**Ba$_{33}$Zn$_{22}$Al$_8$O$_{67}$ with a Framework of ([O(Zn/Al)$_4$]/Ba)(Zn/AlO$_4$)$_4$ Motifs**

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**ABSTRACT:** Single crystals of a new oxide, Ba$_{33}$Zn$_{22}$Al$_8$O$_{67}$ (melting point = 1452 K), were grown in a melt-solidified sample prepared by heating a compact of a BaCO$_3$, ZnO, and Al$_2$O$_3$ mixed powder in a dry air. Ba$_{33}$Zn$_{22}$Al$_8$O$_{67}$ can be handled in dry air, but it decomposes into carbonates, hydroxides, and hydrates in humid air. Single-crystal X-ray structure analysis clarified that Ba$_{33}$Zn$_{22}$Al$_8$O$_{67}$ crystallizes in a cubic cell (a = 16.3328 (3) Å, space group F23) having a three-dimensional Zn/AlO$_4$ framework in which {([OZn$_4$]/Ba)(Zn/AlO$_4$)$_4$} motifs are connected to each other by bridging Zn/AlO$_4$ tetrahedra. A Ba atom or a [OZn$_4$] cluster is statistically situated at the center of the motif with a probability of 0.5. Motifs of another type, {([O(Zn/Al)$_4$]/Ba)(Zn/AlO$_4$)$_4$}, are isolated from the Zn/AlO$_4$ framework. These motifs, {([OZn$_4$]/Ba)(Zn/AlO$_4$)$_4$} and {([O(Zn/Al)$_4$]/(Zn/AlO$_4$)$_4$}, are alternately arranged along the a axis like a checkered cube, and Ba atoms are situated between the motifs. A linear thermal expansion coefficient of 10.4 × 10$^{-6}$ K$^{-1}$ was measured in an Ar gas flow at 301–873 K for a sintered Ba$_{33}$Zn$_{22}$Al$_8$O$_{67}$ polycrystalline sample with a relative density of 73%. A relative permittivity of 31 and a temperature coefficient of 1.5 ppm K$^{-1}$ at 301 K were obtained for another sintered sample (relative density = 70%) in a dry airflow. The electrical conductivity at 1073 K and the activation energy for conduction at 923–1073 K measured for the sintered samples in dry and wet airflows were 6.2 × 10$^{-7}$ S cm$^{-1}$ and 0.65 eV and 2.9 × 10$^{-6}$ S cm$^{-1}$ and 0.59 eV, respectively.

**1. INTRODUCTION**

In many metal oxides, an M-centered oxygen tetrahedron (MO$_4$), in which a cation (M$^+$) is coordinated by four oxide anions (O$^2$), is one of the important building blocks of their crystal structures, and chains, layers, rings, and networks are constructed by sharing the vertex O$^2$-ions of the MO$_4$ tetrahedra. In the case of silicates and phosphates containing SiO$_4$ and PO$_4$ tetrahedra, only two MO$_4$ tetrahedra can share a single vertex O$^2$- because of the high valences of the M cations Si$^{4+}$ and P$^{5+}$. However, in the case of MO$_4$ with lower-valence cations such as Zn$^{2+}$, more than two MO$_4$ tetrahedra can share a single vertex O$^2$- when a vertex O$^2$- is shared with four lower-valence MO$_4$ tetrahedra. When a vertex O$^2$- is shared with four MO$_4$ tetrahedra, an O$^2$-centered cation tetrahedron, [OM$_4$]$,^+$, can also be considered as a structural unit. Recently, a systematic classification of some metal oxides having a structural component with an O$^2$-centered Zn tetrahedron, [OZn$_n$], has been proposed. [OZn$_n$]$_n$-centered motifs of ([OZn$_n$]$_n$)(MO$_4$)$_{3n}$ are formed via the coordination of several MO$_4$ to a [OZn$_n$] tetrahedron, and cations of alkali- and alkaline-earth-metal elements are located between the motifs. Bakakin and Seryotkin proposed two categories based on the valences of the [OZn$_n$]-centered motifs. The first category comprises lower-valence motifs such as ([OZn$_n$]$_n$)(P or AsO$_4$)$_{3n}$, included in alkali-metal phosphate/arsenate hydrates such as K$_2$Zn$_5$(PO$_4$)$_4$(H$_2$O)$_3$, Cs$_2$Zn$_5$(PO$_4$)$_4$(H$_2$O)$_3$, and Li$_2$Zn$_5$(AsO$_4$)$_4$(H$_2$O)$_3$. The second category comprises the higher-valence motifs {([O(Zn/Al)$_4$]/Ba)(Zn/AlO$_4$)$_4$}$_{14}$ and {([OZn$_n$]$_n$)(Al$_{0.87}$Zn$_{0.13}$)O$_4$}$_{18.4}$, included in transition-metal aluminates and gallates such as tululite (Ca$_{14}$(Fe$_{3+}$,Al)(Al$_{1.8}$Zn$_{0.2}$)O$_{35.25}$) and Ca$_4$Al$_2$Zn$_4$O$_{15.5}$. In the present study, a new compound having {([OZn$_n$]$_n$)(Ba$_{0.3}$)(Zn$_{0.67}$/Al$_{0.33}$)O$_4$}$_{18.7}$ and {([O(Zn/Al)$_4$]/Ba$_{0.3}$)(Zn$_{0.67}$/Al$_{0.33}$)O$_4$}$_{18.4}$ motif was found in the Ba–Zn–Al–O system. A [OZn$_n$]$_n$ tetrahedral unit or Ba atom is located at the center of the {([OZn$_n$]$_n$)(Ba$_{0.3}$)(Zn$_{0.67}$/Al$_{0.33}$)O$_4$}$_{18.7}$ motif with a probability of 0.5. The synthesis, crystal structure, thermal expansion, and electronic properties of the new oxide are reported.

**2. RESULTS AND DISCUSSION**

**2.1. Crystal Structure.** The chemical composition measured by electron microprobe analysis (EPMA) for the single-crystal fragment obtained from the transparent part of...
the melt-solidified sample was Ba 63(1), Zn 19(1), Al 2.7(4), and O 15(1) mass % (total 99.7(1) mass %). X-ray diffraction (XRD) spots were indexed using a cubic lattice parameter \( a = 16.3328(3) \) Å. The possible space groups suggested by systematic extinction rules were \( Fm\bar{3}, F23, F\bar{4}3m, F\bar{m}3m, F\bar{4}32 \). The crystal structure was analyzed using a model of space group \( F23 \) having three Ba sites (Ba1–3), one mixed site (Ba4/01) in which Ba and O statistically occupy, one Zn site (Zn1) that coordinates to the O1 site, four Zn/Al sites (Zn/Aln \( n=2–5 \)) statistically occupied by Zn and Al, and five O sites (O2–6). A Ba:Zn/Al:O atomic ratio of 66:44:16:134 was obtained through refinement of the occupancies for Zn1, Zn/Al2–5, and Ba4/O1. This ratio corresponds to a composition of Ba 62.4, Zn 19.8, Al 3.0, and O 14.8 mass %, consistent with the EPMA results within the experimental error. On the basis of these results, the chemical formula of the new oxide was determined to be \( \text{Ba}_{33}\text{Zn}_{22}\text{Al}_8\text{O}_{67} \) (\( Z = 2 \)).

The occupancy parameters for Ba and O in Ba4/O1 (multiplicity and Wyckoff letter, 4c) and Zn in Zn1 (16e) converged to ~0.5 and were therefore fixed at 0.5 in the following refinement. At this stage, the R1 (all data) was 3.5% with large anisotropic displacement parameters for Ba3, and then the Ba3 site was split into two sites, Ba3a (16e) and Ba3b (16e). The occupancies of these two split sites also became ~0.5 and thus the occupancies of Ba3a and Ba3b were also fixed at 0.5 and 0.5. The shape of the anisotropic displacement ellipsoid for O4 situated at the original position of 16e was flat and spread on (111) planes. Therefore, O4 was placed at a general position (48k) with an occupancy of 0.3333. The R1 (all data) for the final refinement was 1.2%. A summary of the single-crystal X-ray structure analysis results is presented in Table 1. The coordination, occupations, and equivalent isotropic atomic displacement parameters are listed in Table 2. The anisotropic atomic displacement parameters and the interatomic distances are listed in Tables S1 and S2 (Supporting Information).

As shown in Figure 1, the Zn\(^{2+}\) and Al\(^{3+}\) cations in Zn1, Zn/Al2, Zn/Al3, Zn/Al4, and Zn/Al5 are coordinated by four O atoms, forming Zn-centered and Al/centered O tetrahedra (ZnO\(_4\)) and Zn/AlO\(_4\)\(_\alpha\) respectively. The average atomic distances are 1.974 Å (Zn–O1), 1.968 Å (Zn–Al2–O), 1.865 Å (Zn–Al3–O), 1.908 Å (Zn–Al4–O), and 1.943 Å (Zn–Al5–O) (Table S2). These distances are plotted on a line connecting the interatomic distances for Al–O and Zn–O calculated from Shannon’s effective ionic radii (Figure 2).

Motifs composed of ZnO\(_4\) and Zn/AlO\(_4\) tetrahedra are recognized in the structure of \( \text{Ba}_{33}\text{Zn}_{22}\text{Al}_8\text{O}_{67} \). In a motif, four Zn/Al2O6(O2)\(_3\) tetrahedra connect to each other by sharing an O atom at O6; in addition, four Zn/Al3O6(O2)\(_3\) tetrahedra connect to the central Zn/Al2O6(O2)\(_3\) tetrahedron by sharing an O atom at O2 (Figure 1a). This motif can be explained with an O6-centered (Zn/Al2)4 tetrahedron, \{O6(Zn/Al2)4\}, which is indicated with dotted red lines in this figure, and four Zn/Al3-centered (O2)4 tetrahedra, \{O6(Zn/Al2)4\}, around the \{O6(Zn/Al2)4\} tetrahedron. This motif is expressed as \{O6(Zn/Al2)4\}\{Zn/Al3O6(O2)3\}. The other motifs, \{Ba4[Zn/Al4O6(O2)3]\} and \{O1(Zn1)4[Zn/Al4O6(O2)3]\}, statistically exist at the same position with 50% probability and are collectively denoted as \{Ba4/O1(Zn1)4[Zn/Al4O6(O2)3]\}. Ba4 is at the center of the \{Ba4[Zn/Al4O6(O2)3]\} motif (Figure 1b). The O1-centered Zn1 tetrahedron, \{O1(Zn1)4\}, is at the center of the \{O1(Zn1)4[Zn/Al4O6(O2)3]\} motif and also surrounded by four Zn/Al4O5(O3)\(_\alpha\) tetrahedra (Figure 1c). The O atom at O3 is shared by Zn/Al4O5(O3)\(_\alpha\) and Zn101(O3)\(_\alpha\) tetrahedra. The atomic arrangement of the latter motif, \{O1(Zn1)4[Zn/Al4O6(O2)3]\}, is similar to that of \{O6(Zn/Al2)4[Zn/Al3O6(O2)3]\}. A motif containing an O-centered cation-coordinated tetrahedron at the center of the motif has also been reported for \( \text{Ca}_{33}\text{Zn}_{22}\text{Al}_8\text{O}_{67} \) (Figures 2 and 3). Using these motif expressions, we can write the crystal structure of \( \text{Ba}_{33}\text{Zn}_{22}\text{Al}_8\text{O}_{67} \) as \( \{\text{Ba}_{63}(\text{Zn}_{0.92}\text{Al}_{0.08})_4\}\{\text{Ba}_{8.5}(\text{OZn}_{4.5}\text{Al}_{0.5})_4\}\{\text{O}_{(\text{Zn}_{0.55}\text{Al}_{0.45})}\}\{\text{Zn}_{0.62}\text{Al}_{0.38}\text{O}_{4.4}\}_4\). The formal charges of the motifs depend on the occupancies of Zn and Al and are in the range \( \{\text{OAI}\}_4^{18–22} \) to \( \{\text{ZnO}\}_4^{18–22} \) and \( \{\text{OAI}\}_4^{18–22} \) to \( \{\text{BaZnO}\}_4^{18–22} \). The largest difference is \( \{\text{OAI}\}_4^{18–22} \) to \( \{\text{BaZnO}\}_4^{18–22} \). These motifs can be related to the \( \{\text{MnO}_4\}_4^{18–22} \) motif categorized as having a valence-matching motif with formal charges from \(-14\) to \(-19\).

The \{Ba4/O1(Zn1)4[Zn/Al4O6(O2)3]\} motifs are connected to each other via Zn/Al5(O5)\(_\alpha\) regular tetrahedra by sharing O atoms at O5 of Zn/Al5(O5)\(_\alpha\) and Zn/Al4O5(O3)\(_\alpha\) tetrahedra of the motifs, forming a three-dimensional network (Figure 3). The \{O6(Zn/Al2)4[Zn/Al4O6(O2)3]\} motifs are isolated from this network. As shown in Figure 3, the \{O6(Zn/Al2)4[Zn/Al4O6(O2)3]\} motifs form a three-dimensional network consisting of \{Ba4/O1(Zn1)4[Zn/Al4O6(O2)3]\} and \{Ba4/O1(Zn1)4[Zn/Al4O6(O2)3]\} motifs.
are alternatingly arranged along the a-axis direction like a checkered cube. Ba atoms at Ba1, Ba2, Ba3a, and Ba3b are aligned around the motifs.

The Ba atoms at Ba1 are in a cuboid arrangement (Figure 4) and are coordinated by eight O atoms with an average Ba1−O distance of 2.903 Å (Table S2). Four O atoms are at O2 of the {[O6(Zn/Al2)4][Zn/Al3O4]4} motif, and the other four O atoms are at O3 of the {Ba4/O1Zn14}[Zn/Al4O4]4 motif. Ba2 is in a distorted gyrobifastigium of eight O atoms: four O atoms at O2 and O4 of two {[O6(Zn/Al2)4][Zn/Al3O4]4} motifs and four O atoms at O3 and O5 of two {Ba4/O6(Zn/Al5)4}[Zn/Al3O4]4 motifs.

Ba3 is in the antiprism of three O atoms at O3 of one {Ba4/O1Zn14}[Zn/Al4O4]4 motif and three O atoms at O4 of three {[O5(Zn/Al1)4][Zn/Al2O4]4} motifs.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for Ba33Zn22Al8O67

| label  | site     | occupancy | x          | y          | z          | U(eq)  |
|--------|----------|-----------|------------|------------|------------|--------|
| Ba1    | 24g      | 1         | 0.00205(3) | 0.25       | 0.25       | 0.01810(6) |
| Ba2    | 24f      | 1         | 0.20530(2) | 0          | 0          | 0.01250(5) |
| Ba3a   | 16e      | 0.5       | 0.40608(4) | 0.40608(4) | 0.40608(4) | 0.0176(2) |
| Ba3b   | 16e      | 0.5       | 0.42322(4) | 0.42322(4) | 0.42322(4) | 0.0318(3) |
| Ba4/O1 | 4c       | 0.5/0.5   | 0.25       | 0.25       | 0.25       | 0.0294(4)  |
| Zn1    | 16e      | 0.5       | 0.31831(4) | 0.31831(4) | 0.31831(4) | 0.0089(2)  |
| Zn/Al2 | 16e      | 0.9211/0.0789(3) | 0.82114(3) | 0.82114(3) | 0.82114(3) | 0.0120(2)  |
| Zn/Al3 | 16e      | 0.4204/0.5796(3) | 0.63625(4) | 0.63625(4) | 0.63625(4) | 0.0119(2)  |
| Zn/Al4 | 16e      | 0.6712/0.3258(3) | 0.13649(3) | 0.13649(3) | 0.13649(3) | 0.0109(2)  |
| Zn/Al5 | 4a       | 0.937/0.063(2) | 0          | 0          | 0          | 0.0115(2)  |
| O2     | 48h      | 1         | 0.1128(2)  | 0.2465(2)  | 0.6128(2)  | 0.0215(6)  |
| O3     | 48h      | 1         | 0.1117(2)  | 0.1116(2)  | 0.2477(2)  | 0.0195(6)  |
| O4     | 48h      | 0.3333    | 0.577(4)   | 0.581(2)   | 0.561(3)   | 0.025(8)   |
| O5     | 16e      | 1         | 0.0687(2)  | 0.0687(2)  | 0.0687(2)  | 0.0165(8)  |
| O6     | 4d       | 1         | 0.75       | 0.75       | 0.75       | 0.017(2)   |

*aUeq = 1/3 (U11 + U22 + U33).*

Figure 1. Atomic arrangements of the (a) {[O6(Zn/Al2)4][Zn/Al3O4]4} motif, (b) {Ba4[Zn/Al4O4]4} motif, and (c) {[O1Zn14][Zn/Al4O4]4} motif. The dotted red lines in (a,c) indicate the central tetrahedron of {[O6(Zn/Al2)4] and [O1Zn14], respectively.

Figure 2. Interatomic distances for Zn/Al−O versus Zn occupancy in tetrahedral sites. Solid circles are Zn/Al−O distances in Ba33Zn22Al8O67, and open squares are Al−O and Zn−O interatomic distances calculated from Shannon’s effective ionic radii.

Figure 3. Crystal structure of Ba33Zn22Al8O67 illustrated for 0 < z < 0.5 with {[O6Zn/Al24][Zn/Al3O4]4} motifs and statistical motifs of {Ba4/[O1Zn14][Zn/Al4O4]4}.
with Ba3a−O and Ba3b−O average distances of 2.693 and 2.714 Å, respectively. These Ba−O distances are comparable to the average Ba−O distances of BaAl2O4 (2.897 Å)13 and BaZnO2 (2.785 Å)14 in six-fold coordination.

Ba4 is at the center of the {Ba4[Zn/Al4O4]} motif and in a cuboctahedron (Figure 4) surrounded by 12 O atoms. The Ba4−O(×12) distance is 3.197 Å, which is the longest of the Ba−O distances in O polyhedra of Ba33Zn22Al8O67 and is similar to the distances of 3.18, 3.16, and 3.18 Å reported for Ba in similar cuboctahedra with 12-fold coordination environments in BaNdGaZn3O7,15 BaCaCo3ZnO7,16 and BaCa(Zn1−xFex)4O7,17 respectively.

2.2. Al Atom Distribution and Local Structure. 1-dimensional 27Al DE-MAS NMR spectrum of Ba33Zn22Al8O67 (Figure 5a) reveals two resonance peaks at 79.2 and 84.9 ppm, which are characteristic of Al in four-fold coordination with O (i.e., AlO4). The positions of the peaks (chemical shifts, δ) are similar to those in the spectrum of Al-doped ZnO powder.18−20 In previous studies, the chemical shifts were interpreted as some of the tetrahedral Zn sites being substituted by Al atoms, where the observed Al environment can be described as a Q4(4Zn) configuration. In the present study, Qn(mT) is defined as follows: Q is the tetrahedral Al, n is the degree of condensation, T is a second neighboring tetrahedral atom (Al or Zn), and m is the number of bonding T atoms via oxygen.

Because the two resonance peaks overlap each other substantially in Figure 5a, we recorded the corresponding 27Al 3QMAS spectrum. Two independent resonance peaks, A and B, were observed (Figure 5b), suggesting that Al atoms in Ba33Zn22Al8O67 can be classified into two local AlO4 environments. The spectral widths along the F2 axis for both peaks are elongated by the substantial quadrupolar interaction. In addition, the large resonance peak A is broadened along the F1 axis, indicating that several resonance peaks associated with different local structures are overlapped.

For convenience, quadrupolar fitting was carried out for the resonance peaks. Several fitting parameters are summarized in Table S3. The resonance peak A was deconvoluted into three components at δiso = 80.9, 81.8, and 83.7 ppm. Given the low Al content in Ba33Zn22Al8O67, most of the peak A is attributable to a Q4 (3Zn or 4Zn) configuration surrounded only by Zn atoms. However, the presence of the three components for peak A suggests Al−O−Al connectivity between adjacent AlO4 tetrahedra,21 the configuration of which is represented as Qn(mAl, (3−m)Zn) (m = 1, 2, 3) and Qn(mAl, (4−m)Zn) (m = 1, 2, 3, 4). The true m value is unclear at present; however, the results suggest that Al atoms may be present simultaneously at adjacent Zn/Al sites to the extent that the occupancy allows.

By contrast, the resonance peak B was fitted by a single peak at δiso = 88.3 ppm, which is not a usual δ value for AlO4 and is shifted considerably to the downfield side as shown in Figure 5b. The same tendency that the chemical shift, δ, increases with increasing Al−O−Ba connectivity for AlO4 tetrahedra, which has been reported in the spectra of Al2O3−BaO glasses.22 The four crystallographic Zn/Al sites determined by the structural analysis must be assigned to the two peaks A and B; however, at present, we could not unambiguously...
determine the distribution of Al atoms because all of the Al atoms partially occupy the Zn sites. However, peak B might be assignable to Q1(0Al, 1Zn) or Q1(1Al, 0Zn) of Zn/Al4 in the {Ba4[Zn/Al4O4]4} motif with a probability of 0.5, three of whose bridging O atoms connect to Ba at Ba4. The A peaks, as previously mentioned, might be assignable to Q3(mAl, (3-m)Zn) (m = 1, 2, 3) and Q4(mAl, (4-m)Zn) (m = 1, 2, 3, 4) for the other Zn/Al sites: Zn/Al2, Zn/Al3, and Zn/Al5 in the {[O6(Zn/Al2)4][Zn/Al3O4]4} motif and Zn/Al4 in the {[O1(Zn1)4][Zn/Al4O4]4} motif with a probability of 0.5.

Ultra-high-field solid-state 27Al and 67Zn NMR measurements would be helpful for further elucidating the distributions of Al and Zn atoms; however, such measurements are left for future work.

2.3. Polycrystalline Sample Preparation. Figure 6a shows a powder XRD pattern for a disk sample prepared by heating the compact of the starting mixture with a Ba/Zn/Al molar ratio of 33:22:8 at 1323 K for 2 h under dry flowing air. The diffraction angles and relative intensities of the XRD peaks in the pattern are explained by the crystal structure of Ba33Zn22Al8O67, except for a few unidentified small peaks indicated with asterisks (*) in the figure. When the sample was left in air with a humidity of 60% for 1 day, it reacted with H2O and CO2 in air and decomposed into BaCO3, BaZn(OH)4·H2O, and BaO2(H2O)2 (Figure 6b). The handling and storage of Ba33Zn22Al8O67 must be carried out in a dry atmosphere.

2.4. Melting Point and Thermal Expansion. The melting temperature of Ba33Zn22Al8O67, as measured by differential thermal analysis (DTA) of the fragments of the disk sample, was 1452 K. A linear thermal expansion coefficient of 10.4 × 10^{-6} K^{-1} from 301 to 873 K was obtained for a polycrystalline square-rod sample (13.80 mm × 3 mm × 3 mm, ∼73% relative density). This coefficient is similar to those reported for alumina [(7–9) × 10^{-6} K^{-1}] and cubic zirconia [(8–10) × 10^{-6} K^{-1}].

2.5. Electronic Properties. The temperature dependence of the electrical resistivity was measured for the disk sample of Ba33Zn22Al8O67 (5 mm in diameter, 2.2 mm in thickness, and ∼70% relative density); the results are shown in Figure 7. The electrical conductivities obtained by the impedance method at 1073 K under dry and wet airflows were 6.2 × 10^{-7} and 2.9 × 10^{-6} S cm^{-1}, respectively. These values agree with the conductivities measured by the direct current two-terminal method at the same temperature. The activation energies for the conductivity in the temperature range from 923 to 1073 K under dry and wet airflows were estimated to be 0.65 and 0.59 eV, respectively. After the conductivity measurement in the wet airflow in the temperature range 923–1073 K, the samples were subjected to the dry airflow and their conductivities decreased to the same values previously measured in the dry airflow. The increase in the conductivity of the sample in the wet airflow might be attributable to the contribution of proton conduction.

The relative permittivities of the disk sample measured at 1 MHz in the temperature range 298–400 K and with the sample in the dry airflow are shown in Figure 8. The relative
permittivity at 301 K was 31. The dielectric loss, tan δ, was approximately constant and less than 0.01 (Figure 8). The temperature coefficient of the relative permittivity change at 1 MHz in the dry airflow was approximately 15 ppm K⁻¹ at 301 K.

3. SUMMARY

A novel quaternary compound, Ba₃₃Zn₂₂Al₈O₆₇, having a three-dimensional network structure formed by sharing the vertex O atoms of Zn/AlO₄ tetrahedra, was synthesized in the Ba–Al–Zn–O system. The melting temperature of the compound, as measured by DTA, was 1452 K. A single crystal obtained from a melted and solidified sample was used for XRD measurements. The crystal structure of Ba₃₃Zn₂₂Al₈O₆₇ (cubic, a = 16.3372 Å, space group F23) was explained on the basis of motifs of \( \{ [OZn_4] [Zn/AlO_4]_4 \} \) and \( \{ [O(Zn/Al)_4] [Zn/AlO_4]_4 \} \). An O-centered Zn tetrahedron \( [OZn_4] \) or Zn/Al tetrahedron \( [O(Zn/Al)_4] \) is present at the center of the motifs. The \( [OZn_4] \) tetrahedron is statistically replaced by a Ba atom with a probability of 0.5 and another motif of \( \{ [Ba] [Zn/AlO_4]_4 \} \) or \( \{ [Ba] [Zn/AlO_4]_4 \} \) motifs and the \( [O(Zn/Al)_4] \) or \( [Ba] [Zn/AlO_4]_4 \) motifs alternatingly align along the \( a \)-axis direction, and Ba atoms are situated between the motifs. The \( ^{27}\text{Al} \) MAS NMR spectra show two types of resonance peaks with a \( \delta_{\text{d}} \) of ~82 ppm (peak A) and \( \delta_{\text{d}} \approx 88.3 \) ppm (peak B). In addition, \( ^{27}\text{Al} \) 3QMAS NMR spectra show that peak B corresponds to a single Al site, whereas the broad peak A represents multiple Al sites. The two peaks could be assigned to the Al(OZn)₄ or \( Q^1(0\text{Al} 1\text{Zn}) \) or \( Q^1(1\text{Al} 0\text{Zn}) \) configurations connecting to the Ba site (peak B).

To the best of our knowledge, the statistical substitution of a Ba atom for an O-centered Zn tetrahedron \( [OZn_4] \) has not been reported in any other oxides. Polycrystalline samples of Ba₃₃Zn₂₂Al₈O₆₇ were prepared by solid-state reaction in a dry air atmosphere coexistence of the single crystals was analyzed by EPMA (JEOL JXA-8200). A single-crystal fragment was sealed in a glass capillary with a 0.5 mm inner diameter in the glovebox, and single-crystal XRD measurements were performed (Bruker D8 QUEST; Mo Ka). The crystal structure was analyzed using the APEX III and SHELXTL-2014 programs and was visualized using the VESTA program.

After BaCO₃, ZnO, and Al₂O₃ powders were weighed out in a Ba:Zn:Al cation molar ratio of 33:22:8, which was determined by single-crystal X-ray structure analyses and EPMA using the single crystal sample of the new oxide, the powders were mixed and pressed into disk-shaped compacts with a diameter of 6 mm and into cuboids with dimensions of 3 mm × 3 mm × 14 mm using molds and a uniaxial pressurizer (~5 MPa). The compacts were placed in an alumina crucible with a lid (Nikkato, SSA-S, 99.6%, 46 mm outer diameter, and 36 mm height) and heated to 1323 K for 3 h in a dry airflow at a rate of 50 mL min⁻¹. The dry airflow was prepared by passing air through a silica-gel-filled container (approximately 30% relative humidity) using an aerator pump (Asone, SA-2000S). The temperature was maintained at 1323 K for 2 h and then the power to the furnace was shut off. After cooling to room temperature, a part of the sample was crushed into powder for XRD analysis (Bruker D2 Phaser, Cu Kα). The crystalline phases that generated peaks in the XRD patterns were identified using TOPAS software.

The local structure around Al atoms was investigated using solid-state magic angle spinning (MAS) NMR measurements. An \( ^{27}\text{Al} \) directly excited (DE) MAS NMR spectrum was recorded under a 9.4 T magnetic field (Bruker Biospin K.K., Japan, AVANCEIII 400WB) at a resonance frequency of 104.267 MHz using a 3.2 mm VT-MAS probe with a zirconia rotor. An \( ^{27}\text{Al} \) 3QMAS two-dimensional (2D) NMR spectrum was also recorded using a \( z \)-filter and a \( \{H\} \) decoupling sequence. The rotor spinning rate was set at 24 kHz for the acquisition of both spectra. A 1.0 M AlCl₃ solution was used as a secondary reference material for the chemical shift of \( ^{27}\text{Al} \) nuclei.

DTA (NETZSCH, STA2500) was carried out for small fragments of a crushed disk-shaped sample. The fragments were placed in an alumina cell with a diameter of 5 mm and a height of 5 mm. A dilatometer (DIL; Bruker, TD5000SA) was used to measure the linear thermal expansion of the square-rod-shaped sample in the temperature range from 301 to 873 K (ramp rate of 20 K min⁻¹) using an Ar flow at 50 mL min⁻¹ (Taiyo Nippon Sanso, 99.9999%). The impedance of the disk sample was measured in the temperature range from 873 to 1073 K in dry and wet airflows with a flow rate of 200 mL min⁻¹ using an LCR meter (Hioki, 3536) and Au electrodes were prepared by heating Au paste (Furuya Metal) at 1073 K for 30 min. The wet airflow was prepared by bubbling air through water at 298 K (~3.2 kPa saturated water vapor pressure) using the aerator pump. The electrical conductivity was determined from Cole–Cole plots of the recorded impedance data. The resistivity was confirmed via the direct current two-terminal method using a digital multimeter (Keithley, 2000). The capacitance and dielectric loss for the disk sample were measured at 1 MHz from 298 to 400 K using the LCR meter.
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Notes
The authors declare no competing financial interest.

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