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快 报

Co_9S_8 单晶片水热还原合成与磁性 *

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摘 要： 以七水合硫酸亚钴（$CoSO_4 \cdot 7H_2O$）和无水亚硫酸钠（Na_2SO_3）为原料，水合肼（$N_2H_4 \cdot H_2O$）为还原剂，在180℃ 水热处理72 h，成功地合成了片状 Co_9S_8 单晶. 产物分别用X射线粉末衍射（XRD）、透射电子显微镜（TEM）和振动样品磁强计（VSM）表征. 实验结果表明，产物主要由直径为0.8～1.5 μm的片状 Co_9S_8 单晶组成，在室温下具有铁磁性，其饱和磁化率（*Ms*）和矫顽力（*Hc*）分别为65 emu/g和333 Oe.

关键词： 合成；Co_9S_8；单晶片；铁磁性
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Hydrothermal-Reduction Synthesis of Co_9S_8 Single-Crystal Flakes and Magnetic Property *

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Key words Synthesis, Co_9S_8, Single-crystal flakes, Ferromagnetism

Co_9S_8 is an important kind of catalyst for hydrodesulfurization and magnetic material[1] among many phases of cobalt sulfides. It has attracted attention for its properties for a long time[2]. Conventionally, cobalt sulfides powders are prepared by traditional solid state methods. For example, cobalt sulfides could be formed by the reaction of stoichiometric amounts of the constituent elements in evacuated silica tubes in the temperature range from 500 ~ 1200℃[3,4]. Cobalt sulfides could be also prepared by the reaction of cobalt or cobalt monoxide with hydrogen sulfide[5,6]. As we know, a midtemperature synthesis route of Co_9S_8 has been reported involving the treatment of anhydrous cobalt sulfate salt in a flowing gas of hydrogen sulfide and hydrogen at 525℃[7], but there are few reports about the formation of Co_9S_8 by low-temperature hydrothermal method[8-12]. Here, we first reported a low-temperature facile synthesis of Co_9S_8 single-crystal flakes using low-cost anhydrous sodium sulfate (Na_2SO_3) to supply sulfur source and hydrazine hydrate ($N_2H_4 \cdot H_2O$) as the reducing and complexing agent.

Single-crystal flakes of Co_9S_8 were synthesized as follows: 0.851 g of cobalt sulfate hydrate ($CoSO_4 \cdot 7H_2O$) was dissolved in 20 mL of distilled water, and then 0.352 g of sodium sulfate (Na_2SO_3) was added under stirring followed by adding 15 mL of hydrazine hydrate ($N_2H_4 \cdot H_2O$, 80%) to form a mixture. The mixture was stirred strongly for 30 min at room temper-

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ature, and then transferred into a Teflon-lined stainless steel autoclave with a capacity of 60 mL, which was filled with distilled water up to 80% of the total volume. The autoclave was sealed and maintained at 180℃ for 72 h. The system was then allowed to cool to room temperature naturally. Black products were collected by filtration, washed with distilled water and absolute ethanol for several times. The final products were dried under vacuum at 60℃ for 3 h.

The obtained samples were analyzed by powder X-ray diffraction (XRD) on Japan Rigaku D/max-γA X-ray diffractometer with Cu-Ka radiation (λ = 1.5418 Å). All of the diffraction peaks in Fig. 1 can be well indexed to a pure cubic phase of Co_9S_8 (space group: Fm3m (225)) with a lattice constant a = 9.927 Å, which is in well agreement with the literature value of a = 9.928 Å (JCPDS cards, No. 73-1442). No characteristic peaks of impurity phases such as cobalt monoxide and other cobalt sulfides are observed. In addition, it is also observed that the intensities of some reflections have changed, compared with those in the PDF card (JCPDS 73-1442). For instance, in the card, but the diffraction peak of (311) is the strongest one, the (420) and (422) peaks are weaker. The relative intensity of the (511) peak for the samples increases significantly, which implies that the as-prepared samples may have orientation.

The size and morphology of as-synthesized products of Co_9S_8 were further examined using a Hitachi Model H-800 transmission electron microscope (TEM) operated at 200 kV. TEM images in Fig. 2 a and b show that the as-prepared samples are mainly composed of Co_9S_8 hexagonal-shape flakes with diameters of 0.8 ~ 1.5 μm. The selected area electron diffraction (SAED) pattern (Fig. 2a, inset) taken from a single hexagonal-shape flake displays single-crystal electron diffraction spots, from which it can be deduced that the prepared hexagonal-shape flakes mainly consist of Co_9S_8 single crystals.

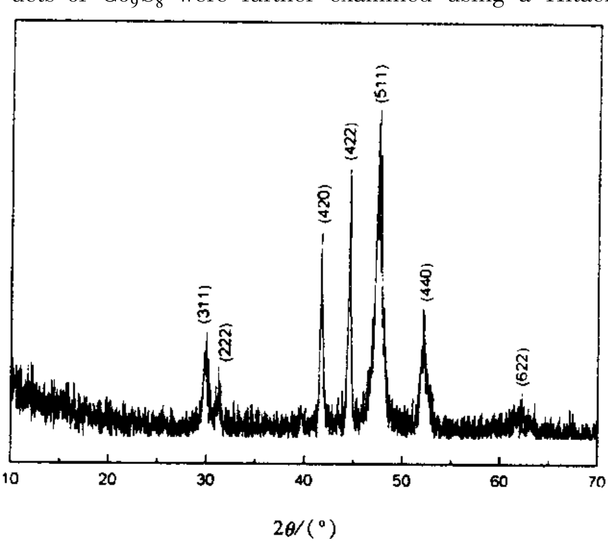
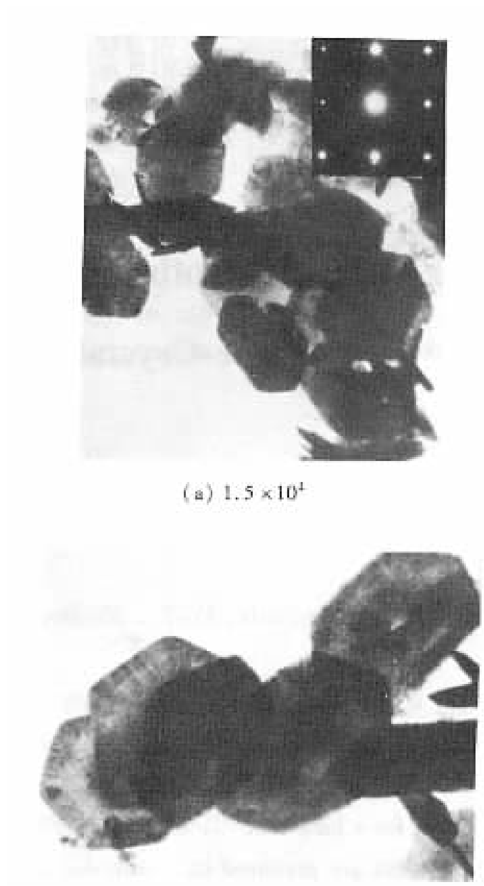


Fig. 1 XRD pattern of the as-prepared samples



(b) 1.0×10^4

Fig. 2 TEM images of the as-prepared products (a) morphology, (inset) SAED pattern of a single Co_9S_8 hexagonal-shape flake, (b) magnification of selected area morphology.

During the formation of Co_9S_8 products, we make use of redox reaction to control S^{2-} concentration, which can be shown as follows:

$$2SO_3^{2-} + 3N_2H_4 \rightarrow 2S^{2-} + 3N_2 + 6H_2O$$

On the basis of the values of E^0, the standard potential of the SO_3^{2-}/S^{2-} couple in alkaline solutions is

−0.61 V. The potential for the redox couple N_2H_4/N_2 (−1.16 V) is negative enough for the SO_3^{2-} reduction to S^{2-}. When $N_2H_4 \cdot H_2O$ is added, Co^{2+}-N_2H_4 complex will be formed. These newly produced S^{2-} will react with Co^{2+}-N_2H_4 complex, then to form the Co_9S_8 products.

Magnetization loop of the products was measured at room temperature using a BHV-55 vibrating sample magnetometer (VSM). The saturation magnetization (Ms) and coercivity (Hc) values of the samples in Fig. 3 are 65 emu/g and 333 Oe respectively, which indicates that the Co_9S_8 products have ferromagnetism.

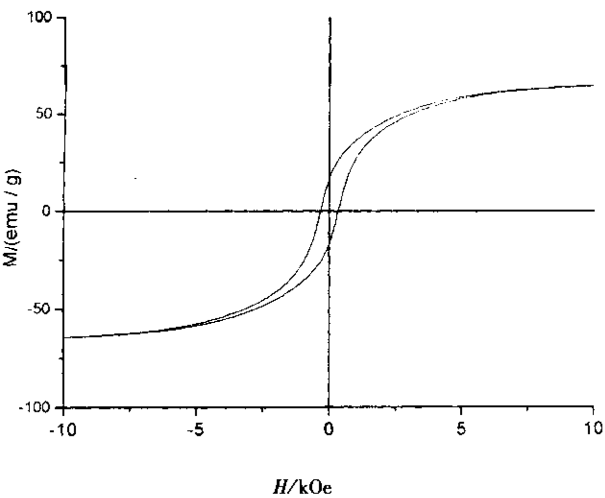


Fig. 3　M-H hysteresis loop of the products at room temperature

In summary, we succeeded in a synthesis of Co_9S_8 single-crystal flakes by the hydrothermal process at 180℃ for 72h. The products are cubic Co_9S_8 single-phase, which consists of Co_9S_8 single-crystal flakes with diameters of 0.8 ~ 1.5 μm. The products have ferromagnetism at room temperature, which might be expected to display many applications in magnetic devices and catalysis.

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