

Short communication

Three rare Ln–Na heterometallic 3D polymers based on sulfate anion: Syntheses, structures, and luminescence properties



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ABSTRACT

Three Ln–Na heterometallic 3D polymers based on sulfate anion, $[\text{LnNa}(\text{SO}_4)_2(\text{H}_2\text{O})]$ (Ln = Gd (**1**); Tb (**2**); Dy (**3**)), were synthesized under hydrothermal conditions, which are the first examples of Ln–Na sulfates. These compounds crystallize in the trigonal $P3_121$ space group, and display a 6-connected *sma* topological structure with a Schläfli symbol of $(4^{10}\cdot 6^5)$. The characteristic analyses reveal that compounds **1–3** display excellent thermal stability, and all exhibit antiferromagnetic interactions between the metal centers. The luminescent properties of **2** and **3** show the characteristic terbium and dysprosium luminescence. The strong luminescence in the green light ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) region for **2** and blue light ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) region for **3** indicate that they may be excellent candidates for green or blue fluorescent materials.

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The design and syntheses of inorganic open-framework materials have attracted great attention over the last few decades because of not only their intriguing varieties of structures but also their potential applications in the areas of catalysis, ion exchange, magnetic properties and luminescence properties [1–4]. Originally, the work mainly focused on selenates, arsenates, silicates and phosphates [5–7]. Recently, the tetrahedral sulfate anions have been demonstrated to be an excellent ligand for the construction of open frameworks with new structures and interesting properties [8,9]. Since the first organically templated cadmium sulfate was synthesized by Rao, a number of transition metal sulfates and rare earth sulfates have been reported, with rich topological structure [10–17]. Compared with transition metals, rare-earth elements can adopt more various coordination numbers from 8 to 12 and flexible Ln–O bond lengths to give lanthanide sulfates with new topologies [4, 8–10]. Moreover, the lanthanide-based compounds usually exhibit interesting luminescence behavior and have important applications as fluorescent probes in many emission-related fields, especially in biochemistry [8,9]. Consequently, it is vital to design novel lanthanide sulfates with intriguing architectures to explore their optical properties and understand the formation mechanism [4,9].

The reported framework materials based on sulfate anions are mainly limited to homo-metal compounds, and the report of lanthanide-containing heterometallic polymers are still rare, which were found

to not only show interesting luminescent properties but also better thermal stabilities than the lanthanide sulfates [18,19]. It is well-known that the inorganic salt of sodium sulfate does not decompose even heated up to more than 1000 °C. Thus, the introduction of Na^+ ion in the lanthanide sulfate may lead to a higher thermal stability, besides retaining the luminescent property of Ln^{3+} ion in the resulting compounds. However, to the best of our knowledge, the Ln–Na heterometallic polymers based on sulfate anion has never been reported up to now. Herein, three isostructural Ln–Na heterometallic 3D polymers $[\text{LnNa}(\text{SO}_4)_2(\text{H}_2\text{O})]$ (Ln = Gd (**1**); Tb (**2**); Dy (**3**)) were successfully prepared by $\text{Ln}(\text{NO}_3)_3$, Na_2SO_4 and methanesulfonic acid with a mole ratio of 1:1.5:1 under hydrothermal conditions.

Single-crystal X-ray diffraction analyses reveal that compounds **1–3** are isomorphous and only the structure of **1** is discussed in detail. Compound **1** crystallizes in the trigonal $P3_121$ space group and features a 3D network which is formed by 6-connected sulfate anion, Gd^{3+} and Na^+ ions (Fig. 1). Each sulfate adopt the rare $\mu_6-\eta_2:\eta_2:\eta_2:\eta_2$ coordination mode to bridge three Gd^{3+} ions and three Na^+ ions. As shown in Fig. 1a, two oxygen atoms of the sulfate firstly chelate one Gd^{3+} ion, and then connect one Na^+ ion respectively. While the other two oxygen atoms chelate one Na^+ ion and further link one Gd^{3+} ion respectively. Each Gd^{3+} ion is nine-coordinated and have a distorted monocapped square antiprismatic $\{\text{O}_9\}$ donor set, built from one terminal water molecule and six sulfate anions. Two of the six sulfates, respectively, use two oxygen atoms to chelate the Gd^{3+} ion, and the other four sulfates only use one oxygen atom to bridge the Gd^{3+} ion. The coordination geometry of the eight-coordinated Na^+ ions can be described as a distorted

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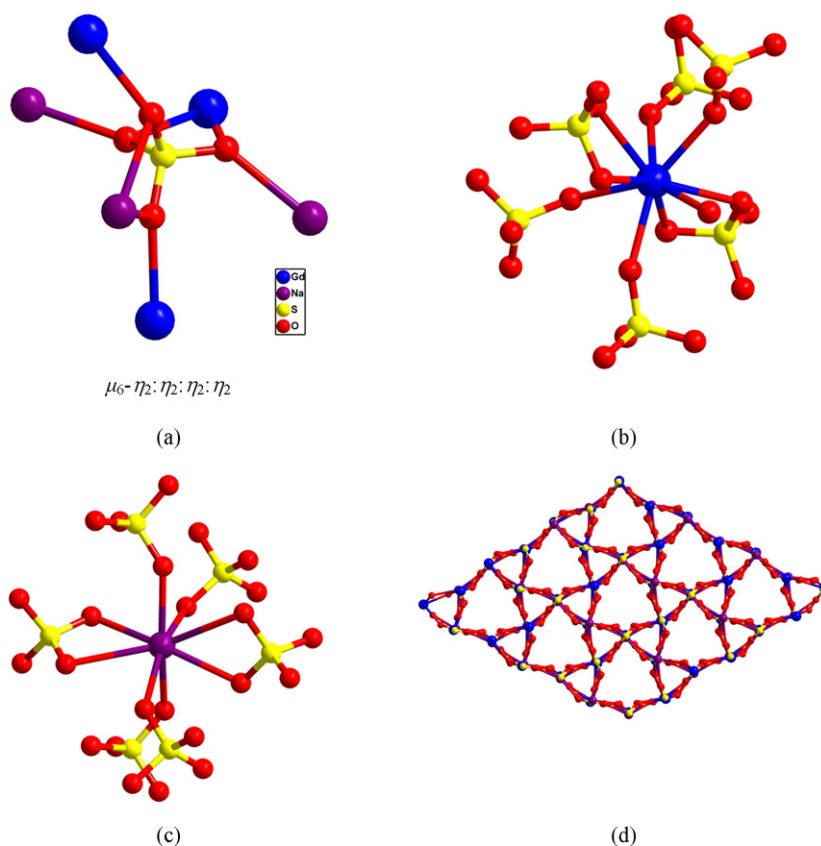


Fig. 1. (a) The coordinate mode of sulfate anion; (b) coordination environments of Gd^{3+} ion; (c) coordination environments of Na^+ ion; (d) view of the 3D framework of **1** viewed along the *c* axis. The coordinated water molecules have been omitted for clarity.

monocapped pentagonal bipyramid, completed by eight oxygen atoms from six sulfates. The Gd–O, Na–O and S–O bond lengths are in the range of 2.404(2)–2.504(2), 2.374(3)–2.869(2) and 1.465(2)–1.482(2) Å, respectively, which are comparable with those reported for other lanthanide and sodium compounds based on sulfate anion [8,9,18,20].

As shown in Fig. 1d, the Gd^{3+} and Na^+ ions are connected in 1:1 ratio by the $\mu_6\text{-}\eta_2\text{:}\eta_2\text{:}\eta_2\text{:}\eta_2$ sulfates to form a 3D neutral framework, bearing two types of equilateral triangle channels (dimensions of about 6.7 and 3.5 Å, respectively) viewed along the *c* axis. The coordinated water molecules are embedded in the big equilateral triangle channels, each of which is surrounded by six small ones. To get better insight of this 3D framework, topology analysis has been programmed by using TOPOS software [21]. If treating sulfate, Gd^{3+} and Na^+ ions as

6-connected nodes, this network can be considered as a 6-connected *sma* topology with a Schläfli symbol of $(4^{10}\cdot 6^5)$ (Fig. 2).

To examine the thermal stabilities of **1–3**, thermogravimetric analysis (TGA) experiments were carried out by heating the crystalline samples in a nitrogen atmosphere from 30 to 1000 °C. As shown in Fig. S3, the TG curves of **1–3** are similar and three mass steps are observed. In the first step, the weight loss of **1–3** in the range of 30–400 °C are 4.46%, 4.78% and 4.98%, respectively, which could be attributed to the loss of one coordinated water molecule for every formula unit (calculated 4.62% for **1**, 4.59% for **2** and 4.56% for **3**). Then, the weights of **1–3** keep constant between 400 °C and 800 °C, indicating that they are thermal stable up to 800 °C, which is higher than the other reported rare earth sulfates [17,18], which may be ascribed to the introduction of Na^+ ion in the lanthanide sulfates. Lastly, the weight loss of **1–3** from 800 to 1000 °C are 24.60%, 25.42% and 22.96%, respectively, corresponding to the release of about one sulfate as SO_3 per unit cell. The formula of the residue could be treated as $\text{Ln}_{1/3}\text{NaSO}_4\cdot\text{Ln}_{2/3}\text{O}$ ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$, calculated 25.12% for **1**, 25.02% for **2** and 24.79% for **3**).

To further examine the thermal stabilities, Powder X-ray diffraction (PXRD) patterns of **1** were recorded in the temperature range of 25–850 °C. As shown in Fig. S4, even heated up to 700 °C, **1** still has almost the same PXRD pattern as that of the room temperature, which confirms that the guest-free frameworks of **1** is thermal stable even up to 700 °C. However, small differences in the intensities of the reflections are observed after 300 °C, which could be ascribed to the removal of the coordinated water molecules from the open framework [22]. After 700 °C, new peaks are observed in the PXRD pattern, suggesting that the framework structure of **1** may begin to be destroyed.

The magnetic susceptibilities of **1–3** were investigated in the temperature range of 2–300 K under an applied direct-current (dc) magnetic field of 1000 Oe (Fig. 3). At 300 K, the $\chi_M T$ values of **1–3** are essentially consistent with the expected values: observed $7.60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **1**

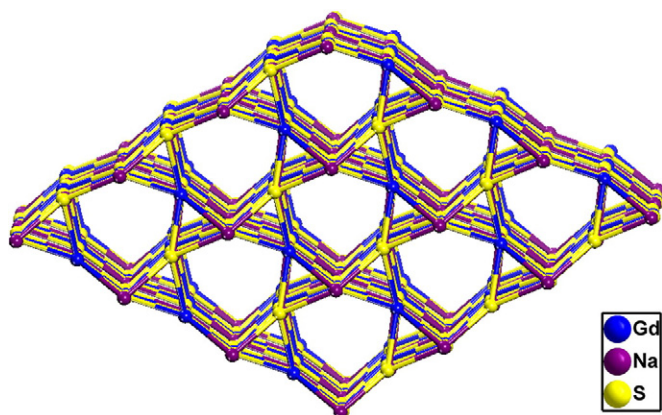


Fig. 2. Schematic view of the 3D 6-connected framework with $(4^{10}\cdot 6^5)$ topology in **1**.

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