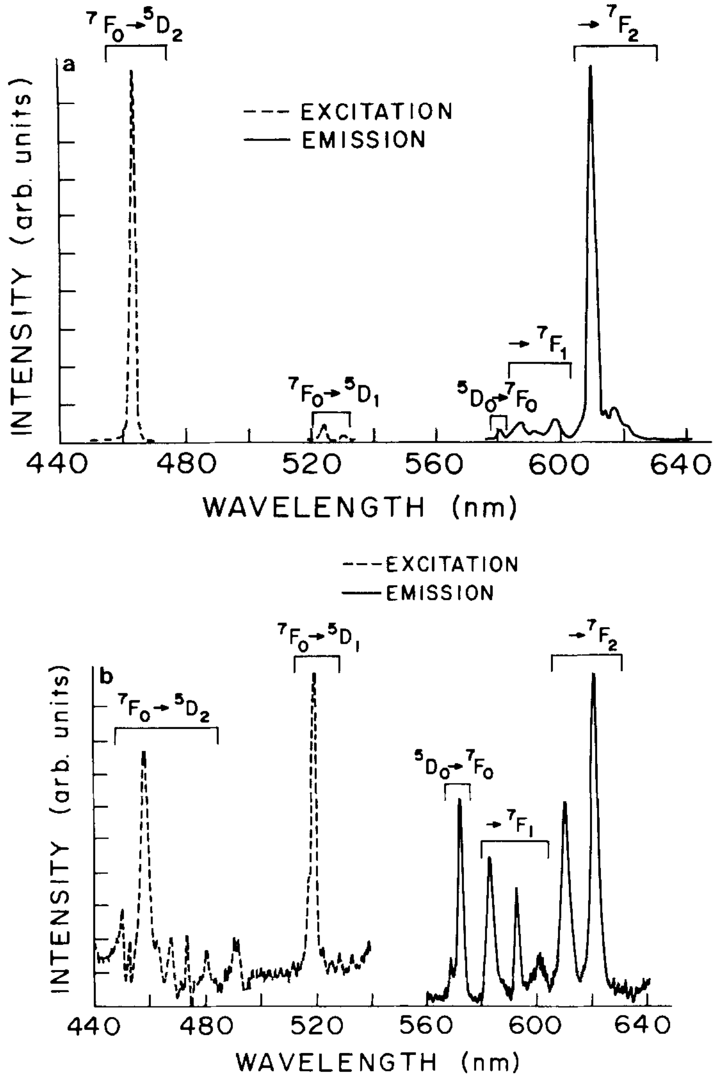

FIG. 4. Excitation and emission spectra of Eu(III) in 60% exchanged Na(I)–Eu(III) β''-alumina: (a) from Eu(III) ions in mO sites and (b) from Eu(III) ions in BR sites.

$\rightarrow {}^7F_0$ transition for Eu(III) ions in mO-type sites in β''-alumina are about 576–579 nm (17,271–17,361 cm^{-1}). These values are similar to some of the highest values reported by Caro *et al.*, indicating that the degree of covalency of the Eu(III)–O bonds of Eu(III) ions in mO sites in β''-alumina is small compared to that of Eu(III) ions in other oxide structures. The position of the $^5D_0$ level for Eu(III) ions in BR sites ($\approx$570–572 nm) indicates that the bonding between these ions and the surrounding oxygens is even less covalent than that in mO sites. The values of the $^5D_0$ position for Eu(III) ions in BR sites are some of the highest values ever reported. This indicates that, while the amount of Eu–O covalency (electron donation) at the mO site is very small

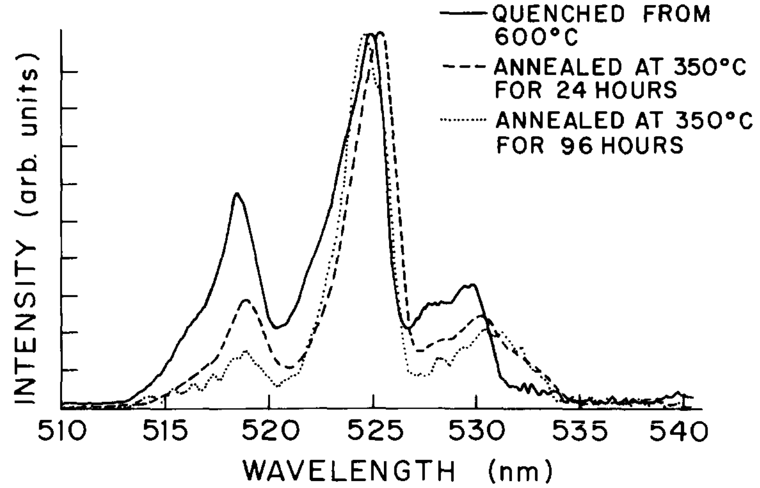

FIG. 5. The effect of thermal history on the $^7F_0 \rightarrow {}^5D_1$ excitation spectrum of 94% exchanged Na(I)–Eu(III) β''-alumina, $\lambda = 612$ nm.

compared with most oxide host lattices, it is still much larger than that at the BR site. It is reasonable to infer that the greater covalency at the mO site should cause the Eu(III) ions to favor this site over the BR site. This is borne out by single crystal X-ray structure analysis (*6*), which shows more than 90% of the Eu(III) ions occupying mO sites. The existence of different "types" of mO and BR sites is probably due to next-nearest neighbor effects, i.e., a variety of arrangements of the mobile ions in the conduction planes surrounding the fluorescent Eu(III) ions.

As described earlier, the mO and BR sites are quite different. The mO site is eight-coordinate, the most common coordination of Eu(III) in oxides. The BR site is essentially four-coordinate, with three in-layer oxygens at a much greater distance from the site. Table I gives the Eu–O distances at each site in fully exchanged Eu(III) β''-alumina, as derived from the single crystal X-ray structure refinement of Cabrillo-Cabrerra *et al.* (*6*). These bond distances are unusually long compared to those of the Eu(III)–O bonds in other oxides, indicating that the Eu(III)–O bonds in β'-alumina are very weak.

Since the lengths of the Eu(III)–O bonds in β''-alumina are known, it is interesting to attempt to estimate the strength and their degree of covalency. Brown and Shannon (*12*) and Brown and Wu (*13*) have developed an empirical method for calculating cation–oxygen bond strengths (hereafter referred to as "bond valences") from measured bond lengths. Their method involves the use of empirical parameters refined from the bond lengths of a large number of

TABLE I

EU(III)–O BOND DISTANCES IN EU(III) β-ALUMINA

Type of site	Oxygen position	Degeneracy	Bond distance (Å)
mO	O(5)	2	2.322(3)
	O(4)	4	2.751(1)
	O(3)	2	2.772(1)
BR	O(4)	3	2.490(6)
	O(3)	1	2.561(8)
	O(5)	3	2.851(2)

oxide structures containing a given cation. The parameters were refined so that the sum of the bond valences around the cations is equal (or close to) the ion's formal valence, as proposed by Pauling's "valence rule" (*14*). Their method is particularly useful for structures in which the coordination of the cation is irregular, as in β″-alumina.

The authors report that the valence of each cation–oxygen bond can be individually calculated using the simple expression

$$s = (R/R_1)^{-N_1},$$

where s is the bond valence (or bond strength), R is the measured cation–oxygen distance, R_1 is an empirically determined cation–oxygen distance parameter, and N_1 is an empirical parameter which varies between 4 and 7 for most ions in the periodic table. The concept of empirically determined bond valence can be seen as an extension of Pauling's "electrostatic bond strength" (*14*) to partially covalent bonds.

In β″-alumina, the fluorescence spectra clearly indicate that the Eu ions are exclusively Eu(III). The valence sums around the Eu ions would thus be expected to be close to 3.0 valence units (v.u.). However, the sums of the bond valences of the Eu(III)–O bonds for Eu(III) ions in mO and BR sites in Eu(III) β″-alumina based on the values of R_1 and N_1 given by Brown and Wu (*14*) are approximately 2.0 v.u. (mO) and 1.6 v.u. (BR), considerably below the value of 3.0 expected for Eu(III) ions in typical ionic structures.

Brown and Wu (*13*) have noted that abnormally small bond valence sums can be found when the size of an ion site is determined by other bonds in the crystal, e.g., K(I) in $K_2PbCu(NO_2)_6$. It is possible that the same effect causes the low Eu(III)–O bond valence sums in Eu(III) β″-alumina. In β″-alumina, since the framework structure is primarily determined by the Al–O and Mg–O bonds in the spinel blocks, the size of the mobile ion sites is, to a first approximation, fixed. Certainly, the column oxygens [O(5)] can distort somewhat toward the mO site in Eu(III) β″-alumina (*6*), because they are not as tightly bound as oxygens in the spinel block, but the spinel block oxygens [O(3) and O(4)] that coordinate the mobile ions are largely restrained from distortion by the spinel block structure. The structure is thus unable to relax fully around the Eu(III) ions, making the Eu(III)–O bonds extremely weak. It should be noted that the O(3) and O(4) positions reported by Carrillo-Cabrerra *et al.* (*6*) may not reflect small, undetected local distortions of some of these ions toward the Eu(III) ions, because the majority of the spinel block oxygens are not coordinated by a Eu(III) ion in this nonstoichiometric material. This may cause the actual Eu(III)–O distances to be slightly smaller than reported.

The bond valences discussed above can also be used to estimate the degree of covalency of the bonds. Brown and Shannon (*12*) have provided an empirical fit of covalency, as calculated from the Pauling (*15*) electronegativity difference between the terminal atoms, versus the mean bond valence of a large number of cation–oxygen bonds. Following their method, the two bonds between the Eu(III) ions and the column oxygen in the mO sites are approximately 33% covalent, while the six Eu(III)–spinel block oxygen bonds in these sites are about 17% covalent. In the BR site, the four Eu(III)–spinel block oxygen bonds are about 30% covalent and the three Eu(III)–column oxygen bonds are 15% covalent. While there is some uncertainty in the Eu(III)–O bond distances used in these calculations, the bond valence sums and covalency percentages calculated here are consistent with the idea that the Eu(III)–O bonds in Eu(III) β″-alumina are among the weakest (and least covalent) ever reported, as experimentally indicated by the $^5D_0 \rightarrow$

$^7F_0$ transition energies in the Eu(III) spectra.

The reasons for the extreme ionicity of the compound can be traced to the unique method used to synthesize Na(I)–Eu(III) β''-alumina. The β''-alumina single crystals which are the starting materials for the syntheses are grown at a very high temperature (≈1700°C), with monovalent Na ions populating the conduction layers. Under these conditions, the oxide ions adopt a layered structure in which the column oxygens are rather far from each other, and there are large open spaces in the conduction layers. When Eu(III) is introduced into β''-alumina, three monovalent Na ions are replaced by each trivalent Eu ion. β''-alumina is unusual in that the relatively low temperature of the ion-exchange reaction does not allow the oxygen framework to rearrange to any great extent, so the metastable, relatively open β''-alumina structure is maintained even in the presence of the Eu(III) ions. Eu(III) β''-alumina is quite certainly not the thermodynamically favored phase at moderate temperatures, but nevertheless is kinetically stable at and below the temperature of the ion-exchange reaction.

This unusual situation requires that in Na(I)–Eu(III) β''-alumina, the trivalent Eu ions are forced into monovalent ion sites. The oxide ions which make up the first coordination shell of Eu(III) are essentially pinned by the framework structure, forcing the Eu(III)–O bonds to be longer than they are in a typical, fully relaxed oxide structure containing Eu(III). The length of the Eu(III)–O bonds makes them extremely ionic, because a large degree of electron sharing is not favored over the relatively long Eu(III)–O distances. When Eu(III) ions occupy four-coordinate BR sites, the effect is even more dramatic, as indicated by the shifting of the $^5D_0$ level to still higher energies and the reduction of the calculated bond valence sum.

Our results also show that the thermal history of a Eu(III) β''-alumina sample has a strong influence on its spectroscopy and structure. The spectroscopy data show that at low temperatures Eu(III) ions do not favor the BR site and only occupy it at high temperatures, when a disordered distribution of Eu(III) ions in the conduction layers is favored from configurational entropy considerations. If the material is cooled quickly, Eu(III) ions are trapped in the BR sites. These trapped ions relax back into mO sites when the sample is annealed at 350°C. Davies *et al.* (*16*) and Queenan and Davies (*17*) have shown that ordered and disordered structures of the mobile ions can be formed in the trivalent β''-aluminas and that the microstructures of the materials are extremely dependent upon thermal history. It appears from our results that the Eu(III) site occupations are also affected by thermal history. We have reported similar effects in the Na(I)–Eu(II) β''-alumina system (*18, 19*).

V. Conclusions

The trivalent β''-aluminas are the only materials yet reported in which trivalent cations are significantly mobile at moderate temperatures (≈400°C) (*1*). This remarkable property is intimately linked to the observations made here that the Eu(III)–O bonds in Eu(III) β''-alumina are among the least covalent reported. The trivalent ions are relatively free to move in β''-alumina at moderate temperatures because there is no site in the conduction layers at which the trivalent ion–oxygen bonding is particularly strong. In these circumstances, configurational entropy considerations favor a disordered configuration of trivalent ions at moderately elevated temperatures.

The origins of this unusual situation can be found in the unique method used to synthesize the trivalent β''-aluminas. The framework structure of β''-alumina is formed at about 1700°C, while the ion-exchange reactions occur at only about 650°C. At the temperature of the ion-exchange reaction, the framework is unable to relax completely when trivalent ions are introduced into the conduction layers. The Eu(III)–O bonds in β″-alumina are thus rather long, and therefore weak and extremely ionic. This unusual coordination and bonding produces Eu(III) fluorescence spectra with $^5D_0$ energy levels that are among the highest ever reported. The site occupations, and thus the optical properties, of the Eu(III) ions in β″-alumina are also sensitive to the thermal history of the samples.

Acknowledgments

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