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Comparison of the Thermal Stability of β- and β″-Alumina at High Pressures

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The high-pressure thermal stability of Na^+ β-alumina and magnesium-stabilized Na^+ β″-alumina was studied from 5 to 50 Kb and from room temperature to 1400°C. Above 5 Kb and 560°C, Na^+ β-alumina decomposes into α-Al_2O_3 and $NaAlO_2$. Magnesium-stabilized Na^+ β″-alumina decomposes at slightly higher temperatures to α-Al_2O_3, $MgAl_2O_4$, and probably $NaAlO_2$. Estimates of activation volume and enthalpy support a model for decomposition that depends on cation vacancies and proceeds by sodium diffusion in quasi-liquid conduction planes.

Introduction

This investigation had its origin in an unsuccessful attempt to hot-press β-alumina in a high pressure "belt" apparatus. The decomposition of β-alumina under these conditions led us to pursue in greater detail the high pressure thermal stability of this unusual ionic conductor. The results of this study are pertinent to: (1) the as yet uncertain thermodynamic stability of both β-alumina (2-block) and β″-alumina (3-block) at one atmosphere; (2) the effect of ionic substitution on the stability of these structures; (3) the possible breakdown of these materials by high local pressures related to high local electric fields; and (4) the possible use of β-alumina as a membrane in a Na pump for producing pressure.

Background and Previous Work

The high ionic conductivity of β-alumina and related materials was described in 1967 by Yao and Kummer (*1*). The magnitude of the sodium ion conductivity at 300°C has made possible the application of this material as a solid electrolyte in a Na–S battery and created great interest in its properties at all levels of understanding. At the application level one of the practical problems lies in producing a dense, strong, ceramic membrane that is stable in charge–discharge cycling. In an attempt to produce high density β-alumina we tried hot pressing at high pressures in the "belt" type apparatus (*2*) and were somewhat surprised by the low temperature of decomposition above 10 Kb. This unpublished work later led us to compare β-alumina and Mg-stabilized β″-alumina under the same conditions. Hereafter these phases will be termed β and β″ for brevity.

The only other high pressure work on these specific materials is the measurement of conductivity in Li-, K-, and Na-β as a function of hydrostatic pressure to about 4 Kb (*3*), and the measurement of compressibility of Na-β parallel to the *C*-axis to about 1 Kb (*4*). However, the work of Goto on the effect of pressure on the $\gamma \rightarrow \alpha$ Fe_2O_3 transformation (*5*), and the studies of Marezio on Li spinels (*6*), are also pertinent and will be referred to later in the text.

β and β″ are phases in the Na_2O–Al_2O_3 system. The former is characterized by a hexagonal unit cell consisting of two spinel-type blocks separated by loosely packed planes of sodium and oxygen (Fig. 1). β″ is

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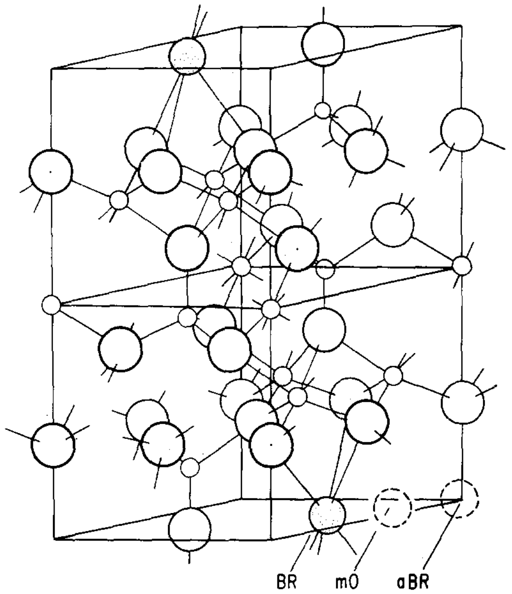

FIG. 1. Atomic arrangement in spinal block and adjacent conduction plane of β-alumina. Large circles are oxygen atoms, small circles are aluminum. For simplicity sodium is shown only in the BR site with mO and aBR sites unoccupied. The conduction plane is puckered in β″-alumina.

rhombohedral and the corresponding hexagonal cell has three spinel blocks. The β″ phase in the binary system decomposes into β above 1580°C (*7*, *8*). The decomposition is not reversible and the equilibrium relation between these phases is still uncertain. Attempts to make single phase β″ have been unsuccessful and the product seems to be a mixture of β and β″; however, ternary compositions with the β″ structure can be grown as single crystals (*8–10*) and appear stable at low temperatures. Mg-stabilized β″ is stable at one atmosphere to >1800°C (*7*, *8*) and was used in the present study. The structure of the ternary compound and the precise location of the Mg^{2+} have been defined in recent publications (*10*, *11*).

Experimental

The source of β was −150 mesh powder prepared by crushing and ball milling Monofrax β-beta alumina (Carborundum Co.). Debye–Sherrer photographs confirmed that the material was nearly pure β.

Mg-stabilized β″ was made from the decomposition and reaction of sulfates. The composition was $Na_2O_{0.787}MgO_{6.16}Al_2O_3$ (8.6 w/o of Na_2O, 4.4 w/o of MgO, 87.0 w/o of Al_2O_3). This mixture was prefired at 1000°C to decompose the sulfates and then reacted at 1400°C. Some experiments were made with crystals grown by isothermal evaporation of Na_2O from a melt of Na_2O–MgO–Al_2O_3 as in the method of Weber and Venero (*8*).

The high pressure cell used in these experiments is shown in Fig. 2. The β and β″ powders were run both individually and simultaneously in the same cell. The latter mode gives a comparison that is free of the inconsistencies of pressure and temperature associated with comparing separate experiments. The powder was tamped into Pt tubes (made from 0.0005-in. Pt foil) which were inserted into BN sleeves, 0.080 in id and 0.200 in. long. The BN sleeve was inserted in a carbon tube heater and encapsulation of the sample was completed with BN plugs. The assembly was then introduced into a standard pyrophyllite high pressure cell and mounted in a 100-ton belt apparatus (*2*). The β-aluminas

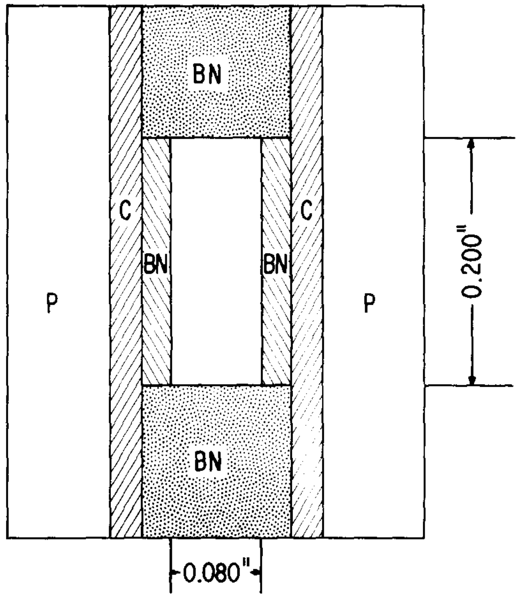

FIG. 2. Cell configuration used in the belt apparatus. C is carbon, P pyrophyllite.

were completely sealed in Pt and never came into contact with the BN or with each other when run simultaneously. Samples were heated by passing a current through the carbon heater, and the temperature was obtained from a calibration of temperature versus input watts.

The β and β'' powders were pressed at temperatures ranging from room temperature to 1400°C and pressures from about 5 to 50 Kb. The low pressure values are close to the limit obtainable with the equipment and are known only approximately. Most samples were maintained at temperature and pressure for 30 min, then quenched to room temperature while still under pressure. Experiments were carried out for as long as 9 hr, but a systematic evaluation of time as a variable was not undertaken.

After the samples were removed from the press, the platinum was stripped off and the product examined with the petrographic microscope and X-ray diffraction. The specimens were found to be completely sealed in the platinum envelope, and there was no evidence for reaction with platinum or loss of sodium. In an open system sodium loss is a definite problem at high temperatures; in this case the belt apparatus is an ideal closed system for studying reactions in the Na_2O-Al_2O_3 system.

Results

The principal finding of the study was that at pressures above 5 Kb, β decomposed into α-Al_2O_3 (corundum), and $NaAlO_2$ (sodium aluminate) at temperatures above about 560°C, and Mg-stabilized β'' decomposed at about 625°C into α-Al_2O_3, $MgAl_2O_4$, and $NaAlO_2$. The Al_2O_3, $NaAlO_2$, and $MgAl_2O_4$ were well crystallized and gave sharp diffraction lines. The results of a series of experiments to map out the pressure–temperature stability region of the two phases are summarized in Fig. 3.

Complete decomposition was obtained in 30 min at 50 Kb of pressure and temperatures of 600, 900, and 1400°C. At lower pressures the reaction was incomplete and some β or β'' remained in the product. The presence of any α-Al_2O_3 was taken to mean that the decomposition region had been reached. The extent of the reaction was estimated from the intensities of the Debye–Sherrer photographs. An isobaric series of experiments at 20 Kb showed that β was approximately 50% decomposed in 30 min at 600 and 900°C, and about 80% decomposed at 1400°C. Similarly, a series of experiments at 600°C showed that the fraction which had decomposed in 30 min increased with pressure from about 25% at 9 Kb, to 50% at 20 Kb, and to 100% at 50 Kb.

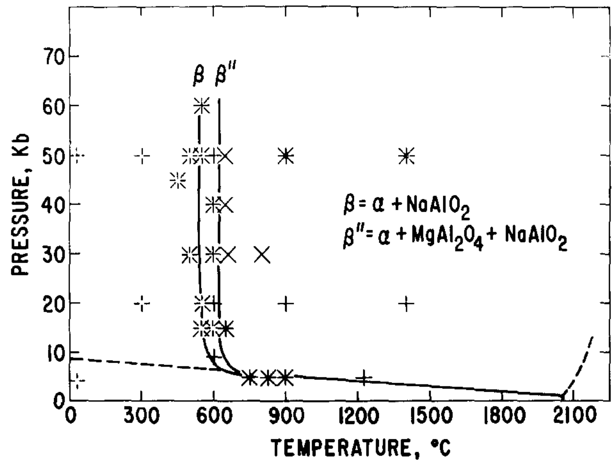

FIG. 3. P–T reaction diagram for β-alumina and magnesium-stabilized β''-alumina. (+) β-alumina, (×) magnesium-stabilized β''-alumina. α-Al_2O_3 was not found in the reactions product of specimens marked with dashes.

The application of high pressure to β at 300°C and room temperature did not result in decomposition in the sense that α-Al_2O_3 or $NaAlO_2$ could be definitely identified in the product. Experiments with β at 300°C and 50 Kb were repeated for 1 and 6.5 h with similar results, and β held at 45 Kb and 450°C for over 9 hr showing no decomposition to α-Al_2O_3. There were, however, indications that both β and β'' had undergone a change as a result of the high pressure. Grains in the pressure-modified product were partially fragmented, showed strain birefringence, and contained small crystallites of a high refractive index. The concentration of high-index particles was below the detection limit of the X-ray technique but appeared to be present in greater concentrations than in the original Monofrax-H powder, and are believed to be α-Al_2O_3. The lines in the Debye–Sherrer photographs of pressure-modified β were diffuse and at large angles the $\alpha_1\alpha_2$ components were no longer resolved. A larger sample was subjected to pressure to provide sufficient material for examination with an X-ray diffractometer. Expanded patterns obtained with the diffractometer confirmed the line broadening but gave no other evidence for structural change. Several attempts were made to restore the sharp diffraction pattern of β by annealing but the lines were still diffuse after heating to 380°C for several hours. Permanent deformation apparently took place in each form without extensive decomposition. If the microscopic evidence for high-index material (α-Al_2O_3?) and X-ray line broadening are interpreted as the initial stage of decomposition, the pressure-modified region should be merged with that of α and the dashed lines in Fig. 3 are the approximate temperatures at which the rate of decomposition was sufficient to produce a barely detectable product.

Discussion

Transformation under pressure forms more closely packed products that occupy a smaller total volume. Table I shows, with the exception of $NaAlO_2$, that this is also true for the individual decomposition products of β and β''.

TABLE I

MOLECULAR VOLUMES AND THEORETICAL DENSITIES AT ATMOSPHERIC PRESSURE AND ROOM TEMPERATURE

Compound	$V(10^{-24}\ cm^3)$	$D(g\ cm^{-3})$
β $Na_{1.22}Al_{11}O_{17.11}$	306.3	3.244
β'' $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$	306.6	3.278
α-Al_2O_3	42.6	3.980
$NaAlO_2$	49.6	2.744
$MgAl_2O_4$	66.1	3.573

In the following analysis, decomposition parameters estimated from the mean stress and volume change should be approximately valid since the latter is relatively insensitive to nonhydrostatic shearing components of the stress.

The range of pressure and temperature at which β and β'' decompose into α-Al_2O_3 and other products was arrived at by the following considerations. The high temperature points at 1 atm are taken from the phase diagram (*7*, *8*) which shows that β forms from the liquid at about 2000°C and atmosphere pressure, is easily synthesized from its component oxides at temperatures above 1650°C, and appears to be stable at higher temperatures up to the melting point (about 2000°C). The data of Weber and Venero (*8*) for Mg-stabilized β'' indicates only that it is stable to at least 1800°C. The point at room temperature is based on the observation that the resistivity of β is independent of pressure from atmospheric pressure to about 4 Kb (*3*)[1]. The temperature at which the latter experiment was performed is not explicitly stated but appears to have been room temperature.

The decomposition of β at high pressures can be discussed in terms of conventional transition state theory. (*13*) Decomposition is assumed to proceed via a transition state and a sequence of first order reactions.

$$\begin{aligned}&\beta \rightarrow \beta^{\#}\\ &\qquad \rightarrow Al_2O_3 + NaAlO_2\end{aligned}$$

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[1] Since this paper was written we have learned of the work of Ihto *et al.* (*12*) which shows resistivity as independent of pressure to about 30 Kb.

The state $\beta^{\#}$ is regarded as an ordinary molecular species, except that in one of the coordinates describing its configuration the potential energy with respect to a change of the coordinate is a maximum instead of a minimum. The transition state is metastable and the "reaction coordinate" is a vibration with no restoring force through which the reaction occurs. The transition state may be a quasi-liquid distribution of sodium ions in the two-dimensional Na–O planes between spinel blocks. Making the usual assumption that $B^{\#}$ is in equilibrium with β, the activation volume $\Delta V^{\#}$ and enthalpy $\Delta H^{\#}$ are obtained from the dependence on the pressure and temperature of the rate constant k.

$$[\delta \ln k/\delta P]_T = -\Delta V^{\#}/(RT).$$
$$[\delta \ln k/\delta(1/T)]_P = -\Delta H^{\#}/R.$$

Above 600°C and 10 Kb the rate of decomposition of β and β'' increases with pressure and temperature. Figure 4 displays the pressure dependence of k measured at 600°C, from which the calculated activation volume is

$$\Delta V^{\#} = -RT[\delta \ln k/\delta P]$$
$$= -3.96 \text{ cm}^3 \text{ mole}^{-1}$$

This result is somewhat exceptional since $\Delta V^{\#}$ for activated transport in solids usually is positive, corresponding to an exponential decrease in rate with increasing pressure (*14*). Negative activation volume implies formation of a transition state with a smaller volume, and the rate constant therefore increases with increasing pressure. It is interesting to note that at 4 Kb the activation volume for conductivity = 0 for $Na^+ - \beta$, <0 for $Li^+ - \beta$, and >0 for $K^+ - \beta$ (*3*). The distribution of Na^+ ions in the conduction plane at high pressure may be similar to Li^+ ions in $Li^+ - \beta$ at low pressure.

Figure 5 displays the temperature dependence of k measured at 20 Kb. The activation enthalpy is

$$\Delta H^{\#} = R[\delta \ln k/\delta 1/T]_P$$
$$= 4970 \text{ cal mole}^{-1}$$

This is a low activation energy for a solid-state reaction in which there is extensive rearrangement of ionic bonds.

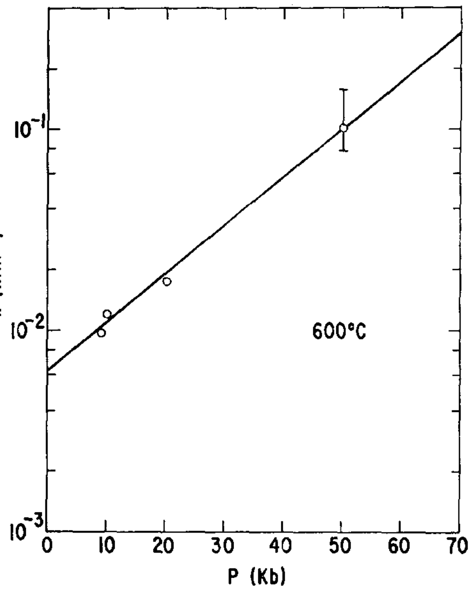

FIG. 4. Pressure dependence of $\alpha \rightarrow \beta$ decomposition at 600°C. No residual β was observed in the 50-Kb decomposition product, and the calculated rate constant assumes 95± 4% decomposition.

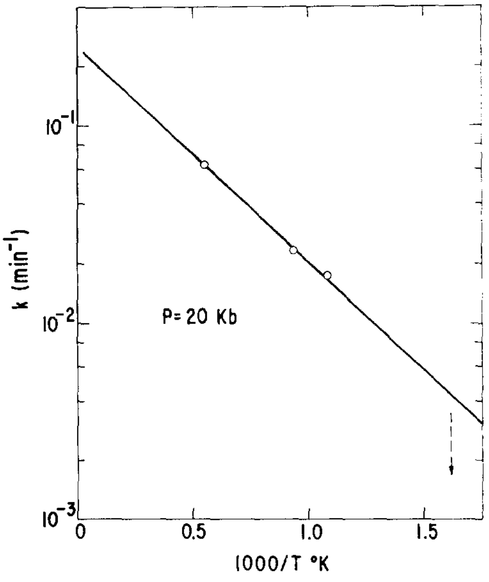

FIG. 5. Temperature dependence of $\beta \rightarrow \alpha$ decomposition at 20 Kb of pressure. α-Al_2O_3 was not detected in the 300°C decomposition product and the rate constant at this temperature is calculated for 10 and 5% decomposition.

We propose the following model for decomposition of β at high pressures: (a) β is metastable at pressures above 8 Kb; (b) Decomposition is nucleated in or near the conduction plane; (c) Reaction proceeds by sodium diffusion in the quasi-liquid conduction plane; (d) Reconstructive transformation of the spinel block is accomplished by the displacement of Al^{3+} ions from four- to six-fold sites.

To discuss the decomposition mechanism we must first consider the structural relationship of β to spinel. The oxygen atoms in spinel are closely packed and Al^{3+} and Mg^{2+} ions barely fill the octahedral and tetrahedral interstices. This nearly ideal packing results in an arrangement which is stable with respect to decomposition to MgO and Al_2O_3 up to 1000°C and 153 Kb (*15*). β is generated from spinel by replacing the Mg^{2+} with Al^{3+} ions and inserting Na–O planes every fifth closely packed layer. The Al^{3+} ions are small and highly charged, and this substitution results in large local strains about four-fold sites, reflected by anomalously short interatomic distances relative to those in spinel (*16*). Decomposition is probably nucleated at one of the strained sites, Al(2) which is near the middle of the spinel block, or Al(3) which is adjacent to the conduction plane (*16*, *17*). Al(3) is coordinated to three oxygen in the spinel block and one in the conduction plane. Nucleation of $NaAlO_2$ at this site would relieve strain and enable the reaction to proceed easily by diffusion of Na^+ ions in the liquid-like conduction plane.

From a crystal-chemical point of view, decomposition requires transfer of Al^{3+} ions from tetrahedrally coordinated sites in β to octahedrally coordinated sites in α-Al_2O_3. This is compatible with Marezio's mechanism for the P–T decomposition of inverse spinels of the type $Li_{0.5}M_{2.5}O_4$ ($M = Fe^{3+}$, Al^{3+}, Ga^{3+}) (*7*), each of which decomposes to M_2O_3 (corundum structure) plus $LiMO_2$ by transfer of trivalent ions from four- to six-fold sites in the products. The reaction also is similar to the transformation γ-Fe_2O_3 to α-Fe_2O_3 at high pressures. γ-Fe_2O_3 is a metastable defect spinel like γ-Al_2O_3;γ-Fe_2O_3 and the β-Al_2O_3 spinel block have many intrinsic vacancies as is evident from their composition, $Fe_{10.67}O_{16}$ and $Al_{11}O_{16}$. The structural transformation involves the movement of Fe^{3+} in four-fold coordination to six-fold sites in α-Fe_2O_3. Goto (*5*) found the transformation kinetics to depend on $P\Delta V$ and determined ΔH from specific heat data to be 5000 cal mole^{-1}. This is comparable to $\Delta H^{\#} =$ 4970 cal mole^{-1} obtained in this study for β decomposition at high pressures. This suggests that the decomposition of β-alumina and γ-Fe_2O_3 depends primarily on high vacancy concentration.

The average vacancy concentration does not give a complete representation of the structure because the vacancies in β-Al_2O_3 are concentrated in planes through which cations diffuse easily. It is interesting to discuss the properties of the $\beta^{\#}$ transition state by considering the conduction plane a quasi-liquid characterized by a melting point of T_m. The liquid-like nature of the conduction planes in β is well established by X-ray and neutron diffraction (*16–18*), and by nuclear magnetic resonance (*19*). Sodium statistically occupies three crystallographically independent sites in the conduction plane and exchanges position rapidly among these sites at temperatures above −163°C. The easy diffusion of Na^+ ions accounts for the exceptionally high conductivity of β, which is 1.4×10^{-2} $(\Omega\text{-cm})^{-1}$ at 25°C. A further refinement of the model would be to describe disorder in the conduction plane by order parameters and the change in state as a second order transition.

The decomposition of β to Al_2O_3 and $NaAlO_2$ results in a 12.3% decrease in the volume.

$$\begin{aligned} Na_{1.22}Al_{11}O_{17.11} &\rightarrow 4.89\ Al_2O_3 \\ &\quad + 1.22\ NaAlO_2. \\ \Delta V &= -306.3 + 4.89(42.6) + 1.22(49.6), \\ &= -37.7\ \text{Å}^3. \end{aligned}$$

This volume decrease is calculated from the data in Table I, neglecting corrections for thermal expansion and compressibility which are estimated to amount to but a few percent. The correction for nonstoichiometry is significant since β typically contains about 22% excess sodium (*17*). The molar volume of β is

184.4 cm^3 and the decomposition of 1 mole results in a 22.7 cm^3 decrease in volume.

The "heat of melting" of the quasi-liquid conduction plane estimated with the Clausius–Clapeyron equation for the data in Fig. 3 over the temperature range 600 to 2000°C, is

$$\Delta H_m = \Delta T_m \, \Delta V \, (\Delta P/\Delta T)$$
$$\Delta H_m \simeq 3050 \text{ cal mole}^{-1}$$

This is comparable to the activation energy for sodium diffusion in β, 3800 cal mole^{-1} (*20*).

The corresponding "entropy of melting" is

$$\Delta S_m = \Delta H_m/T$$
$$= 1.94 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

This appears to be a reasonable value for conduction plane disorder. The conduction plane can approximately be described as a random mixture of N Na atoms and Nx holes arranged in a lattice of $N(1 + x)$ points. By probability theory (*21*), the number of arrangements of atoms and holes is

$$W = \frac{N(1+x)!}{N!\,(Nx)!}$$

and

$$S \simeq Nk[(1+x)\ln(1+x) - \ln x]$$
$$= 1.88 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$\text{for } x = \tfrac{1}{2}.$$

There are three nonequivalent statistically occupied sites in the β conduction plane and an average of about $\frac{1}{2}$ vacant site per sodium is consistent with site occupation parameters measured at high temperatures by neutron diffraction (*17*).

Comparison with Mg-Stabilized β''

The composition of Mg-stabilized β'' is about $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ (*9*). At high pressures and above 600°C the principal decomposition products are α-Al_2O_3, $MgAl_2O_4$, and $NaAlO_2$. Only a few $NaAlO_2$ diffraction peaks were resolved and its identification is less definite than in the β decomposition product. Since spinel forms aluminum-rich phases which can be regarded as solid solutions of $MgAl_2O_4$ and γ-Al_2O_3, the lattice parameter was accurately determined to confirm that the composition was $MgAl_2O_4$. According to the following equation decomposition of Mg-stabilized β'' to Al_2O_3, $MgAl_2O_4$, and $NaAlO_2$ is accompanied by a 7.8% decrease in volume.

$$Na_{1.67}Mg_{0.67}Al_{10.33}O_{17} \rightarrow 3.67\ Al_2O_3 + 0.67\ MgAl_2O_4 + 1.67\ NaAlO_2.$$
$$\Delta V = -306.6 + 3.67(42.6) + 0.67(66.1) + 1.67\,(49.6).$$
$$= -23.76 \text{Å}^3.$$
$$= -14.3 \text{ cm}^3 \text{ mole}^{-1}.$$

Although $\Delta H^{\#}$ for Mg-stabilized β'' was not determined at pressures above 15 Kb, it decomposes at about 65°C higher than β in $\frac{1}{2}$-hr runs. The greater stability of β'' under pressure is probably due to a smaller volume decrease on decomposition and to reduced strain in the spinel block (*16*).

Decomposition by Electrical Stress

Extrapolation of the α-Al_2O_3 stability field to low temperatures indicates that β may be unstable with respect to decomposition into α-Al_2O_3 at pressures above 8 Kb. If $\Delta H^{\#}$ and $\Delta V^{\#}$ retain their high temperature values, approximately 10% of β should have decomposed in 30 min at 300°C and 11 Kb, or at 25°C and 32 Kb. Decomposition rates as large as this were not observed.

Since β is probably metastable at high pressures and low temperatures, it is interesting to question whether electrical stresses across imperfections or grain boundaries could generate sufficient pressure to initiate decomposition. Although β-alumina is extremely anisotropic, we estimate, with a formula derived for an isotropic medium, the magnitude of the pressure developed by electric stress in a dielectric

$$P = \frac{\varepsilon - 1}{8} E^2,$$

where P is the pressure in dynes cm^{-2}, E the electrical intensity in stat volts cm^{-1}, and ε the dielectric constant. For $P = 8$Kb, E is about 0.5×10^8 V cm^{-1}, which is comparable to the dielectric strength of good insulators. Note that β is extremely nonisotropic and in fact may produce local fields in excess of those estimated above for an isotropic dielectric.

Conclusions

β and β'' are unstable with respect to decomposition into α-Al_2O_3 at temperatures above 600°C and pressures above 10 Kb. Neither phase decomposed at high pressures and at temperatures below about 500°C. The phases appear metastable at pressures below 8 Kb, which raises questions regarding the long-term stability of these materials in high electric fields in electrochemical cells at elevated temperatures. Thermodynamically unstable systems may be useful if the barrier to transformation is large and the reactions are slow. This may not always be true for β and β'' if, as suggested by the present results, the reaction rate is determined by the high concentration of vacancies and by sodium diffusion, which is known to be rapid. A study of the decomposition of β and β'' in the 1–10 Kb range would be valuable in further defining the stability of these materials.

Acknowledgements

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