Polycrystalline Sodium–Potassium β/β''-Alumina

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Sodium–potassium β/β''-alumina containing 40 mole% K_2O and 60 mole% Na_2O in the alkali fraction with over 65% β''-phase can be synthesized and sintered by using a commercially feasible spray-drying process for the preparation of the precursor powder. The technique involves the use of finely divided α-alumina ($<2~\mu m$) predoped with about 0.2 wt% of MgO and the incorporation of a large amount (1.3 mole/mole) of MgO as β''-alumina stabilizer and of lithia (0.15 mole/mole) as a sintering aid in a slurry made for spray-drying. Densities in the order of 95% of theoretical are obtained on the sintered products.

Introduction

Alumina (aluminum oxide) has several polymorphs and the most common form is α-alumina (corundum) with a hexagonal crystal structure. Most of the other forms are finely crystalline (such as γ-alumina, δ-alumina) and are unstable at high temperatures; they convert into α-alumina (the most stable form) at about 1200°C. Contrary to convention, β-aluminas are not pure aluminum oxides; they are sodium aluminates. The approximate formula of β-alumina is: $Na_2O:11Al_2O_3$ and of β''-alumina, $Na_2O:5Al_2O_3$. These two can form a series of mixed β/β''-alumina with stoichiometries ranging from 1:4.5 to 1:14.5. The β''-alumina normally requires a stabilizer such as MgO or Li_2O.

β-Aluminas are excellent sodium ion conductors which make them technically important in applications such as thermoelectric generators and the experimental high-energy-density sodium–sulfur battery.

Sodium ion conduction in β-aluminas takes place through NaO layers which separate spinel-like blocks of $Al_{11}O_{16}$ in their hexagonal crystal structure (*1*). β-Alumina has two spinel blocks and β''-alumina has three spinel blocks per unit cell and the β''-form has a sodium ion specific conductivity that is about 1.5 to 2 times that of the β-form. Other β- and β''-aluminas in which the Na ions are displaced by Group I elemental ions (including hydronium and ammonium radicals) of the periodic table are also known.

Hydrogen or hydronium ion conducting β/β''-alumina is an attractive membrane material for devices such as hydrogen–air fuel cells and steam electrolyzers. This material can be prepared in single crystal form by simple ion exchange of their sodium conducting analogs, also in single crystal form (*2*). However, such single crystals are not large enough to be utilized in power devices such as fuel cells. On the other hand, polycrystalline sodium

β/β''-alumina disintegrates on hydronium ion exchange due to the anisotropy in expansion of the sodium ion conductor during ion displacement by the 40% larger hydronium ion. Nevertheless, if potassium β/β''-alumina can be prepared, it is claimed (3) that it can be ion exchanged by hydronium ions without breakdown, because potassium and hydronium ions match very closely in size. Direct synthesis and sintering of pure potassium β''-alumina have so far not been successful due to the unstable nature of the product at the high temperatures ($\approx 1600°C$) required for the sintering. A successful route to the fabrication of potassium β''-alumina has been the ion exchange of the sodium analog by the use of potassium vapor at high temperatures (3). Potassium ion exchange of the pure sodium compound in a molten potassium nitrate bath has been tried, but is not satisfactory due to deterioration of the material at the molten KNO_3 temperature of 350°C (4).

Work by Nicholson et al. (5) has shown that the maximum proportion of potassium that can be incorporated into sodium–potassium β-alumina is about 40 wt% of the total alkali fraction in order to obtain significant amounts of β''-alumina in the product after sintering. They have also shown that such mixed ion products can be fully exchanged into the potassium form by ion exchange in a molten KCl bath. Studies by Bell et al. (6) have indicated that the bulk ionic conductivity of sodium–potassium β-alumina is enhanced dramatically (by about three orders of magnitude) when the $f(\beta)$ value of the product is reduced to less than about 0.37, where

$$f(\beta) = I(\beta)/[I(\beta) + 1.37I(\beta'')]$$

in which $I(\beta)$ and $I(\beta'')$ are, respectively, the intensities of the X-ray diffraction peaks of β- and β''-aluminas corresponding to the d-spacings of 0.269 and 0.260 nm, respectively (7).

The objective of the present study was to fabricate sintered products of sodium–potassium β/β''-alumina with a potassium content of 40 mole% in the alkali fraction and an $f(\beta)$ value of 0.37 or less. A commercially desirable spray-drying process was investigated for the system. This would provide the precursor material required for the synthesis of highly conducting hydronium β/β''-alumina for use as membranes in devices such as hydrogen–air fuel cells and steam electrolyzers.

Experimental Procedures

Reagents. The reagents used in making the compositions were anhydrous sodium carbonate and anhydrous potassium carbonate (Anachemia, ACS reagent grade), aluminum oxide (Reynolds RC-172, Alcan C-71) and also a sample synthesized by the decomposition of aluminum sulfate (Baker Analysed), magnesium oxide (Baker Instra Analysed), acetate (Fisher Certified ACS Reagent), lithium carbonate (Fisher Certified ACS), and acetate (Anachemia Reagent).

Procedure. In the preliminary work, the ingredients were ground into a paste with drops of distilled water in an alumina mortar with an alumina pestle, the paste was dried in an air oven at about 110°C, and the resulting powder was calcined at a temperature of typically 1250°C for 30 min. An X-ray diffraction pattern of the calcined powder was obtained and the $f(\beta)$ of the product was calculated.

In the case of MgO-doping experiments on alumina, the alumina was mixed with the required amounts of MgO or magnesium acetate and ground into a paste as before and calcined at 1250°C.

Aluminum oxide of extreme fineness was prepared by the thermal decomposition of aluminum sulfate crystals. At temperatures below 1000°C, the product was mostly γ-alumina. It was further heat treated at

1100, 1200, 1250, 1300, and 1400°C in order to recrystallize the material to the coarser α-alumina form. These samples were further doped with MgO as required, by the procedure described above.

After obtaining a satisfactory low $f(\beta)$ value on the β-alumina product by calcination, that particular composition was prepared on a larger scale by the spray-drying method. First, carbon dioxide was bubbled through a solution of sodium and potassium carbonates, the required amount of MgO was added and carbon dioxide was passed through again until a clear solution was obtained. Calculated amounts of aluminum oxide were added to the resulting solution and the mixture was shaken in a plastic bottle containing alumina balls for 30 min in order to break up aggregates. The slurry thus obtained was filtered through a 60-mesh screen and spray-dried in a Buchi lab unit at an inlet temperature of about 220°C and an outlet temperature of about 130°C. Aliquots of the powders were calcined at various temperatures in order to ascertain the optimum temperature of calcination for obtaining a powder with the lowest $f(\beta)$ value as determined by X-ray diffraction.

In another procedure, the carbonates of sodium, potassium, and magnesium were dissolved in acetic acid instead of the bicarbonate preparation and alumina was then added as before to make the slurry for spray-drying.

After calcination at the selected temperatures, the samples were uniaxially pressed into disks of about 1.2 cm in diameter and 3 mm in thickness in a steel die at a pressure of about 140 MPa. The disks were then sintered at temperatures ranging from 1600 to 1650°C for 5 to 15 min in a closed platinum crucible, using powder of the same composition for packing. The densities of the disks were determined by measuring the diameter, thickness, and weight of each disk. The $f(\beta)$ values of the fired disks were measured as before by X-ray diffraction and peak intensities of the β- and β''-forms.

Results

The Effect of MgO on the Yield of β''-Phase in the Sodium–Potassium Mixed Composition

The effect of MgO as a stabilizer for β''-alumina with 60 mole% Na_2O and 40 mole% K_2O was studied using RC-172 alumina as the alumina source. The other reactants were sodium carbonate, potassium carbonate, and magnesium oxide. Approximately 80-g batches of the compositions were prepared by spray-drying as described earlier. The $f(\beta)$ values of the various compositions were determined after calcination at temperatures ranging from 800 to 1400°C and also after sintering some of these calcined compositions. The results of these experiments are shown in Table I.

No β''-alumina is formed until the calcination temperature is at least about 1100°C, although small amounts of β-alumina are produced even at 800°C. The highest proportions of the β''-phase are formed at temperatures of 1250 to 1350°C at all MgO concentrations. Although MgO contents of both 0.7 and 1.3 mole/mole produce powders of similar β''-alumina content, on sintering only the 1.3 MgO composition yields a product rich in the β''-phase. The $f(\beta)$ of the 0.7 MgO composition increases on sintering. An MgO content of 1.3 yields a product which has an $f(\beta)$ of even less than the required 0.37. A high MgO content of 1.3 thus has a very strong stabilizing effect on the β''-phase in the 0.60 Na/0.40 K β-alumina composition. It is not clear why an intermediate MgO content of 1.0 yields a product that has a higher $f(\beta)$ than the 0.7 MgO composition, on calcination.

TABLE I

THE EFFECT OF MgO ON THE YIELD OF
β''-ALUMINA IN 60/40 MIXED Na/K COMPOSITIONS

Calcination temperature (°C)	MgO content (mole/mole)	$f(\beta)$	
		Calcine	Sinter
800	0.7	1.0	
	1.0	1.0	
	1.3	1.0	
1000	0.7	1.0	
	1.0	1.0	
	1.3	1.0	
1100	0.7	0.48	
	1.0	0.53	
	1.3	0.46	
1200	0.7	0.42	
	1.0	0.52	
	1.3	0.42	
1250	0.7	0.39	0.65
	1.0	0.45	0.61[a]
	1.3	0.39	0.29
1300	0.7	0.42	
	1.0	0.50	
	1.3	0.40	
1350	0.7	0.38	
	1.0	0.47	
	1.3	0.41	
1400	0.7	0.47	
	1.0	0.51	
	1.3	0.39	

Note. Basic composition: 0.6 Na_2O : 0.4 K_2O : 6.0 Al_2O_3. Alumina used: RC-172.

[a] Powder calcined at 900°C.

The Effect of the Type of Alumina on $f(\beta)$

1. High-purity alumina prepared from aluminum sulfate. The purpose of using high-purity alumina was to prepare very-high-purity β/β''-alumina and to investigate the effect of the particle size and the type of alumina phase (e.g., γ- and α-aluminas) on the yield of sodium–potassium β/β''-alumina. To achieve this, the alumina was prepared by thermally decomposing aluminum sulfate and calcining the sulfate decomposition product at 900, 1200, 1250, and 1400°C. The 900 and 1200°C calcines

contained practically no α-alumina as found by X-ray diffraction. Mixtures were prepared using each sample of these aluminas to make 0.60 Na_2O : 0.40 K_2O : 1.3 MgO : 6.0 Al_2O_3 compositions and then these were calcined at 1250°C for 30 min. Results are listed in Table II.

It is obvious that the γ-type alumina does not produce β''-alumina when the reactants are calcined at 1250°C. On the other hand, the production of β''-phase is related to the presence of α-alumina in the reactants—more β''-phase is formed when higher amounts of α-alumina are present. Also, coarser crystals of α-alumina tend to produce more β''-phase, as indicated by the production of more β''-phase from alumina calcined at higher temperatures.

2. RC-172 alumina. This is a finely divided α-alumina with a particle size of <2 μm. It is known to be excellent for many sintering applications in producing high-density high-alumina bodies. The use of RC-172 alumina in making 0.60 Na_2O/0.40 K_2O : 1.3 MgO : 6.0 Al_2O_3 yielded a product with an $f(\beta)$ of 0.33 on calcination at 1250°C for 1 hr. Thus, RC-172 is much more efficient than high-purity aluminum oxide (prepared from aluminum sulfate) in producing mixed Na/K β''-alumina. The reason for this behavior could be the presence of a small amount of MgO (≈ 0.2 wt%) in the RC-172. In order to verify this theory, the effect of adding MgO to high-purity alumina and

TABLE II

THE EFFECT OF PRECALCINATION TEMPERATURE OF
ALUMINA ON THE YIELD OF β''-ALUMINA

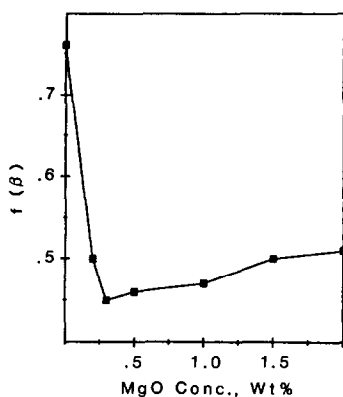| Calcination temperature (°C)	Al_2O_3 type in reactants	$f(\beta)$ of product
900	γ	1.00
1200	γ	1.00
1250	γ + tr. α	0.90
1400	α	0.75

Fig. 1. The effect of doping α-alumina with MgO on the $f(\beta)$ of powder.

calcining it prior to making Na/K β-alumina was investigated.

Pure aluminum oxides made from aluminum sulfate and calcined at various temperatures were used for these tests. Varying proportions of MgO ranging from 0 to 2 wt% of the alumina were mixed with the alumina and calcined at 1250°C for 30 min. (Magnesium acetate was used as the MgO source for these experiments.) The resulting powders were first subjected to X-ray diffraction analysis for phase content and then incorporated into mixtures for the synthesis of 0.60 Na_2O/0.40 K_2O : 1.3 MgO : 6.0 Al_2O_3 β/β''-alumina. Alumina–MgO calcined with less than 0.5 wt% contained no detectable amounts of spinel; traces of spinel were found at the 0.5% level and these increased with further increase in the MgO content. The variation of the $f(\beta)$ with the change in the MgO content of the alumina is illustrated in Fig. 1. As little as 0.2 wt% of MgO in the alumina has a significant effect on the $f(\beta)$; the lowest $f(\beta)$ (highest β''-phase) is obtained after calcination at 1250°C at 0.3–0.5 wt% of MgO.

3. C-71 alumina. This is α-alumina in a considerably coarser form ($\approx$5 μm) than the others used in this study. In one experi-

ment, the Na/K composition was prepared and calcined using untreated C-71 powder. In another, the C-71 was first heat-treated with 0.3% by weight of MgO before making the Na/K β''-alumina reactant mixture. After calcination at the usual 1250°C for 30 min, $f(\beta)$ values, respectively, of 0.34 and 0.36 were obtained with the undoped and doped materials. This shows that when the α-alumina is coarse (5 μm), MgO doping has no effect on the subsequent yield of Na/K β''-alumina. However, the desirable low $f(\beta)$ values are obtained even without any doping, using C-71 alumina.

Sintering of the Powders

The various calcined powders were pressed into disks, which were sintered at 1650°C for 5 min. Table III gives the density and $f(\beta)$ values of these samples. The doped alumina, RC-172, and C-71 all yield products with acceptable $f(\beta)$ values; but none of them has an acceptable density.

Several attempts were made to improve the sintered density by changing the sintering conditions of temperature and time, but no significant improvement in the density could be obtained. It was therefore neces-

TABLE III

Density and $f(\beta)$ of Products Obtained Using Various Al_2O_3 Raw Materials

Alumina sample	Green		Sintered	
	Density	$f(\beta)$	Density	$f(\beta)$
From $Al_2(SO_4)_3$ at 1300°C undoped	1.66	0.45	2.10	0.40
From $Al_2(SO_4)_3$ doped with 0.5 wt% MgO	2.01	0.37	1.99	0.33
RC-172	1.74	0.28	2.70	0.29
C-71 undoped	2.16	0.35	2.13	0.18
C-71 doped with 0.5 wt% MgO			1.93	0.31

Note. Composition: 0.6 Na_2O : 0.4 K_2O : 1.3 MgO : 6.0 Al_2O_3. Calcination temp: 1250°C/30 min. Sintering at 1650°C/5 min.

TABLE IV

THE EFFECT OF Li$_2$O CONTENT ON THE $f(\beta)$ AND SINTERED DENSITY OF Na/K β-ALUMINA

Li$_2$O concentration (mole/mole)	Green		Sintered	
	Density	$f(\beta)$	Density	$f(\beta)$
0.05	1.99	0.52	2.81	0.48
0.10	2.05	0.40	2.97	0.38
0.15	1.84	0.40	3.14	0.48
0.20	1.96	0.42	3.15	0.46
0.30	1.85	0.55	3.22	0.46
0.15[a]	1.93	0.71	3.18	0.87

Note. Reactants: RC-172 alumina; lithium carbonate; magnesium oxide; sodium carbonate and potassium carbonate. Method: hand-mixed paste. Calcination temp.: 1250°C/30 min. Sintering at 1625°C/10 min.

[a] No MgO in mix.

sary to consider a sintering aid for these compositions. Li$_2$O is known to be a sintering agent for several oxide ceramics and hence it was decided to study its influence on the sintering behavior of the mixed sodium–potassium β-alumina compositions. RC-172 was selected as the raw material alumina for these studies. Varying levels of Li$_2$O were incorporated, in the form of lithium carbonate or lithium acetate, into the composition before spray-drying the reagents. After calcination, the various mixtures were pressed into disks and were sintered at 1625°C for 10 min. The results of these experiments are displayed in Table IV. The sintered density is improved by the presence of Li in the system. Although the density of the product increases at least up to 0.3 mole of Li$_2$O per mole, about 0.15 mole/mole is sufficient to obtain approximately 96% sintered density. The $f(\beta)$ of the sintered product, however, is increased by the incorporation of the Li$_2$O. This is in contrast to the effect of Li$_2$O in the synthesis of sodium β''-alumina, where it is used as a β''-alumina stabilizer. An increase of Li$_2$O content from 0.05 to 0.30 mole/mole, nevertheless, does not reduce the β''-alumina content of the sodium–potassium β/β''-alumina. The absence of MgO in the system even when the Li$_2$O is present reduces the β''-phase content. This again shows that in the Na/K β-alumina system, MgO is a stabilizer for the β''-form, but Li$_2$O is not.

Because the use of C-71 alumina produced the highest β''-alumina content of all the alumina raw materials tried, attempts were made to increase the sintered density of the C-71 product by using Li$_2$O as a sintering aid. Three levels of Li$_2$O concentrations, with or without MgO stabilizer, were tried. However, Li$_2$O failed to show its role as a sintering aid in these cases and the β''-phase content of the product decreased considerably with the increase in the Li$_2$O concentration. Table V illustrates these points.

The foregoing experiments indicated that RC-172 alumina was the preferred alumina starting material of the three alumina materials examined for the fabrication of Na/K β-alumina of high-density and high-β''-alumina content. Hence batches of Na/K β-alumina powder compositions were prepared by spray-drying slurries made with RC-172 alumina containing Li$_2$CO$_3$ and the

TABLE V

THE EFFECT OF Li$_2$O ON THE SINTERING OF Na/K β-ALUMINA MADE WITH C-71 ALUMINA

Li$_2$O concentration	MgO concentration (mole)	$f(\beta)$ (powder)	Sinter density	Sinter $f(\beta)$
0.00	1.3	0.35	1.97	0.18
0.05	1.3	0.40	2.14	0.27
0.10	0.0	0.55	2.38	0.87
0.20	1.3	0.53	2.46	0.41
0.30	0.0	0.64	2.11	0.87

Note. Method: Hand-mixed paste. Composition: 0.6 Na$_2$O : 0.4 K$_2$O : 6.0 Al$_2$O$_3$.

TABLE VI

SINTERED DENSITIES AND $f(\beta)$ OF SPRAY-DRIED 0.6
$Na_2O : 0.4\ K_2O :: 1.3\ MgO : 6.0\ Al_2O_3 : 0.15\ Li_2O$
COMPOSITIONS

Slurry type	$f(\beta)$ (powder)	Green density	Sintered	
			Density	$f(\beta)$
Carbonate	0.38	1.84	3.22	0.34
Acetate	0.36	1.91	3.25	0.33
Acetate	0.36	2.00	3.19	0.35

Note. Al_2O_3: RC-172. Calcination: 1300°C/30 min. Sintering at 1625°C/10 min.

other ingredients either in the form of bicarbonates or acetates. A Li_2O concentration of 0.15 mole/mole was used for these preparations. Determination of $f(\beta)$ after calcination of 2-g samples of the powder at various temperatures ranging from 900 to 1400°C for 30 min revealed that calcination at 1300°C produced the powder with the lowest $f(\beta)$ of about 0.35. At 900°C, no β''-alumina was present, but at 1100°C an $f(\beta)$ of about 0.5 was found. No significant differences were observed between the bicarbonate and the acetate processes. The powders were sintered at 1625°C for 10 min in the form of disks and the results obtained are recorded in Table VI. The sintered densities and the $f(\beta)$ values are excellent for the composition.

Discussion

MgO Doping of the Raw Alumina Material

Although MgO is known to be a stabilizer for β''-alumina, the effect of MgO predoping of the reactant alumina on the yield of β''-alumina has not been known before. Interestingly, this effect was discovered through the use of RC-172 alumina and high-purity alumina for the Na/K

β''-alumina synthesis. The RC-172 invariably yielded more β''-alumina when processed with the other reagents although the high-purity alumina sample was a more reactive form of alumina from a surface area point of view. Even when the two types of alumina with equivalent surface areas were used for the preparation, the RC-172 yielded more β''-alumina product. Because the high-purity alumina was prepared by the thermal decomposition of high-purity aluminum sulfate in platinum vessels, no contamination was present. On the other hand, the reported chemical analysis of RC-172 alumina shows the presence of a small amount of MgO in the material. Hence experiments represented in Fig. 1 were carried out on the system by doping the pure alumina with MgO. Although no significant effect of the doping of the extremely fine γ-type alumina is found on β''-phase production, the coarser alumina in the α-form formed by higher temperature calcination does reveal a significant influence. Despite this effect, α-alumina coarser than 5 μm does not show any special influence by MgO. Hence, the mechanism of this effect is uncertain.

The Effect of MgO Concentration

In the case of pure sodium β-alumina prepared by aqueous spray-drying, about 0.8 mole of MgO per mole is sufficient for the stabilization of the β''-alumina. However, as potassium substitutes for the sodium, the MgO requirement increases considerably for β''-form stabilization. Thus, for the 0.6 $Na_2O : 0.4\ K_2O : 6.0\ Al_2O_3$ composition, 1.3 mole of MgO per mole is required to obtain an $f(\beta)$ value less than about 0.37 after sintering. It is not clear why such a high proportion of MgO is needed when 40 mole% of the sodium is substituted by potassium. In addition to the instability of the potassium β''-alumina itself, it appears to have a destabilizing effect on the sodium β''-alumina. An excess

of MgO compensates for this destabilizing effect.

It is interesting that even in the presence of 1.3 mole of MgO, no β''-alumina is formed when the reactants are calcined at 900°C. The formation of β''-alumina starts at temperatures of about 1100°C and the highest proportions of β''-phase are formed at 1250–1350°C. It is therefore inferred that the formation of β''-alumina has a higher activation energy than the β-form, or the alumina raw material has to be in the α-form for β''-alumina formation. Beyond 1400°C the proportion of β''-phase again decreases, which is to be expected because the potassium β''-alumina becomes unstable above that temperature as reported by Nagai and Nicholson (7).

Sintering of the Powders

It is not clear why the compositions that yield a satisfactory β''-alumina content do not sinter under various conditions of temperature and time. It appears that either there is no liquid phase formation in the Na$_2$O–K$_2$O–MgO–Al$_2$O$_3$ system under the sintering conditions tried, or that the vapor pressure in the system is too high for densification. The presence of lithia in the system, however, helps the sintering remarkably, although with a drop in the β''-alumina content of the sinter. Again it is not clear why the lithia does not act as a β''-alumina-stabilizing agent as it does in the sodium β''-alumina. Scanning electron microscopy studies show an increase in the grain boundary phases and it is to be assumed that the lithia stays mainly in these grain boundary phases rather than in the crystal lattice. Unfortunately, EDAX does not detect Li and hence this assumption cannot be easily proved. Nevertheless, a sintered 0.6 Na : 0.4 K β-alumina of acceptable density and $f(\beta)$ can be fabricated by the process described.

It is noteworthy, in Table V, that a sintered 0.6 Na : 0.4 K product with an $f(\beta)$ value of 0.18 can be prepared using the coarse C-71 alumina for the synthesis in the absence of lithia. Although the product has a low density after sintering at 1625°C, the very low $f(\beta)$ of 0.18 shows that potassium β''-alumina can exist at 1625°C.

Conclusions

A sodium–potassium β/β''-alumina containing 60 mole% Na$_2$O and 40 mole% K$_2$O in the alkali fraction can be synthesized and sintered to densities over 95% of theoretical with an $f(\beta)$ value of less than 0.37 by using a spray-drying process for the preparation of the precursor powder. An MgO content of 1.3 mole/mole as a β''-alumina stabilizer and a lithia content of 0.15 mole/mole as a sintering aid are required in the system for the process. A slurry of RC-172 alumina or of α-alumina of crystal size about 2 μm that is doped with at least 0.2 wt% MgO, prepared with the remaining reactants in an aqueous bicarbonate or acetate solution mixture, can be used for the spray-drying.

Acknowledgments

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