Controllable antimicrobial properties of silver ion-exchanged niobate and tantalate compounds

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ABSTRACT
We designed pyrochlore-type potassium niobate (KN) and potassium tantalate (KT) by introducing silver ions to improve their antibacterial efficiency. KN and KT samples were used as ion-exchangeable parent compounds, and molten AgNO₃ was used for the ion-exchange reaction. The formation of silver ion-exchanged compounds with various molar ratios, which was investigated by X-ray diffraction (XRD), indicated a clear structural transformation of KN after complete ion-exchange. The antibacterial efficacy of these samples was investigated using the colony count method, and the relative antibacterial activity was compared based on the area of the inhibition zone. The results indicated that silver ion-exchanged samples with molar ratios of Ag/Nb = 0.05, 0.44, 0.67, and Ag/Ta = 0.07, 0.44 0.64 exhibited complete (100%) antibacterial activity against Staphylococcus aureus (gram-positive) and Escherichia coli (gram-negative). Among the silver ion-exchanged samples, KAN1 and KAT1 exhibited the highest antibacterial activities because of the controlled release of Ag⁺ ions through their tunnel structure. In this study, it was found that tunable silver-release properties of pyrochlore-type niobate and tantalate enable the optimization of discharged Ag⁺ ions, which inhibits the bacterial efficacy in different extents, thus suggesting their use in various biomedical applications.

1. Introduction
The human society is continuously threatened by biological contaminations, such as bacteria, parasites, and viruses [1]. Therefore, the realization of new materials with favorable safety and strong antibacterial properties has been extensively sought [2–4]. Recently, a variety of antibacterial materials, such as carbon-based nanomaterials, cationic polymers, antibacterial peptides, and inorganic materials, have been extensively studied [5–8]. Among these, inorganic materials with antibacterial properties are extremely important owing to their wide range of applications, including applications in building materials, electrical appliances, medical materials, fabrics, and cosmetics [9]. Furthermore, these antibacterial agents have received considerable attention owing to their safety, good stability, wide range of antibacterial activity, and prolonged activity compared with that of organic antibacterial agents [10]. Although several metal ions (Ag⁺, Cu⁺, Zn²⁺, etc.) have been used in antimicrobial ceramics, silver (Ag)-containing materials have gained considerable attention because of their strong antibacterial activity, low cytotoxicity and immunological response [11–14]. Therefore, Ag-containing ceramic materials have multiple potential biomedical applications, such as drug delivery, medical imaging and molecular diagnostic [15,16]. They also used in implantable orthopedic biomaterials, fabrication of artificial joint replacements, wound dressing and burn wound treatment [17,18]. Moreover, Ag-containing materials have exerted strong bactericidal effects on more than 12 species of bacteria, including S. aureus and E. coli [19].

The variety of techniques, such as wet chemical methods, sol-gel methods, thermal or cold spraying techniques, ion-exchange methods, and doping or loading methods, are used to synthesize Ag-containing antibacterial materials [20–22]. Among these methods, the ion-exchange method has been proven to be a simple way to regulate the amount of silver content in potassium tantalate (KT) and potassium niobate (KN) with the pyrochlore-type structure [23]. Although many studies have focused on Ag-containing antibacterial materials, to the best of our knowledge, there have been no studies on the antibacterial properties of Ag-incorporated pyrochlore-type niobate and tantalate compounds. In this study, Ag ions were incorporated into KN and KT structures using small molar ratios and gradually increased to obtain completely ion-exchanged samples. Our aim was to obtain controllable antibacterial properties employing these different ion-exchanged compounds.
and compare their efficiency against *E. coli* and *S. aureus* using the colony count method and inhibition zone method.

2. Experimental section

2.1. Materials and synthesis method

Pyrochlore-type KN and KT were synthesized by a hydrothermal reaction using niobium pentoxide (Nb$_2$O$_5$), tantalum pentoxide (Ta$_2$O$_5$), and potassium hydroxide (KOH) as starting materials according to a previously described method [23]. All chemicals were purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan). Ag ions were doped into KN and KT by an ion exchange process using small molar ratios and gradually increased to obtain completely ion-exchanged samples. To achieve this, the parent compounds (KN and KT) were mixed with different molar ratios of AgNO$_3$, and the resultant mixtures were heated at 300°C for 6 h. Moreover, the ion-exchanged molar ratios of AgNO$_3$/ KN or KT were 0.1, 0.5, and 5.0. The products were filtered, centrifuged several times, and dried at 60°C for 24 h. The final products were denoted as KAN1, KAN2, and KAN3 for KN ion-exchange and KAT1, KAT2, and KAT3 for KT ion-exchange.

2.2. Characterization

The products were identified by X-ray diffraction (XRD), which was performed using an X-ray diffractometer (MiniFlex 600, Rigaku Co., Tokyo, Japan) equipped with CuKα radiation (λ = 0.15418 nm). The morphology, particle size, and chemical composition of the samples were determined using scanning electron microscopy (SEM, JEOL JSM6500) and energy dispersive X-ray spectroscopy (EDX). The optical band gaps were estimated via UV-visible diffuse reflectance spectroscopy (UV–vis DRS, JASCO V–550) and were converted using the Kubelka-Munk function. The amount of Ag$^+$ ions discharged from the powder samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Hitachi SPS3520UV-DD), and surface plasmon resonance (SPR) of silver nanoparticles (NPs) was measured by UV–vis DRS.

2.3. Antimicrobial test

Primary antimicrobial activity was evaluated by the colony count method using *E. coli* (NBRC 3972) and *S. aureus* (NBRC 12732). The bacteria were obtained from National Institute of Technology and Evaluation (NITE), Biological Resource Center (NBRC) and cultured in soybean–casein digest broth with lecithin polysorbate (SCDLP) medium overnight at 37°C in a vibration incubator (150 rpm). To calibrate the initial concentration, the bacterial solution was diluted to 5 x 10$^5$ CFU/ml (colony-forming units per ml). Subsequently, bacterial solutions (0.1 ml) were pipetted into a centrifuge tube with 4.9 ml powder samples soaked in a SCDLP solution, wherein the bacterial solution was filtered using 0.1 g of the powder sample vibrating at 150 rpm overnight at 37°C. After 24 h, 0.1 ml of the resultant bacterial solution was extracted, and bacteria were grown in Standard Methods Agar (SMA) medium overnight at 37°C. The surviving colonies were recorded by counting the number of bacterial colonies on the petri dish (Petri dish 60 mm; Ishi, Japan) and multiplied by the dilution factor to determine the CFU/ml. The percentage of bacteria cell reduction (R(%) was calculated using the following equation (Equation (1)).

$$ R(\%) = \frac{CFU_{control} - CFU_{sample}}{CFU_{control}} \times 100 $$

where $CFU_{control}$ is the number of viable colonies in the control plate (without sample) and $CFU_{sample}$ is the number of viable colonies in the sample plate (with sample). The average value of antibacterial activity was determined in triplicate.

Furthermore, the area of the inhibition zone was determined to calculate the antibacterial efficiency and compare the activity among different samples. In this method, the disks (specimen size: 10 mm in diameter and 2.0 mm in height) prepared using powder samples (0.3 g) were sterilized and placed over the solidified agar medium carefully. Afterward, 1 ml of the bacterial solution with an initial concentration of 10$^6$ CFU/ml was mixed with condensed nutrient agar (9 ml), and the resultant solution was evenly poured over the disks. Thereafter, the plates were incubated at 37°C for 2 d. Subsequently, the relative antibacterial activity was determined by measuring the inhibition zones around the disks. The area of the zones was calculated using ImageJ software (National Institute of Health, MD), and the relative inhibition zone was calculated using the following equation (Equation (2)).

$$ \text{Relative inhibition zone} = \frac{(A_1 - A_2)}{A_2} $$

where $A_1$ is the area of the inhibition zone, and $A_2$ is the area of the test disk.

3. Results and discussion

3.1. Ion-exchange with Ag$^+$ ion

Three different ion-exchanged molar ratios of niobate and tantalate were used to prepare six samples, which included four Ag-doped and two completely ion-exchanged samples. As shown in Figure 1, single-phase pyrochlore-type $K_{0.63}H_{2.35}NbO_5$, $K_{0.63}H_{2.38}TaO_5$ (KN) and $K_{0.63}H_{2.38}TaO_5$ (KT) were prepared by the hydrothermal method (space group
The SEM images (Figure 2(a-c)) show that KN and its Ag ion-exchanged products possessed an octahedral morphology and a particle size of ~50 μm. Furthermore, the fully ion-exchanged product KAN3 (Figure 2(d)) exhibited irregular particle shapes with sizes of approximately 1–5 μm. In the case of KT (Figure 2(e-h)), it can be inferred that the octahedral morphology was preserved while ion-exchange occurred. Moreover, the particle sizes were approximately 1–5 μm in the case of KT.

The pristine white color of KN and KT samples changed with the exchange of ions, turning yellowish for the KN sample and gray for the KT sample. The band gaps decreased from 3.1 to 2.4 eV for KN and 3.8 to 1.8 eV for KT with the addition of Ag ions in these structures. These band gap fluctuations between the samples can be attributed to the Ag d-orbital association in the hybridized energy levels [26,27].

### 3.2. Antimicrobial properties

The antibacterial activities of Ag ion-exchanged and parent compounds were evaluated by the colony count method and further compared through areas of inhibition zones in disk diffusion tests. The activities evaluated using the colony count method are depicted in Figure 3 and summarized in Figure 4. The results indicated almost 100% antibacterial activity by Ag ion-exchanged KAN1, KAN2, KAN3, KAT1, KAT2 and KAT3 compounds. The parent compounds showed relatively lower antibacterial activity against S. aureus (5.6% and 22% for KN and KT, respectively) (Figure 4). However, KN and KT did not show any antibacterial activity against E. coli. This may be due to differences in the bacterial cell walls of gram-negative and gram-positive bacteria [28]. Gram-negative bacteria such as E. coli possess a cell wall that is slightly thinner than that of gram-positive bacteria such as S. aureus. In the literature, there are several explanations for antibacterial mechanisms, such as metal ion antibacterial, nanoparticle antibacterial, and photocatalytic antibacterial mechanisms [29–31]. In this study, antibacterial tests were conducted under dark conditions; therefore, there was no possibility of photocatalytic reactive oxygen species (ROS) production by the samples and antibacterial activity caused by ROS. Hence, it can be

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**Table 1.** Summary of lattice parameters calculated from XRD data.

| Product | Ion-exchanged mole ratio (Ag/Nb or Ag/Ta) | Lattice parameters (Å) | Ag/Nb or Ag/Ta ratio |
|---------|------------------------------------------|------------------------|----------------------|
| KN      | 0.0                                      | 10.611(2)              | 0.00                 |
| KAN1    | 0.1                                      | 10.600(1)              | 0.05                 |
| KAN2    | 0.5                                      | 10.599(4)              | 0.45                 |
| KAN3    | 5.0                                      | 5.117(2)               | 0.67                 |
| KT      | 1.0                                      | 10.629(4)              | 0.00                 |
| KAT1    | 0.1                                      | 10.623(2)              | 0.07                 |
| KAT2    | 0.5                                      | 10.543(3)              | 0.44                 |
| KAT3    | 5.0                                      | 10.515(2)              | 0.64                 |

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*Figure 1.* XRD patterns of parent and silver ion-exchanged samples.

*Fd-3 m, #227*); these findings are similar to the results of our previous studies [21]. The XRD patterns of the Ag-ion-doped KT and KN structures obtained by ion-exchange methods were denoted by sample names KAT1 and KAT2, and KAN1 and KAN2, respectively. The KAT3 and KAN3 samples were completely ion-exchanged with their corresponding KN and KT parent compounds using excess molten AgNO₃. Although the KAN2 sample showed peaks associated with pyrochlore and fluorite mixed structures, the KAN3 sample yielded a fluorite-type structure with space group *Fm-3 m* (#225), whereas the KAT3 sample did not yield this fluorite-type structure. Previous studies have shown that the ordered pyrochlore structure A₂B₂O₇ can be transformed into disordered fluorite structure by changing the radius ratio (r_A/r_B) and relative stability range of the pyrochlore structure from 1.46 to 1.78 (r_K+ = 1.51 Å, r_Ag+ = 1.28 Å, r_NB₅⁺ = 0.64 Å, r_Ta₅⁺ = 0.64 Å) [24,25]. Thus, the KAN3 structure changed to a fluorite-type structure (r_A/r_B = 2), while the KAT3 structure did not change and remained under investigation. A careful comparison of the XRD patterns suggested that the peak position shifted to some degree toward a higher 2θ value (Figure 1) with silver ion-exchange. These changes were due to the larger K ions replaced by the smaller Ag ions (r_K+ = 1.51 Å, r_Ag+ = 1.28 Å), which further confirmed that the ion-exchange reactions were successful. The values of the lattice parameters at different ion-exchange levels are summarized in Table 1, and it could be clearly seen that the lattice parameters decreased with silver ion incorporation.
assumed that the continuous release of Ag ions and Ag nanoparticles (AgNPs) to exert bactericidal effects for niobate and tantalate compounds. The Ag⁺ ions are well-known antibacterial agents against a wide range of microorganisms which can penetrate cell membranes to slow down the active transportation and bacterial metabolism [32–34]. The control releasing properties of ion-exchanged pyrochlore-type structure is maintaining high antibacterial activity while minimizing the cytotoxicity [35–38]. As a smart material, the tunnel pyrochlore-type structure provided structural tunability and possible silver ion migration pathways from the powdered sample to the liquid medium. These migrated ions can attach to the negatively charged bacterial cell wall by coulombic interactions, which can cause an imbalance in the surface charge around the cell. This electrostatic force and unstable surface charge lead to disruption of the cell wall and plasma membrane, causing cell lysis, cytoplasm leakage and bacterial death [39–41]. Moreover, silver ions are strong nucleic acids binders which uptake into cells via channels of the bacterial cell.
membrane can cause intracellular depletion, cell reproduction and condensing DNA to lose its replication [42]. In addition to metal ions, AgNPs with a relatively high surface area led to bacterial death by creating pits, coating and anchor to the cell surface, preventing normal metabolism in the external environment [43,44]. AgNPs also have the capability to penetrate bacterial cell walls, because of their size and change

|          | KN | KAN1 | KAN2 | KAN3 |
|----------|----|------|------|------|
| **E. coli** | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |
| **S. aureus** | ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |
| **E. coli** | ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) | ![Image](image12.png) |
| **S. aureus** | ![Image](image13.png) | ![Image](image14.png) | ![Image](image15.png) | ![Image](image16.png) |

**Figure 4.** Colony-forming units reflecting the antibacterial activities of Ag ion-exchanged and parent samples.

**Figure 5.** Comparison of inhibition zones between KN and KT silver ion-exchanged samples against (a) *Escherichia coli* and (b) *Staphylococcus aureus* after 48 h incubation.
the structure of cell membrane [45]. Furthermore, previous studies show that size of the AgNPs is one of the major factors influence their antibacterial properties and smaller size of the silver nanoparticles is increase their antibacterial activity [46]. Therefore, 100% of the bacterial cells were killed by the Ag ion-exchanged samples.

The reusability of KAN1 and KAT1 was checked by repeating the experiments three times using the same powder samples for colony counting method against E. coli and S. aureus bacteria. KAN1 reused for three times against E. coli and two times against S. aureus, while KAT1 reused for two times for both E. coli and S. aureus.

The antibacterial effects of the samples were further compared using the inhibition zone method. Figure 5 clearly shows the inhibition zones around the silver ion-exchanged samples. It can be understood that the inhibition zones are dependent on the discharged Ag⁺ concentration, which means that the sizes of the inhibition zones decrease with an increase in Ag⁺ concentration. Figure 6(a) illustrates the inhibition zones and their comparison against the silver molar ratio of the samples. All the silver ion-exchanged samples showed inhibition zones against E. coli and S. aureus, whereas the parent KN and KT samples did not show any antibacterial activity. The Ag⁺ ions discharged into the liquid medium from each sample are shown in Figure 6(b). The tantalum phase with a pyrochlore-type structure discharged the highest amount of Ag⁺ ions, which was approximately 44.7 ppm (KAT3). Moreover, the amount of Ag⁺ ions discharged by the niobate phase with a fluorite-type structure (KAN3) was approximately 13.6 ppm. These discharged silver ions are located in the tunnel (16d site) of the pyrochlore-type structure and the 4a site in the fluorite-type structure [47]. Thus, the tunnel structure in the pyrochlore provided possible silver ion migration pathways from the powdered sample to the liquid medium. However, the disordered fluorite structure hosted Ag and Nb cations at the 4a site, and it also showed some capability to release Ag⁺ ions into the solution. Although the KAT3 and KAN3 samples discharged the highest amounts of silver ions, their relative antibacterial activities were lower than those of the other ion-exchanged samples. This surprising result is an indication of AgNP agglomeration. The AgNPs discharged into the liquid medium tend to minimize the surface energy by aggregation, which leads to a decline in the antibacterial properties of the samples. Moreover, the reduction and aggregation of Ag⁺ ions into metal clusters also lead to the formation of AgNPs [48]. To investigate the AgNP and Ag⁺ behavior during the antibacterial experiment, surface plasmon resonance (SPR) measurements were conducted by UV–vis spectroscopy. UV–vis spectroscopy is one of the main techniques for structural analysis of silver AgNPs. To investigate the AgNPs, pellets were prepared according to the method described in the previous section and kept at 37 °C in distilled water (10 ml) solution to obtain pale-yellow solutions. Figure 7 shows the absorption spectrum of the pale-yellow silver colloids solutions at different samples. The extra light absorbance peaks at approximately 400–425 nm in the UV–vis spectra (Figure 7) were indicative of AgNP formation in KAT3 and KAN3 samples. Furthermore, the SPR band intensity (at 425 nm) decreased in the case of other samples (KAT2, KAN2, KAT1, and KAN1). To further confirm AgNP agglomeration, XRD of the pellets was performed after Ag⁺ ions were released (Figure 8). The XRD patterns clearly showed an intense silver peak, as evidenced by the peaks at 2θ values of 38.3° and 44.0° (denoted by *), which corresponded to the (111) and (200) Bragg reflections, respectively. These XRD results further confirmed that AgNPs were formed by the reduction of

Figure 6. (a) Relative inhibition zone of each sample against Escherichia coli and Staphylococcus aureus after 48 h incubation and (b) Ag⁺ and K⁺ ions released from niobate and tantalate sample pellets after 48 h.
Ag⁺ ions during the antibacterial test. When high concentrations of Ag⁺ ions are released, they tend to reduce to nanoparticle-forming nanoparticle agglomerates. Because the KAT1 and KAN1 samples discharged the lowest amounts of silver ions into the liquid medium, it can be inferred that these samples managed to minimize AgNP agglomeration, which increased the antibacterial activity. AgNPs are not only used as an application in antibacterial field but also food packaging, textile fibers and health care industries [49,50]. This tunable property of niobate and tantalate compounds enables the optimization of Ag⁺ ions discharged into a liquid medium for various applications, including clinical applications such as drug delivery, antibacterial-resistant bacteria, and other biomedical industries. *S. aureus* possesses lower antibacterial-resistance capability than *E. coli*, which can be attributed to the differences in the bacterial cell walls of gram-negative and gram-positive bacteria. Honda et al. [18] reported the antibacterial capability of silver-containing hydroxyapatites against *S. aureus*, which exhibited the highest inhibition zone of approximately 1.6. Based on comparison with these results, it can be inferred that KAN1 and KAT1 possess the best antibacterial ability, with inhibition zone values of approximately 2.6 and 2.5, respectively.
4. Conclusions

The Ag ion-exchanged samples from pyrochlore-type $K_{0.65}H_{0.35}NbO_3$, $0.29H_2O$ (KN) and $K_{0.62}H_{0.38}TaO_3$, $0.53H_2O$ (KT) exhibited antibacterial properties superior to those of their corresponding parent compounds. The antibacterial test results indicate that the amount of $Ag^+$ ions discharged and the minimization of AgNP aggregation are crucial factors for antibacterial activity. The KAN3 and KAT3 samples showed the lowest relative antibacterial activity owing to agglomeration of the discharged AgNPs, while the KAN1 and KAT1 samples showed good antibacterial activity. This controllable bactericidal effect can be attributed to their distinct structure, where pyrochlore-type structures have been considered as hosts for $Ag^+$ ions and capable of regulating their release through their tunnel structure. Furthermore, the study shows that Ag ion-exchanged samples play a major role in enhancing the antibacterial activity against $E. coli$ and $S. aureus$. Moreover, this study reveals a new pathway for designing pyrochlore-type niobates and tantalates as efficient antibacterial materials. Thus, these pyrochlore-type compounds might be effective candidates for combating bacteria-induced infections and for various other bioengineering applications.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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