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STRUCTURE AND SURFACE PROPERTIES OF DUAL OXIDE

GELS IN THE SYSTEM BeO-Ir₂O₃

by

Charles Rex Adams

A THESIS

SUBMITTED TO THE FACULTY

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W.O. Melgen
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INTRODUCTION
The phenomenon of mutual protective action (1) in dual systems of hydrous oxides has been studied extensively at The Rice Institute. A variety of systems has been studied and in many of these systems each oxide prevents or retards the crystallization of the other. The degree of mutual protection varies from system to system and also depends upon the temperature level at which the dual gels have been heated. The system BeO-In₂O₃ was first studied in 1947 by Watt (2) by x-ray diffraction techniques. Marked mutual protection was observed in this system in two composition zones. Only the diffraction pattern of cubic In₂O₃ was observed for any sample containing In₂O₃, agreeing with the observations of Ensslin and Valentiner (3).

Extensive sorption-desorption studies have been made by the author (4) on the system BeO-In₂O₃, heat-treated for 2 hours at 500°. From these studies surface areas, specific adsorptive capacities, differential and integral heats of adsorption, and pore size distributions were obtained. Enhanced adsorptive capacities, surface areas, and differential and integral heats of adsorption were observed in the same composition zones which had previously shown protection against crystallization (2). Figure 1 shows a plot of surface area, as well as specific adsorptive capacity at two different pressures, as a function of composition. From these curves it is noted that there are two major regions of increased surface area and adsorptive capacity, at a region corresponding to 40-60% BeO and at a region corresponding
to 90% BeO. The enhanced surface area and adsorptive capacity has been explained on the basis of mutual protection against crystallization (5), utilizing the concept of adsorption of one oxide on the other in the solid state.

In Figure 2 are shown plots of the differential and integral heats of adsorption as a function of composition at various values of the relative pressure. Two maxima exist, one between 30% BeO and 60% BeO, the other between 80% BeO and 90% BeO. These are essentially the same composition ranges in which there is mutual protection against crystallization and an increase in surface area and adsorptive capacity. If these zones correspond to smaller crystal size, and it will be shown that this is the case, the increase in heat of adsorption may be explained on the basis of increase of heterogeneity of the surface, due to a larger predominance of cracks, crevices, sharp edges and the like for an assembly of smaller crystals.

The purpose of the present investigation is an attempt to elucidate the structure of these gels, especially in the zones of mutual protection.
ELECTRON MICROSCOPE STUDIES
EXPERIMENTAL

The dual hydrous oxide gels employed in these studies were the identical samples used in the previous adsorption studies (4). Briefly, measured amounts of ammonium hydroxide were added rapidly to solutions of indium nitrate and beryllium nitrate and the resulting gels were washed free of nitrate ion. These gels, after drying in air, were then heated at 500° for a period of 2 hours. Dilute suspensions of the samples dispersed in hydrochloric acid at a pH value of 6.0 were allowed to dry on thin collodion films mounted on metal grids. Most of the photographs were taken on Process Ortho film with an exposure time of 4 seconds or less, using 100 kv electrons, and a calibrated magnification of about 16,000 diameters. Optical enlargements of 13 diameters were made from the center portion of the negative, where the rotational distortion was less than 2 per cent. Statistical counts and measurements were made directly on the positive prints, approximately 700-1000 pores or particles being counted for each sample.
RESULTS

In Figures 3-13 are shown electron micrographs (200,000 diameters) of the gels in the system BeO-In₂O₃, heat-treated at 500° for two hour periods. The gels consist of small, spheroidal particles packed in a random, non-close-packing manner. Occasional cubic pseudomorphs were found in the gel formed from heating the pure indium hydroxide, known to crystallize in the cubic system (6), but no pseudomorphs were found in the heat-treated products of the other gels which are essentially amorphous to X-rays (2). The absence of many mono-disperse particles indicates strong cohesion between the secondary particles. The strength of the aggregates is shown by the fact that the degree of dispersion of the secondary particles varies but little upon suspension in water and subsequent evaporation to dryness, as shown below by a comparison of pore sizes measured in the electron microscope with those measured by adsorption methods.

In Figure 14 are plotted the area distributions of the secondary particles found in this system, assuming the particles to be smooth spheres. The most frequent particle radii for pure BeO and pure In₂O₃ were 60 Å and 84 Å respectively. The most frequent particle radii for the dual gel series are a linear function of composition within the precision of the data. In Figure 15 is given the electron microscope "surface area" per mole and BET water adsorption "area" per mole as a function of composition. The microscope surface area is a linear
function of composition, indicating the absence of interaction as the secondary particle size increases. Also in Figure 15 is plotted a "roughness factor", here defined as the ratio of the BET water "surface area" to the electron microscope "surface area", as a function of composition. Two pronounced maxima exist at the same compositions which had previously shown protection against crystallization (2), enhanced surface area (4), and enhanced integral and differential heats of adsorption (4). Noting the magnitude of the "roughness factor maxima", it is apparent that the aggregates as viewed in the electron microscope must be composed of still smaller particles whose area is in part accessible to water molecules. This point is investigated in the third part of this thesis.

In Figure 14 are also given the pore volume size distributions obtained graphically from the desorption isotherms by means of the Kelvin equation (points) and from electron microscopic count (bars). The desorption radii have been corrected for two monolayers of adsorbed water. The total pore volume obtained from electron microscopic measurements has been equated to the pore volume obtained from the desorption branch of the water vapor isotherm, thereby placing both pore distributions on the same quantitative basis. The volume of the pores was calculated assuming right circular cylinders of height proportional to the radius.

The most frequent pore radii for pure BeO and pure In₂O₃ are found to be 25 Å and 125 Å, respectively. As the BeO content is increased
the pore radii decrease in size uniformly, the largest changes occurring at compositions of 10 and 90 mole per cent BeO. Excellent quantitative agreement is obtained between the two completely independent measurements. This is taken to be a strong justification of the Kelvin equation for calculating pore radii from desorption isotherms of this type. Foster (7) has shown that the Kelvin equation gives correctly the relative dependence upon the physical properties of the condensed liquid. The adsorption work (4) has shown the temperature coefficient to be correct. Finally, the present electron microscopic studies have shown the absolute magnitude of the radii of the pores as given by the Kelvin equation to be satisfactory. In view of these data it is difficult to question the validity of the Kelvin equation when it is applied to pores in the size range studied here.
ANALYTICAL EXPRESSION FOR PORE SIZE DISTRIBUTIONS
CALCULATIONS

Most of the commonly occurring distribution functions have been used to represent pore size distributions. Many of them, however, are restricted in either of two respects: (a) they are insufficiently versatile to cover both sharp and broad distributions of different size ranges, or (b) they are cumbersome and tedious to handle either in the integrated or differentiated form. The Gaussian distribution, widely used to represent pore size distributions, cannot be integrated into a closed form, thus making it difficult to compare calculated cumulative pore volumes with the experimentally measured values. Furthermore, it is usually too wide at the top and too narrow at the bottom to fit well most experimental distributions. The Maxwellian distribution, along with the Gaussian distribution, has been used by Shull (6) to represent pore size distributions, but this equation lacks versatility in that the spread cannot be controlled independently of the most frequent pore size.

Dr. W. O. Milligan has suggested the use of the hyperbolic tangent equation. This equation:

\[ \frac{dV}{dR} = h k \text{sech}^2 [k(R-r_o)], \]

where,

\( V = \) cumulative pore volume of all pores having radii equal to or less than \( R, \)
\[ 2h = \text{total pore volume excluding adsorption}, \]
\[ k = \text{factor determining the sharpness of the distribution}, \]
\[ r_o = \text{most frequent pore radius}, \]
\[ v_o = \text{cumulative pore volume of all pores having radii equal to or less than } r_o, \]

possesses wide versatility in that the spread, amplitude, and position of the distribution can be varied independently. Furthermore, the integrated expression,

\[ v - v_o = h \tanh \left[ k(R - r_o) \right], \]

possesses a very simple closed analytical form, and calculated cumulative pore volumes can be easily compared with the experimental values. In Figure 16 the distribution, \( \frac{dV}{dR} = hk \text{sech}^2 \left[ k(R - r_o) \right] \), is shown with a Gaussian distribution (dashed line) having the same height and area. It is seen that the new expression is closely similar to the Gaussian distribution. The main difference is that the new expression is a little sharper at the top and a little broader at the bottom, thus approximating more closely many experimental distributions.

Since cumulative pore volumes are usually the only quantities accessible by methods commonly employed to determine pore sizes, it is desirable to work with the integrated form of the distribution function instead of the distribution function itself. The proposed equation is particularly adapted to such ends. The integrated expression
may be fitted to the experimental values and the distribution function
obtained analytically from the fitted equation.

The integrated expression may be fitted by numerical and/or graphi-
cal methods. In the present case two parameters, \( k \) and \( r_o \), were found
graphically and the other two, \( h \) and \( v_o \), were determined by the method
of least squares. Cumulative pore volumes obtained for eleven gels
in the system BeO-In\(_2\)O\(_3\) by gas adsorption (4) and electron microscope
techniques have already been presented. The methods used in determin-
ing the parameters were as follows.

Approximate values of \( v_o \), \( k \) and \( r_o \) were picked and the quantity
tanh \( k(R-r_o) \) was plotted vs. \( V-v_o \), using only absolute values of the
two quantities so that the points below \( r_o \) were "folded" back on the
same graph paper as the points above \( r_o \). If the curves have a curva-
ture upward (toward the \( V-v_o \) axis), the value of \( k \) must be decreased.
If the slope of the negative values is higher than the slope of the
positive values, the value of \( r_o \) must be decreased. Both the slope
and curvature are very sensitive to the chosen values of \( k \) and \( r_o \) so
that correct values of \( k \) and \( r_o \) are obtained in only about four graph-
ings. In the present case special hyperbolic tangent graph paper was
used, eliminating the necessity of obtaining from tables the values
of the hyperbolic tangent. When the best values of \( k \) and \( r_o \) had been
obtained by the above methods the values of \( h \) and \( v_o \) were obtained
by the method of least squares.
RESULTS

As an example of the agreement obtained with the new equation calculated and observed values for the cumulative pore volumes for the electron microscope results on the gel composed of 10 mole % BeO and 90 mole % In$_2$O$_3$, heat-treated at 500° for two hours are given in Table I. In Table II are given the most frequent pore size ($r_o$), the amplitude of the distribution ($h_k$), the width of the distribution at half-height (1.7628/k), and the standard deviation of the calculated cumulative pore volumes as compared with the observed ones. Most of the deviation occurs at the extreme ends of the distributions. In Figures 17-27 are shown in graphical form the results of the eleven gels. The open points correspond to cumulative pore volumes obtained from two desorption isotherms at two different temperatures (4). The closed points represent cumulative pore volumes obtained from electron micrographs. The curves are the calculated values using the new equation. The radius of the experimental points corresponds to the standard deviation from the calculated values. In the inset are given the distribution functions obtained by various methods. The solid curve represents the analytical derivative of the new equation fitted to the desorption pore volumes by the method described. The points represent counted distributions obtained from high magnification electron micrographs. The dashed curve represents the new function fitted to the electron microscope pore volumes.
The overall agreement is satisfactory. The largest deviations occur at the extreme ends of the distributions, where it would be expected that secondary effects, such as aggregation or clumping, would have a pronounced effect. In summary, the flexibility, ease of applicability, and the simple analytical forms of the new equation appear to justify its addition to the existing distribution functions.
ELECTRON DIFFRACTION STUDIES
EXPERIMENTAL

The electron diffraction patterns were taken in a Philips electron microscope using 100 kv electrons. The photographic densities were obtained from the plates by the use of a Moll microphotometer and a "Photopen" recorder. The photographic densities were converted to relative electron intensities and transferred to large graph paper. The incoherent scattering was obtained by drawing in a smooth curve and the structure-sensitive diffraction peaks obtained by subtracting.

Figure 28 shows the diffraction patterns for the system heat-treated for 2 hours at temperature levels of 500° and 600°. The prints have been masked by the rotating sector method to obtain an even background. In Figure 29 are plotted, on a relative intensity basis, the coherent scattering patterns for the system.

It will be noted in Figures 28-29 that enhanced line broadening occurs at compositions corresponding to the two previously observed zones of mutual protection. The increased line broadening may result from smaller crystal size, or from strains and distortions. The position of the diffraction lines are identical, within the limits of observation, with those obtained from large, well-formed crystals of In₂O₃. In the following interpretations of the observed line broadening, it is assumed that broadening from strain or distortion may be neglected, or is independent of the temperature of heat-treatment. The assumption accounting the line broadening to crystal size effects leads to
results agreeing closely with water surface areas measured previously by gas adsorption techniques (4). It appears reasonable that the line-
broadening may be interpreted on the basis of crystal size.

To obtain a measure of the crystallite size from line broadening
one must know the instrumental broadening due to the particular experi-
mental apparatus. The instrumental broadening was obtained in this
case for each particular line by heating samples of pure In$_2$O$_3$ and
BeO to a sufficiently high temperature to obtain single crystals large
enough to see and measure in the electron microscope. In the samples
employed for standardization the single crystal cubes of In$_2$O$_3$ were
about 250 Å on an edge. The single crystals of BeO tended to be plate-
like and were about 250 Å in length. In these samples the broadening
due to crystal size amounted to only a few percent of the total broaden-
ing. The electron diffraction rings were slightly spotty in appearance.
RESULTS

In Figures 28-29 are shown the coherent scattering patterns for the system heat-treated at 500° and 600°. From a consideration of the patterns for the system heat-treated at 500° it is apparent that the same zones of composition which had previously shown enhanced adsorptive capacity, surface areas and differential and integral heats of adsorption, correspond to a more poorly crystalline condition. Visual inspection of the patterns suggests that the crystal size is much smaller in these regions. In a previous study with x-rays (2) no pattern for BeO as a separate phase was detected in the dual gels at any heat-treatment. From an examination of the 90 mole % BeO sample heated at 500°, it is apparent that the stronger diffracting power of electrons has detected the presence of a crystalline phase of BeO. However, the crystal size is very small for the samples heated at 500°, and therefore, a complete electron diffraction study was carried out on samples heat-treated for two hours at 600°. From these latter patterns it is apparent that the BeO exists as a separate crystalline phase to as low a concentration as 60 mole % BeO, although x-ray diffraction patterns of these samples fail to show the presence of a separate crystalline phase of BeO for any samples containing In₂O₃. The apparent contradiction of these experiments is attributed to the much greater diffracting power of BeO for electrons relative to x-rays. Figure 30 shows the size of the crystallites as measured by line-broadening
for the system heated at 500° as compared to the secondary particle size. The open points give the volume average of the secondary particle diameter as measured in the electron microscope $\frac{32}{33}$. The closed points give the edge of a crystalline cube of $\text{In}_2\text{O}_3$ as deduced from line broadening. The half-open circles give the diameter of a sphere of BeO. It is noted that the secondary particle size is a linear function of composition, thus indicating that the interaction has no effect on the secondary particle size. However, the crystallite size shows a decided decrease in the regions of the zones of mutual protection. It follows that the secondary particles are composed of several smaller crystallites, the number rising very rapidly in the zones of mutual protection, as shown in the top part of Figure 30.

In Figure 31 is shown a plot of the fraction of crystallite surface accessible to water vapor as measured by a calculation of the water surface area (4). It is noted that more than half of the crystallite surface is accessible to water vapor. In view of the uncertainty of the crystallite size measurements (15-20%) and a lack of a detailed knowledge of the exact shape of the crystallites, one can only conclude that most of the crystallite surface is accessible to water vapor. However, since all of the crystallite surface is not accessible to water vapor, a consideration of the packing of the crystallites in the secondary particle must account for this area which is not accessible to the water vapor. Since the water vapor does have access to a much larger area than the external area of the secondary particles, it
follows that the water molecule (or OH groups) can penetrate around at least part of the area of the crystallites. The closed points in Figure 31 give the value of the fraction of surface area available to a water molecule for close-packed spheres of diameter equal to the crystallite size. The fair agreement indicates that the crystallites are fairly tightly packed in the secondary particles, but it would be difficult to distinguish between similar idealized models.
SUMMARY
The primary and secondary structure of the gels formed in the system BeO-In₂O₃ seems to be well established. The gels consist of small spheroidal particles, here called secondary particles. The size of these secondary particles is a linear function of composition, indicating that the phenomenon of mutual protection does not result from variations in secondary particle size as viewed in the electron microscope. The secondary particles are made up of smaller crystallites, the size of which are directly related to mutual protection. The zones of maximum mutual protection correspond to regions having much smaller crystal size, this smaller crystallite size accounting for "amorphous" x-ray diffraction patterns, enhanced surface areas and adsorptive capacities and enhanced differential and integral heats of adsorption. These crystallites are fairly tightly packed in the secondary particle, although loose enough that most of the crystallite area is still accessible to the water molecule.

A new pore size distribution equation has been used to express the pore sizes found in the system BeO-In₂O₃. The expression is believed to be more readily applied than most other equations that have been used to express pore size distributions.

The mechanism of the protective process is still not completely understood, although the final structure of the heat-treated gels is fairly certain. Since the secondary particle size is not effected by the mutual protection, it is apparent that the governing mechanism must occur within the secondary particle. If the secondary particles
are formed upon precipitation the mutual protective process may occur in the secondary particle by adsorption of one oxide on the other, as postulated by Weiser, Milligan and Mills (5). This adsorption may be destroyed by high temperatures and the formation of small crystals can occur. It is obvious that compositions which favor maximum adsorption would give rise to smaller crystal size for a given heat-treatment. This would give rise to two zones of mutual protection.

Many questions remain to be answered before the phenomenon of mutual protection against crystallization is fully understood. The air-dry gels are known to be amorphous to x-rays (2), but it must be determined whether this is due to extremely small crystals, with perhaps an adsorbed layer of the other oxide, or whether it is due to disorder on the molecular level. In other words, it should be determined at just what stage the phenomenon begins to have an effect on the structure of the gels; whether it begins at the inception of precipitation, or whether it begins when the molecules begin to order themselves into crystals through thermal energy. The effect of the temperature of heat-treatment, from the air-dry stage onward, on the secondary, or aggregate, size would throw much light on the question of where the mutual protection takes place. If the secondary particle size remains constant for various temperatures of heat-treatment, the protective action must be localized within the secondary particle. This would indicate that the protective action begins when the small crystals begin to grow, since the secondary particle size of the heat-treated gels have been shown to be unaffected by the mutual protection.
TABLE I

10 Mole % BeO - 90 Mole % In₂O₃, heated 500°C.

<table>
<thead>
<tr>
<th>Electron Microscopic Pore Size</th>
<th>Pore Volume, V, cc/g</th>
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<tr>
<td></td>
<td>obs.</td>
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<tr>
<td>R , Å</td>
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<tr>
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\[ \sqrt{\sum(\Delta V)^2/n} = 0.002 \]
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<th>Sample heated 2 hrs., 500°C.</th>
<th>Most Frequent Pore radius, ( r_0 ), Å</th>
<th>Amplitude, ( h_k )</th>
<th>Width, ( 1.7628/k )</th>
<th>( \sqrt{\Sigma(\Delta Y)^2/n} )</th>
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<tbody>
<tr>
<td>Mole % Mole %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BeO</td>
<td>In(_2)O(_3)</td>
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<td>EM</td>
<td>des</td>
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avg. = 0.011 0.010

des = desorption isotherm ; EM = electron microscope
FIGURES
Figure 1. Specific adsorptive capacities and surface areas in the system BeO-In$_2$O$_3$, heat-treated for 2 hours at 500°.
\[ x/m \text{ at } 12^\circ C \]

\[ x/m \text{ at } 2^\circ C \]

\[ \text{BET Surface Area at } 12^\circ C \]

\[ \text{BET Surface Area at } 2^\circ C \]

(A) \( P/P_0 = 0.1 \)

(B) \( P/P_0 = 0.0 \)
Figure 2. Differential (dashed line) and integral (solid line) heats of adsorption in the system BeO-In$_2$O$_3$, heat-treated for 2 hours at 500°.
Figure 3. Electron micrograph of 100 mole % In$_2$O$_3$, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 4. Electron micrograph of 10 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å
Figure 5. Electron micrograph of 20 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 6. Electron micrograph of 30 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 7. Electron micrograph of 40 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 8. Electron micrograph of 50 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 9. Electron micrograph of 60 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 10. Electron micrograph of 70 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 11. Electron micrograph of 80 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 12. Electron micrograph of 90 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 13. Electron micrograph of 100 mole % BeO, heat-treated for 2 hours at 500°. Magnification: 200,000 diameters, one millimeter corresponds to 50 Å.
Figure 14. Pore volume and particle area distributions of gels in the system BeO-In$_2$O$_3$, heat-treated for 2 hours at 500°. The points represent a graphical evaluation of the pore volume size distributions from the desorption isotherms by means of the Kelvin equation, while the bars represent distributions obtained from the electron micrographs.
Figure 15. Electron microscopic (A) and water adsorption (B) surface areas, and roughness factors (C) of gels in the system BeO-In$_2$O$_3$, heat-treated for 2 hours at 500°.
Figure 16. The distribution, $\frac{dV}{dR} = h k \text{sech}^2 [k(R-r_0)]$, (solid line), compared with a Gaussian distribution (dashed line) having the same height and area.
Figure 17. Calculated and observed cumulative pore volumes and pore size distributions for 100 mole % In$_2$O$_3$, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 18. Calculated and observed cumulative pore volumes and pore size distributions for 10 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 19. Calculated and observed cumulative pore volumes and pore size distributions for 20 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 20. Calculated and observed cumulative pore volumes and pore size distributions for 30 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 21. Calculated and observed cumulative pore volumes and pore size distributions for 40 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 22. Calculated and observed cumulative pore volumes and pore size distributions for 50 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 23. Calculated and observed cumulative pore volumes and pore size distributions for 60 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 24. Calculated and observed cumulative pore volumes and pore size distributions for 70 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 25. Calculated and observed cumulative pore volumes and pore size distributions for 80 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 26. Calculated and observed cumulative pore volumes and pore size distributions for 90 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 27. Calculated and observed cumulative pore volumes and pore size distributions for 100 mole % BeO, heat-treated for 2 hours at 500°. Open points are cumulative pore volumes from desorption data, closed points are pore volumes from electron microscope data; the radius of the experimental points corresponds to the standard deviation from the calculated values. The points in the inset represent counted distributions from electron micrographs.
Figure 28. Electron diffraction patterns for the system BeO-In₂O₃, heat-treated for 2 hours at 500° and 600°.
Figure 29. Relative coherent electron diffraction intensities for the system BeO-In$_2$O$_3$, heat-treated for 2 hours at 500° and 600°.
Figure 30. Particle sizes in the system BeO-In₂O₃, heat-treated for 2 hours at 500°. Open points are secondary particle diameters. Closed points are edges of In₂O₃ cubes. Half-open points are diameters of spheres of BeO. The top graph gives a measure of the number of crystallites per secondary particle.
- Secondary Particle Size
- In$_2$O$_3$ Crystal Size
- BeO Crystal Size
- Number of Crystals per Secondary Particle
Figure 31. Fraction of crystallite surface area accessible to water vapor, $F$, as a function of composition. The closed points are the fractions available for close-packed spheres of the same size as the crystallites.
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REFERENCES