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Synthesis of Di- and Trivalent β''-Aluminas by Ion Exchange

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Many of the mono-, di-, and trivalent cations in the periodic chart diffuse rapidly in the β''-alumina structure. β''-Aluminas containing multivalent cations can be synthesized by ion exchange reactions starting with the sodium form of the compound. These facile reactions make it possible to prepare a wide variety of β''-alumina compositions, many of which are metastable and inaccessible by normal synthetic means. This paper describes the methods used to synthesize multivalent β''-aluminas and the preparation of a number of specific transition metal and lanthanide forms of these compounds. © 1986 Academic Press, Inc.

1. Introduction

Most high-conductivity solid electrolytes conduct only a single ion. For example, Li(I) diffuses rapidly in Li_3N, and Ag(I) in $RbAg_4I_5$. In contrast, the β- and β''-alumina structures conduct many different cations. Early investigations of ion transport in sodium β- and sodium β''-alumina demonstrated that the entire sodium content of each can be exchanged with a variety of monovalent cations, including Li(I), K(I), Ag(I), Tl(I), and Cu(I), as well as with various protonic species (*1*, *2*). It is also possible to replace the sodium content of β-alumina (*1*) with divalent cations, although the resulting divalent β-aluminas are poor ionic conductors (*3*). In contrast, divalent cations diffuse quite rapidly in β''-alumina (*3*, *4*).

Recently it was shown that trivalent cations also diffuse rapidly in β''-alumina (*5*). β''-Aluminas containing transition metals [Cr(III)], a Group V element [Bi(III)], and lanthanides [Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), etc.] have been produced from sodium β''-alumina by ion exchange. The lanthanide β''-aluminas are particularly interesting because of their potential applications in solid-state lasers and optoelectronic devices.

Multivalent cations diffuse rapidly in β''-alumina because of its unusual structure. Details of the structure of β''-alumina and its isomorphs have been discussed extensively elsewhere (*6*, *7*). Briefly, β''-alumina is a layer structure composed of so-called

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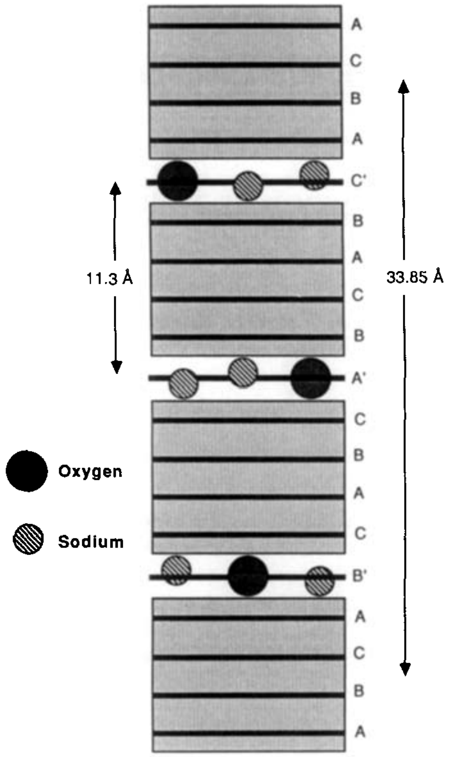

FIG. 1. A schematic representation of the structure of sodium β''-alumina. The Al–O spinel-type blocks are represented by the shaded rectangles. They are separated by the conduction planes which contain the bridging O(5) species and the mobile cations.

"spinel blocks" made up of Al, O, and Mg in a close-packed spinel structure, stacked and held together by Al–O–Al groups (see Fig. 1). The oxygens in the bonds that link successive spinel blocks are called bridging or column oxygens and are generally denoted as O(5). The bridging oxygens define relatively open regions within which the mobile ions can diffuse in two directions. Ionic diffusion is rapid within these quasi-two-dimensional regions, but many orders of magnitude slower between them.

The rapid diffusion of many different cations in the β''-alumina structure makes it possible to prepare a range of compositions and structures that are inaccessible by direct synthetic reactions. These materials demonstrate the power of ion exchange as a synthetic approach for preparing unusual solid-state materials. Relatively few materials support the rapid ionic diffusion essential for such ion exchange reactions; but, for those materials that do, ion exchange is a synthetic technique of subtlety and elegance.

Previous papers have described the conductivity (*3*), spectroscopy (*5, 8*), structure (*9*), and laser characteristics (*8*) of various trivalent β''-aluminas. This paper presents the first detailed discussion of the methods used to synthesize them. It presents new results of attempts to prepare various β''-alumina compositions containing transition metal cations and describes the factors that influence their chemical stability.

2. Experimental Procedure

2.1. Crystal Preparation

Multivalent β''-aluminas were prepared by the ion exchange of single crystals of sodium β''-alumina. Sodium β''-alumina crystals, typically $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$, were grown by a flux evaporation method in which a mixture of Na_2CO_3, MgO, and Al_2O_3 was heated in a Pt crucible in air at 1700–1710°C for 14–21 days (*2*). Specimens were generally about 3 × 3 × 0.2mm, and each weighed approximately 7 mg.

The sodium contents of selected crystals from each growth were determined by measuring the weight change upon ion exchange of Ag^+ for Na^+. This exchange reaction occurs rapidly when sodium β''-alumina crystals are immersed in molten $AgNO_3$ at 250°C. These measurements indicated that the compositions of individual crystals selected for this work vary over a small range. In the general formula, $Na_{1+x}Mg_xAl_{11-x}O_{17}$, values of x ranged from 0.61 to 0.70. Alden *et al.* (*10*) have directly analyzed the sodium content of sodium β''-

alumina crystals from similar growths and found x to vary over a slightly wider range, 0.59 to 0.72.

2.2. Determining the Extent of Ion Exchange

The ion exchange reactions of β''-alumina are described by

$$Na_{1.67}Mg_{0.67}Al_{10.33}O_{17} + (1.67/n)M^{n+} \rightarrow M_{1.67/n}Mg_{0.67}Al_{10.33}O_{17} + 1.67Na^{+} \quad (1)$$

Three methods have been used to monitor the progress of ion exchange in β''-alumina crystals and to determine its extent. Each has particular advantages and complications. They are compared and contrasted in the following discussion.

2.2.1. Weight change. Measuring the change in weight that results from the ion exchange process is an experimental technique that has been frequently used to determine the extent of ion exchange in samples of β- and β''-alumina. For example, if the entire Na^+ content of a crystal of sodium β''-alumina ($Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$) is replaced by Pb^{2+}, its weight should increase by 22.2%.

For weight change to accurately measure the extent of ion exchange, several conditions must be met. The identities and oxidation states of the ions entering and leaving the sample must be known. Samples must be large enough that the weight difference can be measured accurately, and no extraneous weight loss from crystal degradation can occur during the exchange process. Since ion exchange is typically carried out in molten salts, any salt that adheres to a crystal must be completely removed after exchange. This is generally accomplished by washing in an appropriate solvent.

Weight change is, in fact, a reliable indicator of the extent of ion exchange for a few reactions. One is the replacement of Na^+ with Ag^+ in β- and β''-alumina. Weight change measurements are not reliable, however, when the oxidation state of the ion entering the crystal is not well defined, when ion exchange produces only a small weight change, when samples are damaged during exchange, or when it is difficult to remove residual salt after exchange. These conditions are often encountered with reactions involving protonic species or multivalent cations, in particular, transition metal ions. Simple weight change measurements can then be misleading and grossly inaccurate.

2.2.2. Radiochemical analysis. An alternative approach for monitoring ion exchange involves labeling the mobile ion content of the starting crystals with a radioisotope, such as labeling sodium β''-alumina crystals with ^{22}Na(I). The extent of sodium replacement can then be determined by measuring the radioactivity of the samples (*11*). This technique is free of many of the problems associated with weight change measurements. It can be quite reliable and convenient, particularly when the ion initially in the sample is Na(I), because ^{22}Na-doped salts are widely available, and the isotope has a reasonable long half-life. It also is possible to label other ions diffusing out of or into the crystals. Unfortunately, convenient isotopes are not available for many elements, so the radiochemical technique has principally been used with ^{22}Na(I).

2.2.3. X-ray mapping. A new method that monitors ion exchange by mapping the X-ray absorption of a sample before and after exchange has recently been described (*12*). It is based on a simple principle. If the X-ray absorption coefficient of the ion entering the crystal is sufficiently different from that of the ion leaving, as is generally true, the change in X-ray absorption is a direct measure of the distribution of mobile ions and their concentrations. This method has proven to be more versatile and reliable than either weight change or radiochemical measurements.

The technique is quite straightforward: a beam of Mo$K\alpha$ radiation with an elliptical spot size of approximately 50 × 100 μm is directed at the large face of a β''-alumina crystal (typically 3 × 3 × 0.5 mm). The X-ray absorption of the sample is then measured, point by point, by translating the sample in steps. The crystal is first scanned before any ion exchange has occurred, and then again after ion exchange. If the ions entering and leaving the crystal are known, the change in the X-ray absorption values can be converted to a map of ion concentration. The technique works because ion diffusion in the β-aluminas proceeds from the edges of the samples, and the X-ray beam is perpendicular to the planes of fast diffusion.

The X-ray mapping technique is a simple, nondestructive, and reliable method for measuring the distribution of mobile ions in the β-aluminas and related materials. Unlike radiochemical analysis, X-ray mapping can be used to study the diffusion of many different ions in these materials. It can be very reliable when weight change measurements are not, one example being when the oxidation state of the ion entering the crystal is not known. This situation frequently occurs with exchange reactions involving transition metal and lanthanide ions.

2.3. Experimental Conditions for Ion Exchange Reactions: Molten Salt and Vapor Phase Exchange

The ion exchange reactions of β- and β''-alumina crystals have generally been carried out by immersing crystals in molten salts or in the vapors generated by solid or molten salts. Molten salt exchanges have been most successful with salts that melt at relatively low temperatures, typically less than 500°C. These include the halides and nitrates of many monovalent and divalent cations. Salts of trivalent cations and of many divalent cations, particularly the transition metal cations, generally have much higher melting points, 600°C and above. At these temperatures, molten salts generally etch β''-alumina crystals and cause them to crack apart. It is possible to avoid these problems by carrying out exchanges in mixed salts that melt at lower temperatures, such as $NdBr_3$ dissolved in molten NaBr. But, mixed salts never yield complete ion exchange.

The chemical attack that occurs with crystals in high-melting salts can frequently be avoided by carrying out ion exchange in the vapor generated by the salts. In this technique, a crystal is either suspended above the ion exchange salt if the salt is molten or buried in the salt if it is solid. The exchange reaction proceeds by vapor phase transport of the species entering and leaving the sample, and the process produces crystals of high optical and mechanical quality.

In vapor phase exchanges, some salts sinter and soften, particularly around the edges of the crystals. As the exchange proceeds, it appears that a local region of mixed salt composition with a depressed melting point forms near the crystal edges. The mixed salt often coats the edges of the crystal and retards the rate of ion exchange, which can be accelerated by cleaning the crystal.

All of these reactions can be conveniently carried out in quartz tubes or in high purity α-alumina crucibles. Frequently it is necessary to evaculate and seal the tubes to exclude moisture and oxygen. A reactive gas atmosphere is sometimes necessary to maintain the desired oxidation state of the ion entering the samples. A good example is that of the exchange of sodium β''-alumina in $EuCl_3$. This reaction must be carried out in an atmosphere of Cl_2 to maintain Eu in the +3 oxidation state.

2.4. Kinetics of Ion Exchange Reactions

Ion exchange from molten salts is generally rapid. For example, in one experiment

TABLE I

ION EXCHANGE REACTIONS OF β''-ALUMINA WITH DIVALENT CATIONS[a]

Ion	Melt Composition	Temperature	Time	% Exchange	Note	Reference
Ca(II)	$CaCl_2$	770	23 hr	100	*b*	*3*
Sr(II)	$Sr(NO_3)_2$/ $SrCl_2$[47 : 53]	550	20 hr	100		*3*
Ba(II)	$Ba(NO_3)_2$/ $BaCl_2$[62 : 38]	550	20 hr	100		*3*
Zn(II)	$ZnCl_2$	500	24 hr	100	*b*	*3*
Cd(II)	$CdCl_2$	600	20 hr	100		*3*
Pb(II)	$PbCl_2$	525	20 hr	100	*h*	
Mn(II)	$MnCl_2$	600	5 days	100	*f,h*	
Eu(II)	EuI_2	500	5 days	99.8	*c,f,h*	
Ni(II)	NiI_2	600	6 days	32	*c*	
Co(II)	$CoBr_2$	500-550	18 days	100	*d,f,h*	
Sn(II)	$SnCl_2$	400	1 min	10	*e*	

[a] Starting materials were small (typically 2 × 2 × 0.2 mm) single crystals of sodium β''-alumina.

[b] Starting material was silver β''-alumina.

[c] Vapor phase exchange.

[d] Reaction involved two exchange, wash, anneal steps.

[e] Rapid exchange occurred, but crystal severely cracked.

[f] Exchanged under vacuum.

[g] Exchanged under chlorine.

[h] Oxidation state of ion in crystal depends on thermal history.

over 50% of the sodium in a β''-alumina crystal (2.6 × 2.8 × 0.60 mm) was exchanged by Cd^{2+} when the crystal was immersed in molten $CdCl_2$ at 600°C for 1 min.

Exchange reactions are slower when vapor phase transport is involved and when trivalent cations are diffusing. For example, a sodium β''-alumina crystal (2 × 2 × 0.5 mm) that was buried in solid $NdBr_3$ underwent about 90% sodium replacement within 24 hr at 650°C. A second 24-hr exchange in fresh salt produced 99+% exchange.

3. Results of Specific Exchange Reactions

3.1. Divalent Cations

Initial reports (*3*) of the high divalent cation conductivity of β''-alumina described the preparation of single crystals of Ca(II), Ba(II), Sr(II), Cd(II), Zn(II), and Pb(II) β''-alumina. This list now includes Sn(II), Mn(II), Eu(II), Ni(II), Co(II), Cu(II), and Hg(II) (see Table I). Of these, it has not yet been possible to prepare completely exchanged forms of Hg(II) and Cu(II) β''-alumina.

3.2. Trivalent Cations

Trivalent β''-aluminas that have been prepared include the Gd(III), Nd(III), Eu(III), Yb(III), Sm(III), Tb(III), Dy(III), Er(III), Pr(III), Bi(III), and Cr(III) forms. Nearly 100% ion exchange in samples with good optical and mechanical quality has been achieved with most of these ions. The conditions for exchange are summarized in Table II.

3.3. Complications Encountered in the Ion Exchange Reactions

It would be misleading to suggest that all of the exchange reactions proceed without

TABLE II

Ion Exchange Reactions of β''-Alumina with Trivalent Cations[a]

Ion	Melt Composition	Temperature	Time	% Exchange	Note	Reference
Gd(III)	$GdCl_3$	615	5 hr	100		*5*
Nd(III)	$NdBr_3$	720	0.5 hr	95		
Eu(III)	$EuCl_3$	600	5 days	92	*c,d*	
Yb(III)	$YbCl_3$	740	24 hr	90		*5*
Sm(III)	$SmCl_3$	700	20 hr	90		*5*
Tb(III)	$TbCl_3$	740	48 hr	90		*5*
Bi(III)	$BiCl_3$	270	12 hr	70		*3*
Cr(III)	$CrCl_3$	530–550	14 days	75	*b,c*	
Er(III)	$ErCl_3$	600	8 days	96	*d*	

[a] Starting materials were small (typically 2 × 2 × 0.2 mm) single crystals of sodium β''-alumina. Exchanges were carried out under vacuum unless otherwise noted.

[b] Reaction required two exchange, wash, anneal steps.

[c] Exchanged under chlorine.

[d] Oxidation state of ion in crystal depends on thermal history.

complication. Some reactions are straightforward, but many others are more complex and more interesting for what they suggest about the chemistry of β''-alumina. Patterns of behavior have emerged which indicate that the exchange process is strongly influenced by the number and nature of the oxidation states of the exchanging ion.

In general, ion exchange is simplest for those species that have a single-cation state for which the reduction reaction to the parent metal has a large free energy. These include the alkali metal cations, as well as Ca(II), Ba(II), Sr(II), Cd(II), Gd(III), Nd(III), Yb(III), Tb(III), Dy(III), and Pr(III). Preparing these forms of β''-alumina is generally quite straightforward. The most common complication is encountered with ions that have higher melting salts, especially the trivalent lanthanides. The higher exchange temperatures required with these salts accelerate direct chemical attack of the samples, which mechanically and physically degrades them. Fortunately, vapor phase exchange at temperatures no higher than about 650°C generally avoids these problems.

The most frustrating and intriguing complications arise when the entering ion has several cation oxidation states and/or a single oxidation state with a relatively low free energy of reduction to the metal. We have observed that the oxidation state of such an ion can change as it enters the β''-alumina structure and that, in some cases, it can be reversibly cycled between two or more oxidation states after it is in the structure. For example, when Eu(III) β''-alumina is heated in vacuum at 400–600°C, the Eu(III) is reduced to Eu(II) (*15*). It can then be reoxidized to Eu(III) by heating in oxygen. A crystal of Pb(II) β''-alumina turns purple when heated in vacuum and bleaches when subsequently heated in oxygen. Similar reactions have been observed with Er(III), even though this ion has only one common cationic state. Exchanges involving Cu(I), Mn(II), Ni(II), Co(II), Cu(II), Sm(III), Er(III), and Cr(III) are also complicated by reactions of this sort. For all of these ions, the conditions of exchange are extremely important, in particular, the atmosphere surrounding the crystal as it is being exchanged or annealed at elevated temperature.

The cationic reductions observed when crystals of Eu(III) and Pb(II) β''-alumina are heated require that an oxidation reaction proceed simultaneously. All of the reactions can be rationalized by suggesting that oxygen ions from the β''-alumina structure can be lost from the structure and reincorporated into it. Carrillo-Cabrera *et al.* have already speculated that such a reaction might occur in these materials (*15*). The proposed reactions are summarized in Eqs. (2) and (3) using Kroger-Vink notation. The O(5) or column oxygens that exist within the conduction plane are likely candidates for the predominant mobile oxide species. The two electrons left behind for each oxygen lost can be trapped, either in a defect in the structure, such as an O(5) vacancy (Eq. (2)), or by the mobile cations in the conduction plane (Eq. (3)).

$$2\mathrm{O_O} = \mathrm{O_2} + 2\mathrm{V_O}^{\cdot\,\cdot} + 4e \qquad (2)$$

$$2\mathrm{O_O} + 2M_M = \mathrm{O_2} + 2\mathrm{V_O}^{\cdot\,\cdot} + 2M_M'' \qquad (3)$$

We have not definitively shown that these reactions occur. But, qualitative evidence suggests that they do. We are currently studying whether oxygen loss does actually take place under certain conditions and, if it does, how it can be controlled.

3.4. Specific Ion Exchange Reactions

The following ion exchange reactions illustrate the complexity of preparing various multivalent β''-aluminas. Simple reactions that proceed without difficulty have been summarized in Tables I and II.

3.4.1. Cu(I) and Cu(II) exchanges. Attempts to prepare pure Cu(I) and Cu(II) β''-alumina have had mixed success. Many of the complications that can occur during ion exchange in these materials combine to frustrate attempts to prepare pure samples either composition. To start, the thermal instability of CuCl and $\mathrm{CuCl_2}$, which are the logical salts to use for ion exchange, restricts the range of temperature than can be used for exchange. CuCl melts above about 430°C; $\mathrm{CuCl_2}$ decomposes into CuCl and chlorine above about 425°C. Also, it appears that the more stable copper state at elevated temperatures in β''-alumina is Cu(II). As a result, Cu(I) may disproportionate into Cu and Cu(II) in the β''-alumina structure.

For example, in one experiment, a 3.5 × 3 × 0.3 mm crystal of sodium β''-alumina was sealed in the side arm of a quartz reaction tube. A mixture of CuCl and Cu was placed in the main tube which was then evacuated, sealed, and heated to 500°C for 12 hr. The crystal was then tipped into the melt, and the temperature maintained at 500°C for 2 weeks. After the crystal was cooled and cleaned, radiochemical analysis showed that 35% of its initial sodium content had been replaced. Weight change measurements, however, indicated that the effective oxidation state of the copper in the crystal was two. Its color was a metallic reddish-orange.

An examination of the crystal with an optical microscopy showed that it was not homogeneous. The metallic appearance was caused by small copper-colored islands in the crystal. Their size and shape varied, but they were thin and about 20 μm in diameter. Analysis of the crystal in cross section indicated that the islands were about 8600 Å thick.

Similar results were observed in a number of other experiments. The data are by no means consistent. However, it does appear that Cu(I) exchanges into β''-alumina and then disproportionates to form Cu and Cu(II). Perhaps oxygen loss with the coupled reduction of Cu(I) and Cu(II) also occurs, in reactions similar to those observed with Eu(III) and Pb(II). It is clear that the copper β''-aluminas are fascinating and complex systems for studying the chemical reactions fundamental to understanding the preparation and stability of the multivalent forms of this material. We are currently approaching the synthesis of the copper β''-aluminas using milder routes and hope to report success in our efforts shortly.

3.4.2. Pb(II) exchange. The replacement of Na(I) in β''-alumina by Pb(II) proceeds rapidly and completely in molten $PbCl_2$ at 550°C, when carried out in air. The Pb(II) exchange reactions have been studied using X-ray mapping, radiochemical analysis, and weight change measurements. Pb(II) β''-alumina samples are clear and colorless and contain the right amount of Pb(II) expected based on the simple exchange of two Na(I) for one Pb(II).

However, when the exchange is carried out in vacuum at 100°C or higher the resulting crystals are purple. Colorless samples that have been exchanged to greater than about 90% Na(I) replacement also turn purple when heated in vacuum at >500°C. When the purple crystals are heated in air, they quickly bleach. As with the example of Eu(III) β''-alumina previously discussed, the coloration of Pb(II) β''-alumina crystals during heating in vacuum is consistent with a model in which oxygen ions can be lost from the structure and leave behind electron pairs that are trapped either in lattice defects or on Pb(II) species. These processes are currently being studied in detail in this laboratory.

3.4.3. Cr(III) exchange. Substantial replacement of sodium in β''-alumina by Cr(III) has been achieved by burying samples in anhydrous $CrCl_3$ (Cerac, 99.99%) and heating them to 550°C under a chlorine atmosphere. Under these conditions 14 days of exchange produced 62% exchange in one experiment and 75% exchange in another. After annealing in air at 550°C, the resulting crystals were green and were somewhat degraded physically. The insertion of the small Cr(III) ion (radius = 0.53 Å) into Na(I) β''-alumina must produce a major contraction in the *c*-lattice parameter, which increases the risk of cracking, delamination, and conduction plane collapse. At this time it is clear that Cr(III) exchange into β''-alumina is possible, but the process and its consequences are not well understood.

3.4.4. Eu(III) exchange. Eu(III) β''-alumina forms readily by ion exchange in $EuCl_3$ powder (Cerac, 99.9%, nom. mp = 850°C) under chlorine. Substantial exchange was observed over a wide range of temperatures, from 300 to 650°C. The crystals appeared clear and colorless with no obvious evidence of mechanical degradation. They fluoresced bright red under broadband UV illumination, and absorption spectroscopy measurements showed that at least 95% of the Eu was in the +3 state.

However, when crystals of Eu(III) β''-alumina were heated to 400–600°C under vacuum, the Eu(III) content was slowly reduced to Eu(II), beginning at the edges of the crystals and proceeding inward. The change in oxidation state was revealed by a change in fluorescence from the red of Eu(III) to the green color of Eu(II). The fluorescence of the crystals could be restored to red by reheating in oxygen, although this does not demonstrate that the process is truly reversible. The reduction is accompanied by considerable microscopic degradation, and spectroscopic measurements have shown that reoxidation does not truly restore a sample to its original state.

3.4.5. Co(II) exchange. The exchange of Co(II) for Na(I) is straightforward. Samples buried in $CoBr_2$ (Cerac, 99.9%, nom. mp = 678°C) and heated to 500–550°C *in vacuo* underwent essentially 100% exchange after 18 days. The exchanged crystals were deep blue and in good mechanical condition.

3.4.6. Mn(II) exchange. Mn(II) exchange occurs readily when crystals of sodium β''-alumina are buried in $MnCl_2$ (Cerac, 99.5%, nom. mp = 650°C) at 500–625°C under vacuum. Virtually complete ion exchange was observed at after 5 days at 600°C or 4 days at 625°C. In general, crystals in which essentially all of the Na(I) had been replaced are colorless or pale pink, if annealed in air at 600–620°C, but turn black if annealed in vacuum at the same temperature. This observation is additional evidence that oxygen ions may be able to move out of the β''-alumina structure, leaving behind trapped electrons or reduced transition metal ions.

3.4.7. Er(III) exchange. β''-Alumina crystals in which essentially all Na(I) has been replaced by Er(III) can be formed by exchanging crystals in $ErCl_3$ (Cerac, 99.9%, nom. mp = 774°C) powder for 6–8 days at 550–600°C. If annealed at 550–650°C in air, the crystals appear cloudy and pink. If annealed at the same temperature but in vacuum, they turn black. They can be restored to their original cloudy pink by subsequent heating in air. These reactions resemble those of the Pb(II) and Mn(II) β''-alumina samples previously described.

3.5. *Re-exchange of Trivalent Cations*

In general, trivalent cations readily replace one another in the trivalent β''-aluminas, and it also is possible to re-exchange the trivalent cations with sodium ions. The relative rates of the re-exchange reactions suggest that the c-lattice parameter strongly influences the rate of ion migration.

Trivalent cations easily replace each other in the structure at rates similar to those at which sodium is replaced by a trivalent cation. For example, we have observed that Tb^{3+} and Eu^{3+} almost completely replace Nd^{3+} within 24 hr at 700°C. However, the rate at which a trivalent cation is replaced by sodium ions is much slower than that of the reverse reaction. A sample of Nd^{3+} β''-alumina, about $2 \times 2 \times 0.2$ mm in size, immersed in molten NaBr at 760°C for 5 days underwent 80% replacement of the Nd(III) by Na(I). In contrast, a comparable crystal of sodium β''-alumina in molten $NdBr_3$ at 684°C underwent 97% exchange of Nd(III) for Na(I) in 24 hr.

These differences may be related to changes in the c-lattice parameter of the structure. The trivalent lanthanide cations ($r = 0.85$–1.01 Å) are about the same size as Na(I) ($r = 0.95$ Å). But, because of their much larger tripositive charge, the c-lattice parameter decreases when tripositive cations replace sodium in the structure. For example, the c-lattice parameter of Na(I) β''-alumina is 33.54 Å, while that of Gd(III) β''-alumina is 33.13 Å (*10*). The exchange of one trivalent cation for another produces an insignificant change in the c-lattice parameter. The replacement of a trivalent cation by Na(I) results in an expansion of the crystal, initially around the edges. We have observed that crystals appear to crack and cleave much more during the re-exchange process than during the initial exchange. Apparently, expansion which starts at the edges degrades the crystal much more than compression.

4. Conclusions

The experiments summarized in this paper illustrate some of the varied solid-state chemical reactions that proceed in the β''-alumina structure and influence its ion exchange chemistry. They also suggest general patterns of behavior for the multivalent forms of this material. For example: (1) the larger the change in c-lattice parameter upon ion exchange, the greater the likelihood of crystal fracture, delamination, and degradation; (2) ion exchange reactions are simplest when they involve species that have single oxidation states that are not easily reduced to the parent metal form; (3) exchange of ions with multiple oxidation states or ions that are easily reduced to the metallic form can produce mixed oxidation states in β''-alumina crystals. This situation occurs frequently with transition metal cations and also with a number of main group and lanthanide elements.

The mechanism by which multivalent cations can change oxidation state within the β''-alumina structure is not well understood. Considerable evidence suggests that it may involve a relatively facile loss of structural oxygens, a process that is not likely to be reversible.

All of these results point out that the simplicity of the ion exchange process is deceptive. It is easy to demonstrate that an ion exchange reaction has replaced some or all of the sodium in β''-alumina by another species, but much more difficult to find out what that species is, how it is distributed in the crystal, and whether the crystal has sustained damage as a result of the reaction. The risk in all of these experiments is that sophisticated and difficult measurements may be carried out on poorly characterized materials. The preparation of high-quality crystals of β''-aluminas containing transition metals therefore requires considerable care and control of the conditions of exchange. In any investigation of the properties of a multivalent β''-alumina crystal, it is essential that careful attention be paid to its preparation and characterization before other studies begin.

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References

1. J. T. Kummer, *Prog. Solid State Chem.* **7**, 153 (1972).
2. J. L. Briant and G. C. Farrington, *J. Solid State Chem. 33*, 385 (1980).
3. G. C. Farrington and B. Dunn, *Solid State Ionics* **7**, 267 (1982).
4. B. Dunn and G. C. Farrington, *Mat. Res. Bull.* **15**, 1773 (1980).
5. G. C. Farrington, B. Dunn, and J. O. Thomas, *Appl. Phys. A* **32**, 159 (1983).
6. C. R. Peters, M. Bettman, J. W. Moore, and M. D. Glick, *Acta Crystallogr. Sect. B* **27**, 1826 (1971).
7. K. G. Frase, J. O. Thomas, and G. C. Farrington, *Solid State Ionics* **9/10**, 307 (1983).
8. M. Jansen, A. Alfrey, O. M. Staffsud, B. Dunn, D. Yang, and G. C. Farrington, *Optics Lett.* **9**, 119 (1984).
9. W. Carrillo-Cabrera, J. O. Thomas, and G. C. Farrington, *Solid State Ionics* **9/10**, 245 (1983).
10. M. Alden, Thesis, University of Uppsala, Uppsala, Sweden, 1985.
11. K. G. Frase and G. C. Farrington, *Annu. Rev. Mat. Sci.* **14**, 279 (1984).
12. J. Tegenfeldt, M. Underwood, and G. C. Farrington, *Solid State Ionics,* in press.
13. G. C. Farrington and J. L. Briant, *Science* **204**, 1371 (1979).
14. J. L. Briant and G. C. Farrington, *J. Electrochem. Soc.* **128**, 1830 (1981).
15. W. Carrillo-Cabrera, J. O. Thomas, and G. C. Farrington, *Solid State Ionics,* in press.