



Short communication

A study on electrical conductivity of chemosynthetic $\text{Al}_2\text{O}_3\text{-2SiO}_2$ geopolymer materialsXue-Min Cui^{a,*}, Guang-Jian Zheng^a, Yao-Cong Han^a, Feng Su^a, Ji Zhou^b^a School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China^b State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, PR China

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ABSTRACT

$\text{Al}_2\text{O}_3\text{-2SiO}_2$ amorphous powders are synthesized by sol-gel method with tetraethoxysilane (TEOS) and aluminum nitrate (ANN) as the starting materials. The microstructure and phase structure of the powders are investigated by SEM and XRD analysis. Geopolymer materials samples are prepared by mechanically mixing stoichiometric amounts of calcined $\text{Al}_2\text{O}_3\text{-2SiO}_2$ powders and sodium silicate solutions to allow a mass ratio of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.4, 0.375, 0.35, 0.325, 0.288, 0.26, 0.23$ or 0.2 separately, and finally to form a homogenous slurry at a fixed $\text{H}_2\text{O}/\text{Na}_2\text{O}$ mole ratio = 11.7. The results show that the synthetic $\text{Al}_2\text{O}_3\text{-2SiO}_2$ powders have polycondensed property and their compressive strengths are similar to that of nature metakaolin geopolymer materials. The results also show that the water consumption is not the main influencing factor on electrical conductivity of harden geopolymer materials but it can intensively affect the microstructure of geopolymer materials. In addition, the electrical conductivity of harden geopolymer sample is investigated, and the results show that the geopolymer materials have a high ionic electrical conductivity of about $1.5 \times 10^{-6} \text{ S cm}^{-1}$ in air at room temperature.

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1. Introduction

Fast ionic conductors are powerful materials for the fabrication of the secondary high-energy solid-state batteries and other solid-state electrochemical parts [1]. Park fabricates a type of inorganic silicophosphate- HClO_4 (SiP-HClO_4) gel fast ionic conductor with electrical conductivity of $2 \times 10^{-2} \text{ S cm}^{-1}$ by sol-gel process, which provides a good method to fabricate the inorganic fast ionic conductors [2]. However, there are some problems in the preparation of those materials such as costly raw materials, high synthesis temperature, etc. Recently, a type of aluminosilicate geopolymer materials is attached importance to apply because of its free sintering, easy fabrication and low cost. In fact, the aluminosilicate geopolymer material is a type of cross-linked long-chain inorganic polymer materials between tetrahedral $[\text{AlO}_4]$ and $[\text{SiO}_4]$ unit, built in three-dimensional structures with excellent property of high strength, anticorrosion, standing fire and long life [3–8]. At present, we investigated the electrical conductivity and dielectric performance of metakaolin geopolymer materials in the frequency range of 1–1000 MHz. The experimental results show that this geopolymer material has high ionic conductivity, low dielectric constant and high dielectric loss in air circumstance at room tempera-

ture. If its ionic electrical conductivity is higher than the level of $10^{-6} \text{ S cm}^{-1}$, this materials are expected to play important roles on the preparation of fast ionic conductor used for all solid-state batteries, electrochemical sensors and so on.

In the aluminosilicate geopolymer materials, the M^+ (Li^+ , Na^+ or K^+), water molecule and hydroxy are the most important factors to influence electrical conductivity and dielectric property at room temperature. The existent way of alkali ion M^+ in molecular structure of geopolymer materials is not clearly theoretically at present. Usually, the accustomed viewpoint is that the alkali metal ions play a charge-balancing role or are actively bonded into the matrix; hence the typical geopolymer composition is expressed as $n\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ (M is alkali metals element such as Li, Na or K) [3–5]. Generally, the ^{27}Al and ^{29}Si MAS-NMR has been used to determine the molecular structure of the geopolymer materials synthesized with different alkali cations [3–5]. The molecular structure of geopolymers is described as a matrix of alumina and silica tetrahedra joined at the corners with oxygen. Alkali cations are associated with aluminum, where the AlO_4 groups have a single negative charge due to aluminum(III) being in tetrahedral co-ordination. A study of the effect of alkali cations (sodium and potassium) on the molecular ordering of the geopolymer gel concludes that the concentration of silicon in the activating solution plays an important role in aiding the incorporation of aluminum into the matrix via solution phase speciation with silicon [3–5]. Similarly, the alkali cation also contributes to the level of reaction

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of the solid aluminosilicate source, as well as the level of aluminum incorporation [4–6]. Hence, the balanced M^+ (Li^+ , Na^+ or K^+) maybe move along the pore in aid of the water in geopolymer materials, and improve the ionic electrical conductivity of geopolymer materials.

Usually, the Metakaolin is fabricated by calcined process with Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) at 600–900 °C [7,8]. However, the type of metakaolin is not pure and the Al/Si atom ratio is not fixed because the forming age and site of kaolin mine are different. So, this study designs the sol–gel method for synthesizing and purifying the $Al_2O_3-2SiO_2$ amorphous powders with tetraethoxysilane (TEOS) and aluminum nitrate nine-hydrate (ANN) as the starting materials [9].

2. Experimental

Starting materials for the sol–gel synthesis are tetraethylorthosilicate (TEOS) and aluminum nitrate (ANN). Solvents for the synthesis are anhydrous ethanol and distilled water. Starting materials and solvents are mixed in the following ratios: the molar ratio of Al_2O_3 to SiO_2 is 1:2 and the molar ratio of SiO_2 to H_2O and EtOH is 1:18:6. Typically, two solutions are prepared under stirring: solution A formed by TEOS and EtOH; and solution B by ANN and distilled water. Once these solutions are homogenized, solution B is added to solution A slowly under stirring and the obtained mixture reacted at 70 °C until gel is formed. The gel is first dried at 93 °C for 2 h by azeotropic distillation processing, and then increased to 117 °C with a hold time of 0.5 h. At last, the dried product is calcined in air at 800 °C for 2 h to fabricate the amorphous powders.

The microstructure of the amorphous powders is then investigated by SEM and XRD analysis. In order to examine the activity of the powders, alkali-activation tests are performed, with the calcined powders reacting with the water glass (the atom ratio of silicon/sodium is about 1:2) to form geopolymer materials. Geopolymer materials samples are prepared by mechanically mixing stoichiometric amounts of powders calcined at 800 °C and sodium silicate solutions to allow the mass ratio of $Na_2O/Al_2O_3 = 0.4, 0.375, 0.35, 0.325, 0.288, 0.26, 0.23$ and 0.2 to form a homogenous slurry on the condition of a fixed molar ratio of $H_2O/Na_2O = 11.7$, respectively; in addition, the deionized water consumption must ensure the same thickness or viscosity of geopolymer materials paste. After 15 min of mechanical mixing the slurry is vibrated for 5 min to remove entrained air before being transferred to moulds, which are cured in air at room temperature. Specimens used in conductivity experiments are molded with a diameter of about 20 mm and polished so that their ends are flat and parallel to ensure the accuracy of electrical measurement.

In this paper, we measure the free Na ions by ICP-AES (inductively coupled plasma atomic emission spectrometry) by water solutions, and the electrical conductivity of harden geopolymer materials paste of $Al_2O_3-2SiO_2$ is investigated by LCR821 (that frequency is from 25 Hz to 200 kHz) after coated graphite paste. Equipment and test fixture calibrations are carried out before each experiment.

3. Results

In this experiment, we gain nanometer drying-gel particles whose D_{50} is about 80 nm by sol–gel method, but it is improved to 400–500 nm after calcined at 800 °C for 2 h. Compared with the microstructure of synthetic powders with nature metakaolin, it is found that the alternate Al_2O_3 and SiO_2 layer structure shown in nature Metakaolin but not obvious in the synthetic powders

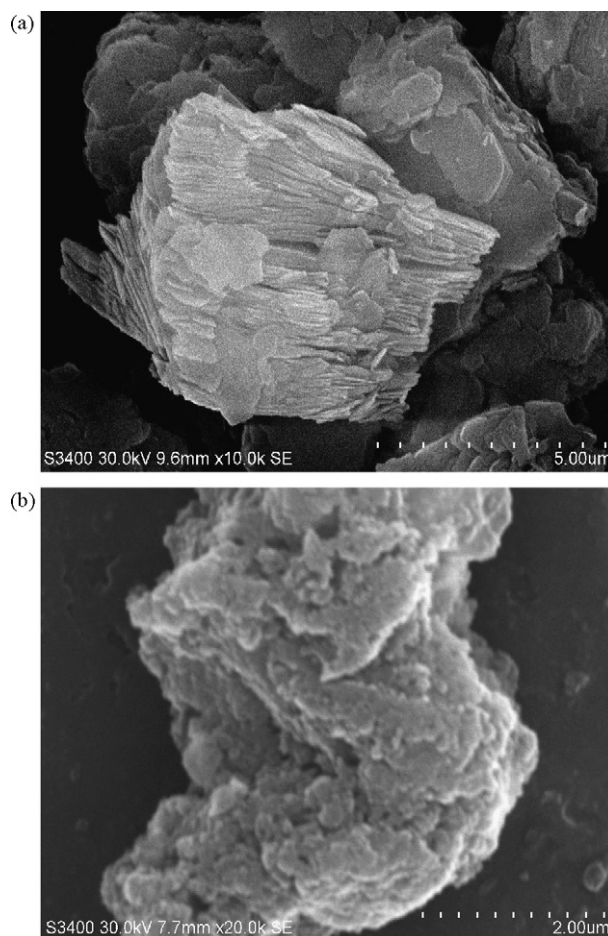


Fig. 1. SEM photo of erosional $Al_2O_3-2SiO_2$ powders in 10 M sulphuric acid for 10 h: (a) nature Metakaolin and (b) synthetic $Al_2O_3-2SiO_2$ powders.

even if the synthetic powders is treated by acid leaching method (immersed in 10 M sulphuric acid for 10 h). The reason is that the alumina can be dissolved but silica cannot be dissolved by sulphuric acid. The SEM images are shown in Fig. 1a and b. The experimental results show that the synthetic $Al_2O_3-2SiO_2$ powders also have irregular layer structure, which are different from that of nature Metakaolin, and the single layer is likely to be composed of many clusters, as is shown in Fig. 1b.

A typical powder X-ray diffraction pattern of the synthetic powders is shown in Fig. 2. There is no significant difference of curves shape between the XRD patterns of powders before and after calcined at 800 °C; but the XRD patterns of calcined $Al_2O_3-2SiO_2$ powders at 800 °C shows some shift in peak position. According to the Scherrer equation, the 2θ angle changing can reply to increasing of the molecular orderly structure with the calcined temperature increment. However, the molecular structure of the synthetic powder is typically amorphous, lacking periodically repeated atomic ordering and its phase structure is similar to that of metakaolin. In order to synthesize a geopolymer with a high compressive strength, synthetic powders with a high reactivity are required [10]. The non-calcined synthetic powders, with a comparatively lower reactivity that do not occur condensation reaction and ultimately do not form geopolymerization. However, the reactivity of synthetic powders after calcined at 800 °C significantly improve the compressive strength of harden geopolymer materials paste in this experiment. The changing of molecular orderly structure leads to the different reactivity that will be studied in latter work.

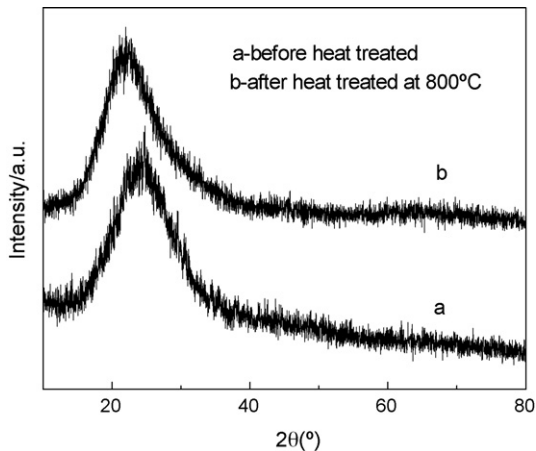


Fig. 2. XRD patterns of synthetic $\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ powders: (a) non-calcination and (b) calcined at 800°C .

Usually, the geopolymers consist of aluminum and silica tetrahedrally interlinked alternately by sharing all the oxygen atoms. A polymeric structure of Al-O-Si formed constitutes the main building blocks of geopolymeric structure [3–8]. Sodium silicate and/or hydroxide are necessary for the dissolution of Si-O bond and Al-O bond to form aluminosilicate gel as well as for the catalysis of the condensation reaction. The gel phase is thought to be highly reactive and produced by co-polymerization of individual alumina and silica from their source, dissolved by the sodium salts. Some Na ions must be presented to keep the structure neutrality (since aluminum is fourfold), and other Na ions maintain this neutrality.

It is still not clear if these Na ions simply play a charge-balancing role or are actively bonded into the matrix. The mechanism of immobilization is expected to be the combination of chemical and physical interaction. Cation is either bonded into the matrix via Al-O or Si-O bond or present in the framework cavities to maintain electrical charge balance. The coordination number of the silica and alumina in the source material is of great importance. It is believed that the alkali solutions act as a catalyst and leach out from the hardened alkali activated cement in more or less amount as that was added during synthesis. Ions such as Na ions that are incorporated into the matrix in one way or another balanced ions maybe dissociate from materials structure by water solvent [11,12].

In order to validate the free Na ions on geopolymer structure, we attempt to measure the free Na ions by ICP-AES, as shown in Fig. 3. We break up the hardened geopolymer materials paste for different cured time and dissolve the free Na ions to deionized

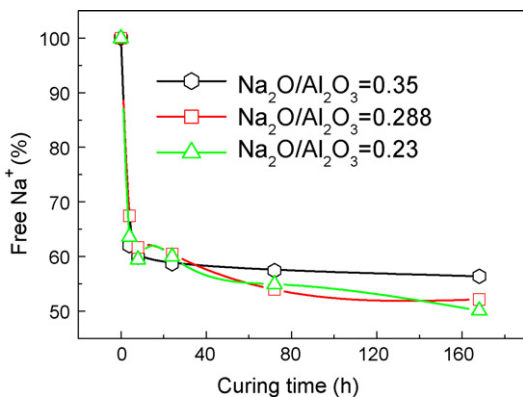


Fig. 3. The free Na ions of geopolymer materials changing with the increment of cured time.

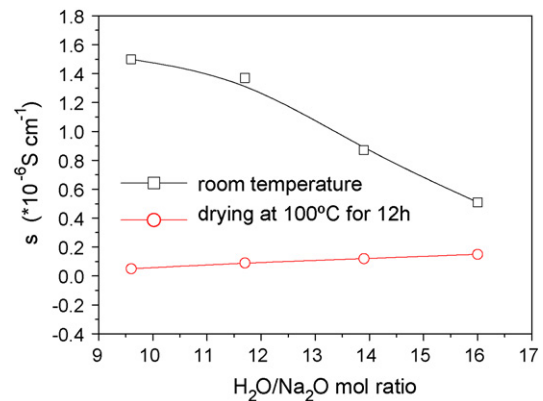


Fig. 4. The relationship between $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio and electrical conductivity in geopolymer materials.

water so that sample compositions are fixed with a molar ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O} = 11.7$ and different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. With different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of geopolymer materials, the fraction of free Na ions almost hold constant after cured for 4 h, when the cured time exceeds 168 h, the free Na ions will be increased with the increment of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. The experimental result is shown in Fig. 3.

In fact, the water consumption is an important factor to influence ionic electrical conductivity of this geopolymer material. In our work, we fix the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.288$, and change the molar ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ from 9.6 to 16 as shown in Fig. 4. The relationship between $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio and electrical conductivity has different changing tendency before drying when the sample is cured after 168 h. The result shows that the electrical conductivity decreases with the increment of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio but it would be increased with the increment of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio after drying for 12 h at 100°C . It is found that the increment of water consumption cannot improve the electrical conductivity but the porous microstructure formed at high $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio maybe the main factor to impact electrical conductivity. In other words, the water consumption is not the main influencing factor to electrical conductivity but it can intensively impact on the microstructure of geopolymer materials.

In this work, we measure the electrical conductivity of the geopolymer materials with different $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio after cured for 168 h, as shown in Fig. 5. The experimental results show that the electrical conductivity is out of proportion to the free Na ions. For holding the constant viscosity, the added water consumption is fixed in starting paste materials, and with the increment of

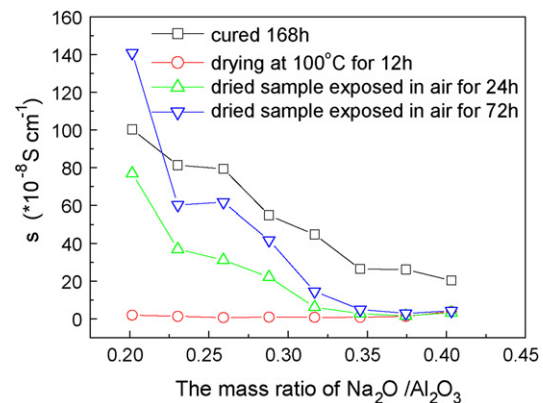


Fig. 5. The relationship between $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio and electrical conductivity geopolymer materials.

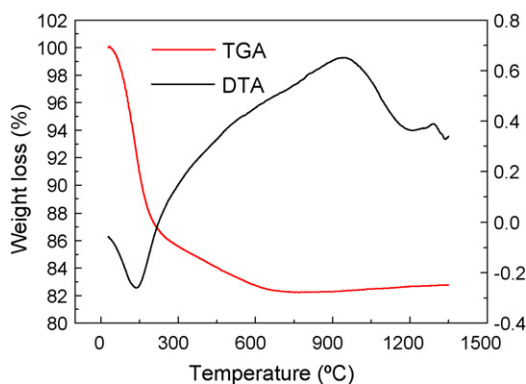


Fig. 6. The TGA/DTA curve of geopolymer materials in air.

$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio in this experiment, the gross of water is increased in geopolymer materials paste. Because the different water consumption in geopolymer materials impact on the microstructure, the influence of water would exceed the influence of free Na ions to the electrical conductivity. In this experiment, the electrical conductivity is rather depressed with the increment of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. The influence of water on the electrical conductivity of geopolymer materials can be depressed or eliminated by heat treatment. In Fig. 5, the drying process at 100°C of geopolymer materials obviously reduces the electrical conductivity from 10^{-6} S cm^{-1} to 10^{-8} S cm^{-1} but the electrical conductivity of dried sample increases with the increment of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. Hence, the influence of water on the electrical conductivity conceals the contribution of free Na ion on the electrical conductivity. In fact, the influence of water and hydroxy can be entirely eliminated if geopolymer materials is treated at 600°C as shown in Fig. 6. However, holding structure water in geopolymer materials body can make up its strength. Owing to the porous structure of geopolymer materials, dried sample can adsorb water when it is exposed in air. When the dried sample is exposed in air for more than 72 h, the electrical conductivity of the sample (with $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.288$ and molar ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O} = 11.7$) develops acutely change that exceeds the electrical conductivity before dried because of water adsorption. Therefore, the geopolymer materials have high electrical conductivity while water exists in geopolymer materials body. In other words, the geopolymer materials can be acted as fast ionic conductor when the solid object includes pore and liquid phase.

4. Discussions

As fast ionic conductors, the electrical conductivity of harden geopolymer materials paste is low. Fan [3] studied the similar aluminosilicate with a layered structure and high conductivity of $2.76 \times 10^{-3}\text{ S cm}^{-1}$. Metakaolin is a kind of aluminosilicate with a layered structure and consists of two layers of Si–O tetrahedra between which Al–O octahedra are sandwiched; the frames charge negatively because of isomorphous replacement of octahedra and the cations are attracted in interlayers to balance the negative charge on the frame. Examining the literature about aluminosilicate with a layered structure, we see the hypothesis that the compensated cations in aluminosilicate were in thermal disturbance. For example, Sheffield and Howe [12] measured the conductivity of H-montmorillonite with 13% water content to be $1 \times 10^{-3}\text{ S cm}^{-1}$ to $4 \times 10^{-3}\text{ S cm}^{-1}$ at 296 K, and they considered its use in electrochemical devices as a solid electrolyte; however, the acid exchange of the montmorillonite results in leaching of Al^{3+} and Mg^{2+} from the layers and this disturbs the bulk of the clay structure.

In this paper, the free Na ion content in geopolymer is only about 50%, as shown in Fig. 3, other part of Na ion is bonded to crystal structure, hence, the mobile Na ions content relatively reduce in geopolymer materials. Another reason is that the formation of porous microstructure because of the water vaporizing, which will impede the Na ion moving. In order to improve the activity of the ionic electrical conductivity, composites alkali-activation tests are performed, with the chemosynthetic powders reacting with the sodium plus lithium silicate solutions (the molar ratio of silicon/(sodium + lithium) is holding about 1.2). The experimental results show that compared with the sodium silicate solutions, the ionic electrical conductivity only improves to a limited value at the same conditions. However, the added lithium hydroxy can restrain and stay the geopolymerization between Al_2O_3 – 2SiO_2 powders and alkali silicate solutions. So, we abandon this experimental project.

Whittingham [13] has pointed out that these high conductivities, approaching those of bulk aqueous solution, are associated with the outside surface of the clay, not the bulk. With this view in mind, we will further discuss how to improve the conductivity of aluminosilicate in next work. In fact, the 10^{-6} S cm^{-1} levels that are not enough for fast ionic conductor. New experiment results show that the ionic electrical conductivity of geopolymer materials is improved to 10^{-4} S cm^{-1} by controlling the fabricated processing and microstructure of geopolymer materials, and it will be reported in next paper.

5. Conclusions

A sol–gel method is used to effectively fabricate pure Al_2O_3 – 2SiO_2 inorganic materials with amorphous phase structure, good geopolymerization, and higher ionic conductivity at room temperature. The experiment results indicate that the increment of water consumption cannot improve the electrical conductivity but the porous microstructure maybe the main factor to impact electrical conductivity, which is formed due to the high $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio. In other words, the water consumption is not the main influencing factor on electrical conductivity but it can intensively impact on the microstructure of geopolymer materials. If fixed the water consumption, the electrical conductivity of geopolymer materials will be increased with the increment of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio when the free water is eliminated by drying. In this geopolymer materials system, because a part of alkali cations must be presented to keep the structure neutrality (since aluminum is fourfold) and other cations maintain this neutrality, the balanced alkali cations can move along the pore and interface. Therefore, the geopolymer materials can be acted as fast ionic conductor when the solid object includes pore and liquid phase and its ionic electrical conductivity can arrive at 10^{-6} S cm^{-1} .

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