Structure and antibacterial activity of new layered perovskite compounds

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Abstract: New layered perovskite compounds, Ag$_x$Na$_{2-x}$La$_2$Ti$_3$O$_{10}$ ($x$=0.2, 0.3 and 0.5) were synthesized by an ion-exchange reaction of Na$_2$La$_2$Ti$_3$O$_{10}$ with AgNO$_3$ solution and characterized by energy dispersive X-ray analysis(EDX), X-ray diffractometry(XRD), scanning electron microscopy(SEM) and X-ray photoelectron spectroscopy(XPS). The ion-exchange processes were optimized, and the antibacterial activity, light permanency and water-resistance were evaluated. Surprisedly, no significant changes in crystal structure of Na$_2$La$_2$Ti$_3$O$_{10}$ are found by the exchange of silver ions. The Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$ particles conglomerate obviously with irregular shape and size. Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$, possessing the minimum inhibitory concentrations(MICs) against Escherichia coli (E. coli), Staphylococcus aureus (S. aureus) of 180 mg/L and 240 mg/L, has high antibacterial activity, good light permanency and water-resistance. The ionic state silver in Ag$_x$Na$_{2-x}$La$_2$Ti$_3$O$_{10}$ is the antibacterial active component.

Key words: layered perovskite compound; structure; antibacterial activity; ion-exchange

1 Introduction

It is widely known that inorganic antibacterial agents carrying silver have high antibacterial activity to microorganisms[1–4] and display no or little side effects on tissue[5]. The applications of the inorganic antibacterial agents are limited because of discoloration and high cost though they are used as sterilizing and antibacterial agents in paper, plastic, paint, ceramic and so on. Therefore, it is important to develop new antibacterial agents with low cost, high antibacterial activity and light permanency.

Layered perovskite compounds with Ruddlesden-Popper phase of $A_2[A'_{m-1}B_mO_{3m+1}]$, where $A$ is an exchangeable alkali metal cation, $A'$ is an alkali metal, alkaline earth, main group and/or rare earth, and $B$ is a transition metal, have been investigated extensively in recent years[6–7]. These compounds possessing interesting structure and ion-exchange property have been explored as ionic conductors[8–9], photocatalysts [10–12], and super-conductors[13]. However, there have been few reports on the study of the antibacterial activity, and the influence of silver valence state on antibacterial activity is not clear so far. In this paper, new layered perovskite compounds, Ag$_x$Na$_{2-x}$La$_2$Ti$_3$O$_{10}$ ($x$=0.2, 0.3 and 0.5) carrying low content silver were synthesized and characterized. And the antibacterial activity, light permanency and water-resistance of the compounds were investigated.

2 Experimental

All reagents used were of analytical purities. The parent compound (carrier) of Na$_2$La$_2$Ti$_3$O$_{10}$ was prepared by conventional solid-state reaction[9,14]. The raw materials of sodium carbonate, lanthanum oxide, and titanium oxide were mixed at the mole ratio of 1.6:2:3. A 60% (mole fraction) stoichiometric excess of sodium carbonate was added to compensate for the loss due to the evaporation of the sodium component, which can act as an oxidizing flux also[15]. The mixture was ground into powder, and heated at 105 °C for 10 h in air. The obtained powder was placed into alumina crucible, calcined in air at 500 °C for 10 h, heated at 1 000 °C for another 5 h, and then cooled. At last, the product was synthesized by an ion-exchange reaction of Na$_2$La$_2$Ti$_3$O$_{10}$ with AgNO$_3$ solution.
washed with deionized water and dried at 105 °C for 10 h.

Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} was synthesized by an ion-exchange method. 1 mol Na\textsubscript{2}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} was added into deionized water to obtain a 10% suspension, and intermixed with 0.1−0.3 mol AgNO\textsubscript{3}, and then maintained at 40−70 °C for 1−7 h in a dark vessel. The products were filtered out, washed with deionized water, and dried at 105 °C for 10 h. After grinding and sieving, the portion with average size of 5 μm was used in property tests.

The Ag\textsuperscript{+} content in reaction solution was measured by a HITACHI 180-80 atomic absorption spectrophotometer. After a certain time of an ion-exchange reaction, the Ag\textsuperscript{+} exchange fraction (\(\eta\text{(Ag\textsuperscript{+})}\)) was calculated according to the following equation:

\[
\eta\text{(Ag\textsuperscript{+})}=m_1\text{(Ag\textsuperscript{+})}/m_2\text{(Ag\textsuperscript{+})}×100\%
\]

where \(m_1\text{(Ag\textsuperscript{+})}\) and \(m_2\text{(Ag\textsuperscript{+})}\) are the mass fraction of Ag\textsuperscript{+} in Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} and initial reaction solution, respectively.

The crystal structures of the samples were characterized by XRD on a MASL-XD2 X-ray diffractometer using Cu K\(\alpha\) radiation (36 kV, 24 mA, \(\lambda=0.154\) nm), and a scanning rate of 0.08 (°)/s was used to record the patterns in the range of 5°−65°; the components and silver content were analyzed by EDX using an Oxford ISIS-300 energy-dispersive X-ray detector; the surface morphologies of Na\textsubscript{2}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} and Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} were observed using a JSM-6360 scanning electron microscope; the silver valence state in Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} was determined with an ESCALab220i-XL electron spectrometer.

The antibacterial activity (minimum inhibitory concentrations, MICs) of Na\textsubscript{2}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} and Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} as functions of the mole ratio Ag to Na, was estimated by a two-fold diluting method[16], and the bacteria of E. coli ATCC25922 and S. aureus ATCC6538 were selected as indicators. The light permanency was carried out by exposing the samples under fluorescent ultraviolet lamp (351 nm) for a certain time and observing the discoloration. 0.1 g Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} was soaked in 20 mL deionized water in a polypropylene bottle at 37 °C and rotated with a diameter of 3 cm and a rotating speed of 120 r/min. After 1−10 d of rotation, the Ag\textsuperscript{+} concentration in solution was measured by a HITACHI 180-80 atomic absorption spectrophotometer.

3 Results and discussion

3.1 Ion-exchange process

The antibacterial activity of Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10}, which is directly associated with the silver content, is affected by the ion-exchange process. The influences of reaction temperature, reaction time, AgNO\textsubscript{3} dosage on Ag\textsuperscript{+} exchange fraction (or the silver content of Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10}) were investigated as follows.

When the mole ratio of Ag to Na in initial reaction solution was 0.2:1, Ag\textsuperscript{+} exchange fraction was determined as functions of reaction temperature (40−70 °C) and reaction time (up to 7 h). As shown in Fig.1, Ag\textsuperscript{+} exchange fraction increases with the increase of reaction temperature and reaction time. Furthermore, at relatively high temperature (60−70 °C), Ag\textsuperscript{+} exchange fraction levels off above 6 h. The results suggest that the ion-exchange reaction reaches a high Ag\textsuperscript{+} exchange fraction at 60 °C for 6 h.

![Fig.1 Effect of reaction temperature and reaction time on Ag\textsuperscript{+} exchange fraction (\(\eta\text{(Ag\textsuperscript{+})}\))](image)

Ag\textsuperscript{+} exchange fraction and the mass fraction of Ag\textsuperscript{+} in Ag\textsubscript{0.3}Na\textsubscript{1.7}La\textsubscript{2}Ti\textsubscript{3}O\textsubscript{10} as functions of the mole ratio Ag to Na in initial reaction solution at 60 °C for 6 h are shown in Fig.2. With the increase of mole ratio of Ag to Na, Ag\textsuperscript{+} exchange fraction declines and the mass fraction of silver increases. Surprisingly, a further increase in mole ratio of Ag to Na (beyond 0.2) led to a sharp decline in Ag\textsuperscript{+} exchange fraction. It may be explained that the silver ion concentration on carrier surface tended to rise with the increase of mole ratio of Ag to Na, and then more silver ions exchanged with carrier causing the increase of mass fraction of Ag\textsuperscript{+}. At the same time, the silver ions remaining in solution might be reduced to metallic silver, which would choke exchange sites when they deposited on carrier surface. Therefore, with the increase of mole ratio of Ag to Na, more metallic silver particles and more choked exchange sites result in the decrease of Ag\textsuperscript{+} exchange fraction.

According to the aforementioned results, the optimized ion exchange process is as follows: reaction temperature 60 °C, reaction time 6 h, mole ratio of Ag to Na 0.2.
Fig.2 Effect of mole ratio of Ag to Na on Ag⁺ exchange fraction and mass fraction of Ag⁺ in AgₓNa₂₋ₓLa₂Ti₃O₁₀

3.3 Structure analysis

The results of EDX analysis for Na₂La₂Ti₃O₁₀ and AgₓNa₂₋ₓLa₂Ti₃O₁₀ are shown in Table 1. According to the mole ratio of Na, La and Ti, the molecular formula of Na₂La₂Ti₃O₁₀ (sample 1) can be confirmed. The molecular formulae of AgₓNa₂₋ₓLa₂Ti₃O₁₀ (samples 2, 3 and 4) can also be determined because the mole ratios of Ag, Na, La and Ti are almost in accordance with the molecular formulae of Ag₀.2Na₁.₈La₂Ti₃O₁₀, Ag₀.₃Na₁.₇La₂Ti₃O₁₀ and Ag₀.₅Na₁.₅La₂Ti₃O₁₀.

Table 1

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molecular formula</th>
<th>Na</th>
<th>Ti</th>
<th>Ag</th>
<th>La</th>
<th>Total</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Na₂La₂Ti₃O₁₀</td>
<td>27.80</td>
<td>43.29</td>
<td>-</td>
<td>28.91</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Ag₀.₂Na₁.₈La₂Ti₃O₁₀</td>
<td>25.11</td>
<td>43.40</td>
<td>2.77</td>
<td>28.72</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Ag₀.₃Na₁.₇La₂Ti₃O₁₀</td>
<td>23.07</td>
<td>43.37</td>
<td>4.46</td>
<td>29.10</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Ag₀.₅Na₁.₅La₂Ti₃O₁₀</td>
<td>20.99</td>
<td>43.45</td>
<td>6.61</td>
<td>28.95</td>
<td>100</td>
</tr>
</tbody>
</table>

The XRD patterns of Na₂La₂Ti₃O₁₀ and AgₓNa₂₋ₓLa₂Ti₃O₁₀ (x = 0.2, 0.3 and 0.5) are shown in Fig.3. Obviously, the diffraction peaks of AgₓNa₂₋ₓLa₂Ti₃O₁₀ (x = 0.2, 0.3 and 0.5) are almost the same as that of Na₂La₂Ti₃O₁₀, which are consistent with the earlier determined pattern of compound Na₂La₂Ti₃O₁₀ with tetragonal crystalline[17]. However, small changes are observed in the unit cell parameters of AgₓNa₂₋ₓLa₂Ti₃O₁₀ (x = 0.2, 0.3 and 0.5) because of the different sizes between Na⁺ (0.098 nm) and Ag⁺ (0.113 nm), as can be seen in Table 2. As a result, no significant changes in crystal structure of Na₂La₂Ti₃O₁₀ are found by the exchange of silver ions.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>a/ nm</th>
<th>c/ nm</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂La₂Ti₃O₁₀</td>
<td>0.383</td>
<td>2.864</td>
<td>18</td>
</tr>
<tr>
<td>Na₂La₂Ti₃O₁₀[17]</td>
<td>0.384</td>
<td>2.858</td>
<td>82</td>
</tr>
<tr>
<td>Ag₀.₂Na₁.₈La₂Ti₃O₁₀</td>
<td>0.383</td>
<td>2.865</td>
<td>01</td>
</tr>
<tr>
<td>Ag₀.₃Na₁.₇La₂Ti₃O₁₀</td>
<td>0.384</td>
<td>2.865</td>
<td>75</td>
</tr>
<tr>
<td>Ag₀.₅Na₁.₅La₂Ti₃O₁₀</td>
<td>0.384</td>
<td>2.866</td>
<td>17</td>
</tr>
</tbody>
</table>

The SEM images of Na₂La₂Ti₃O₁₀ and Ag₀.₃Na₁.₇La₂Ti₃O₁₀ are shown in Fig.4. Fig.4(a) corresponding to Na₂La₂Ti₃O₁₀ particles display some conglomeration with flocculent shape and uneven size due to the high temperature solid-state reaction. Moreover, Ag₀.₃Na₁.₇La₂Ti₃O₁₀ particles conglomerate obviously with irregular shape and size because of the import of silver ions, as shown in Fig.4(b).

3.3 Properties evaluation

The antibacterial activity and light permanency of Na₂La₂Ti₃O₁₀ and AgₓNa₂₋ₓLa₂Ti₃O₁₀ (x = 0.2, 0.3 and 0.5) are listed in Table 3. The MICs of AgₓNa₂₋ₓLa₂Ti₃O₁₀ against E. coli and S. aureus are all less than 300 mg/L, in contrast with that of higher than 2 g/L for Na₂La₂Ti₃O₁₀. On the other hand, Na₂La₂Ti₃O₁₀, Ag₀.₂Na₁.₈La₂Ti₃O₁₀ and Ag₀.₃Na₁.₇La₂Ti₃O₁₀ show no discoloration while Ag₀.₅Na₁.₅La₂Ti₃O₁₀ displays a little discoloration after exposing to UV light for 24 h. These results indicate that the antibacterial activity of AgₓNa₂₋ₓLa₂Ti₃O₁₀ improves with the increase of silver content or the value of x. But at the same time, the trend to discoloration increases. It is interesting that the MICs of Ag₀.₃Na₁.₇La₂Ti₃O₁₀ against E. coli and S. aureus are 180 mg/L and 240 mg/L, respectively, and its discoloration is not observed after exposing to UV light for 24 h. Therefore, Ag₀.₃Na₁.₇La₂Ti₃O₁₀ has the potential to be commercially used in future.
Table 3 Antibacterial activity and light permanency of Na$_2$La$_2$Ti$_3$O$_{10}$ and Ag$_x$Na$_{2-x}$La$_2$Ti$_3$O$_{10}$ (MIC/(mg·L$^{-1}$))

<table>
<thead>
<tr>
<th>Property</th>
<th>Na$_2$La$_2$Ti$<em>3$O$</em>{10}$</th>
<th>Ag$<em>{0.2}$Na$</em>{1.8}$La$_2$Ti$<em>3$O$</em>{10}$</th>
<th>Ag$<em>{0.3}$Na$</em>{1.7}$La$_2$Ti$<em>3$O$</em>{10}$</th>
<th>Ag$<em>{0.5}$Na$</em>{1.5}$La$_2$Ti$<em>3$O$</em>{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. coli</td>
<td>&gt;2 000</td>
<td>250</td>
<td>180</td>
<td>125</td>
</tr>
<tr>
<td>S. aureus</td>
<td>&gt;2 000</td>
<td>300</td>
<td>240</td>
<td>150</td>
</tr>
</tbody>
</table>

Discoloration No No No A little

3.4 Exploration of antibacterial active component

The silver valence state in Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$ was analyzed by XPS, and the Ag 3d spectrum is shown in Fig.6. The binding energies of Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ are 367.59 eV and 373.63 eV, respectively, which are in accordance with standard parameters of ionic silver[18]. This result suggests that the silver in Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$ exists as ionic state.

The effect of silver valence state on antibacterial activity was further estimated as shown in Table 4. With the lapse of UV irradiation time, for Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$, the MICs increase and the discoloration becomes serious. These results can be explained that when Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$ is exposed to UV light, some ionic silver is reduced to metallic silver, and the metallic silver content in Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$ increases with the increase of UV irradiation time. Unfortunately, the color

Table 4 MICs and discoloration of Ag$_{0.3}$Na$_{1.7}$La$_2$Ti$_3$O$_{10}$ at different UV irradiation time (MIC/(mg·L$^{-1}$))

<table>
<thead>
<tr>
<th>Property</th>
<th>0</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>96</th>
</tr>
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<tbody>
<tr>
<td>E. coli</td>
<td>180</td>
<td>180</td>
<td>200</td>
<td>240</td>
<td>400</td>
</tr>
<tr>
<td>S. aureus</td>
<td>240</td>
<td>240</td>
<td>300</td>
<td>320</td>
<td>500</td>
</tr>
<tr>
<td>Discoloration</td>
<td>No</td>
<td>No</td>
<td>A little</td>
<td>A little</td>
<td>Serious</td>
</tr>
</tbody>
</table>
becomes deep, and the antibacterial activity declines. Therefore, it is evident that the ionic state silver in Ag$_{2}$Na$_{2-x}$La$_{2}$Ti$_{3}$O$_{10}$ is the antibacterial active component.

4 Conclusions

1) New layered perovskite compounds, Ag$_{2}$Na$_{2-x}$La$_{2}$Ti$_{3}$O$_{10}$ ($x$=0.2, 0.3 and 0.5) are synthesized by an ion-exchange reaction of Na$_{2}$La$_{2}$Ti$_{3}$O$_{10}$ with AgNO$_{3}$ solution; the optimized ion exchange process is as follows: reaction temperature 60 °C, reaction time 6 h, mole ratio of Ag to Na 0.2.  
2) The molecular formulae of Ag$_{2}$Na$_{2-x}$La$_{2}$Ti$_{3}$O$_{10}$ ($x$=0.2, 0.3 and 0.5) are confirmed; no significant changes in crystal structure of Na$_{2}$La$_{2}$Ti$_{3}$O$_{10}$ are found by the exchange of silver ions; Ag$_{0.3}$Na$_{1.7}$La$_{2}$Ti$_{3}$O$_{10}$ particles conglomerate obviously with irregular shape and size.
3) Ag$_{0.3}$Na$_{1.7}$La$_{2}$Ti$_{3}$O$_{10}$ possessing the MICs against E. coli, S. aureus of 180 mg/L and 240 mg/L, has high antibacterial activity, good light permanency and water-resistance.
4) The ionic state silver in Ag$_{2}$Na$_{2-x}$La$_{2}$Ti$_{3}$O$_{10}$ is the antibacterial active component.

References

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