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ALMATIS PREMIUM ALUMINA expands its calcined aluminas into a higher purity range

By Nils Rosenberger and Marius Schustereder

Emerging and developing technical applications require improved purity levels of specialty alumina. To address the increasing need for higher purity alumina, Almatis has focused on generating cost-effective alumina powders with alumina content purities greater than 99.9%.

Alumina is the most extensively used ceramic material.

A major reason for the success of alumina over other technical ceramic materials is its excellent material properties in combination with its lower price, which is due to the use of the Bayer process for synthesis.

For the vast majority of alumina applications, a purity range of 99.6–99.8% is sufficient to achieve the desired properties. However, some specialty applications, such as lithium-ion batteries, require higher purities to achieve the desired properties.

The demand for higher purity alumina has been increasing recently due to new emerging applications, such as 5G, as well as the advancement of existing applications, such as semiconductor processing equipment.

An increase in purity to more than 99.9% typically comes at a significantly higher cost—i.e., by an order of magnitude—caused by either more expensive feed that must be used or complex processing steps to remove impurities from the alumina. For example, purities of 99.99% or greater are typically produced by methods that use ammonium alum, aluminum metal, or aluminum salts as feed instead of the cost-effective Bayer feed from a refinery.

To address the increasing need for higher purity alumina, Almatis focused on improving the purity levels of Bayer-based materials to generate cost-effective alumina powders with alumina content purities greater than 99.9%.

In previous work,[1–3] it was reported how impurities and dopants such as Na_2O, SiO_2, CaO, and MgO affect the sintering behavior and microstructure evolution in specialty aluminas derived from the Bayer process. However, limited work has been done on how impurities in this concentration range affect properties of alumina.

For applications in semiconductor processing and 5G, the dielectric loss tangent is an important property, and it is reported that the impurity concentration in the alumina has a major impact on it.[4–6] Therefore, we investigated the dielectric loss tangent of alumina with different purity levels and impurities.

This work led to the development of a proprietary process that allows us to selectively remove impurities from a Bayer-based feedstock and reach purity levels of 99.9–99.99%.

Higher purity specialty calcined aluminas produced at Almatis

Table 1 shows the overall purity of five alumina powders and the concentration of their impurities. The five powders are chosen to cover the purity range of 99.78–99.97%. Note that MgO is typically not considered an impurity due to its use as a sintering aid. MgO was intentionally added to powders 1, 2, and 5 for this reason. The physical parameters of the five powders are shown in Table 2.

Table 1. Purity levels of five alumina powders used for dielectric measurements. Credit: Almatis

in ppm	Na_2O	Fe_2O_3	B_2O_3	SiO_2	MgO	TiO_2	CaO	Li_2O	% Al_2O_3
Powder 1	790	184	12	204	761	34	241	2	99.78
Powder 2	80	133	14	214	563	15	105	2	99.89
Powder 3	150	67	11	60	14	4	19	20	99.96
Powder 4	70	193	10	79	16	34	59	2	99.95
Powder 5	80	187	8	83	595	34	63	2	99.89

Table 2. Particle size values by laser diffraction and specific surface are measured by the BET method. Credit: Almatis

	d10 (µm)	d50 (µm)	d90 (µm)	d100 (µm)	BET (m2/g)
Powder 1	0.12	0.5	2.11	10	6.56
Powder 2	0.09	0.45	2.08	12	7.92
Powder 3	0.1	0.49	1.62	12	4.80
Powder 4	0.08	0.43	1.84	10	8.57
Powder 5	0.08	0.43	1.93	10	8.28

Microstructures and densities of higher purity Bayer alumina

Figure 1 shows microstructures of samples prepared from Bayer process alumina with purities of A) 99.78% (powder 1) and B) 99.97% (powder 3). The samples were prepared by freeze granulation, uniaxial pressing of freeze granulated powder at 90 MPa, and firing at 1,600°C for 1 hour.

It can be seen that the impact of the overall purity on the microstructure of the samples investigated here is small. The grain size and shape of samples with a purity level of 99.78% (A) are similar to samples with a higher purity level of 99.97% (B). After investigating a larger sample area, a higher number of facetted grains similar to the grain in the center of image (A) in Figure 1 was observed in the alumina with lower purity.

The formation of a small amount of second phases, most likely sodium aluminate, calcium aluminate, and spinel phases,[2–3,7] was observed in samples with the lower purity of 99.78%. No second phase formation was observed in the sample with a higher purity of 99.97%.

To determine the impact of the purity on the sintered density, 10 pellets of each powder were uniaxially pressed at 90 MPa and sintered at 1,600°C for 1 hour in an electric kiln. The samples made from the powder with a purity of 99.78% had an average density of 3.91 g/cm^3 (standard deviation = 0.01 g/cm^3), whereas the samples made from the powder with a purity of 99.97% had an average density of 3.93 g/cm^3 (standard deviation = 0.01 g/cm^3). The difference in the sintered density can be attributed to the effects of impurities on sintering mechanisms, as described in the literature.[1–3,7]

Effects of impurities on properties: Example dielectric loss tangent

Figure 2 shows the dielectric loss tangent of samples that were prepared from the five alumina powders described in Tables 1 and 2. The dielectric loss tangent was determined at 10 GHz using split-cylinder resonator measurements as described by Janezic and Baker-Jarvis.[8] We estimate the accuracy of this measurement to be about 10%.

It can be seen that the dielectric loss tangent decreases with increasing purity. The sample prepared from powder 1 (99.78% purity) has a dielectric loss tangent of 3.5 x 10^{-3}, whereas the samples prepared from powders with a purity of 99.89% or higher have dielectric loss values that are one order of magnitude lower.

However, it can also be seen that the dielectric loss tangent does not solely depend on the overall purity of the alumina. In other words, it is not the purest sample (made from powder 3) that has the lowest dielectric loss tangent. This observation indicates that the type of impurities present is more important for the dielectric loss than the total amount of impurities.

Powder 3 has the lowest overall impurity concentration and the lowest impurities for every individual impurity, except for Na_2O and Li_2O. This finding indicates that Na_2O and Li_2O have a more severe impact on the dielectric loss tangent than other impurities. Powder 1

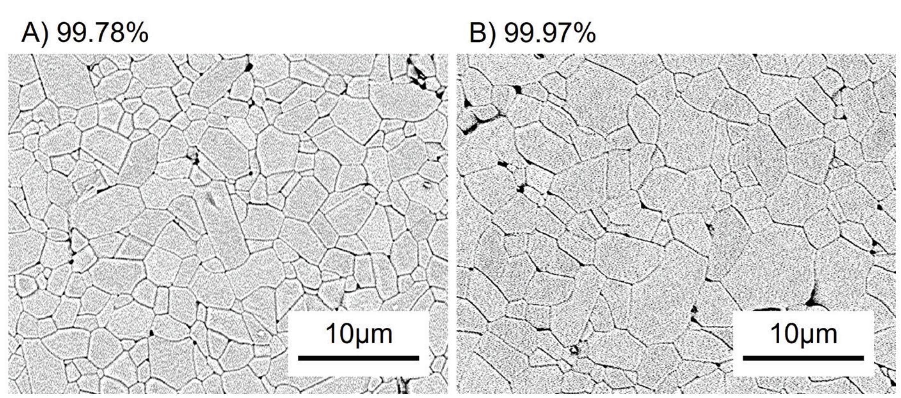

Figure 1. Microstructures of alumina samples with purities of A) 99.78% and B) 99.97%.

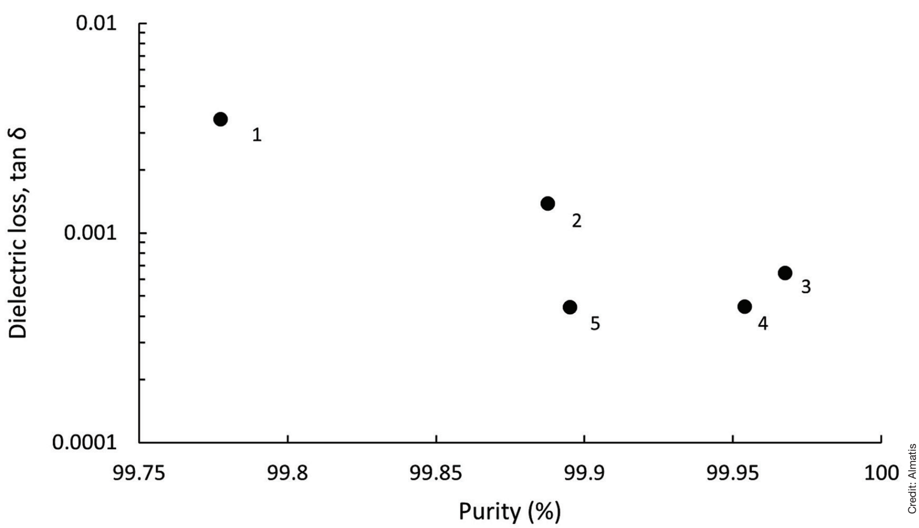

Figure 2. Loss tangent and purity of the alumina samples. The numbers indicate the powders used to prepare the samples.

has the highest Na_2O concentration with 790 ppm and also shows the highest loss tangent, which further supports the claim that Na_2O has a significant impact on the dielectric loss tangent.

It is also apparent that Na_2O and LiO_2 are not the only impurities that affect the dielectric loss. Samples from powders 1 and 2 have a higher SiO_2 and CaO concentration than samples from powders 3, 4, and 5. This finding indicates that higher SiO_2 and CaO concentrations led to higher dielectric loss tangents as well.

Powders 4 and 5 have similar impurity levels, except for the MgO concentration. Powder 5 was intentionally doped to the reported MgO level, as it is common practice for reactive aluminas due to the positive effect of MgO on the sintering behavior and microstructure development of alumina (Figure 1A). Powder 4 was not doped with MgO, and the difference in MgO concentration did not affect the dielectric loss tangent at 10 GHz for these samples. This finding contradicts the observation by Molla et al.,[4] who reported a negative effect of MgO on the dielectric loss tangent of alumina. However, further investigations are necessary to understand this discrepancy.

The data analyzed in this study shows no indication that Fe_2O_3, TiO_2, or B_2O_3 have any impact on the dielectric loss tangent at 10 GHz within the impurity ranges (see Table 1).

Summary

The data presented here suggests that Na_2O, CaO, SiO_2, and Li_2O are the main impurities that affect the dielectric loss tangent at 10 GHz. The dielectric loss tangent can be reduced from 3.5 x 10^{-3} to 4.4 x 10^{-4} by avoiding/removing the mentioned impurities.

However, more detailed investigations are necessary to fully understand the effects of single impurities and cross-effects of different impurities with each other and how they influence the dielectric loss tangent over a wider range of frequencies of alumina.

About the authors

Nils Rosenberger and Marius Schustereder are global technical director and application & market development manager, respectively, at Almatis GmbH. Contact Rosenberger at nils.rosenberger@almatis.com.

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