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A convenient co-reduction route to nanocrystalline neodymium disilicide

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Abstract

Nanocrystalline neodymium disilicide was synthesized by co-reducing anhydrous neodymium trichloride and sodium fluorosilicate with metallic sodium in an autoclave at 650 °C. The as-prepared product was characterized and studied by X-ray powder diffraction, transmission electron microscopy and thermogravimetric analysis.

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1. Introduction

Rare earth (RE) silicides have attracted interest during the last few years for both fundamental and technological properties [1], such as their metallic resistivity, a small lattice mismatch (−2.55–+0.83%) [2] and very low Schottky barrier (∼0.3 eV) on n-type silicon [3]. Since, Tu et al. [4] and Norde et al. [5] found the potential device applications in infrared detectors, rare earth silicides became very attractive for electronic applications [6] in the field of ohmic contacts. As one of this kind of rare earth silicides, neodymium silicides also have these unique properties. Furthermore, Nd_5Si_4 and $NdSi_{1.4}$ exhibit magnetic behavior, while $NdSi_{2-x}$ exhibits an antiferromagnetic transition at a Neél temperature of $T_N = 10$ K.

Traditionally, neodymium silicide can be prepared by different methods, such as a mechanical alloying (MA) route [7] by mixing and heating rare earth metal and silicon powders under protective atmosphere, arc-melting synthesis [8] of the constituent elements under a high-purity argon atmosphere, MEVVA (metal vapor vacuum arc) ion source method of thin film followed by rapid thermal annealing from 900 to 1200 °C. However, there are few reports on the synthesis of nanocrystalline neodymium disilicide.

In this paper, we have developed a route to prepare nanocrystalline neodymium disilicide via co-reducing anhydrous neodymium trichloride and sodium fluorosilicate by metallic sodium in an autoclave at 650 °C. This reaction can be described as follows

$$NdCl_3 + 2Na_2SiF_6 + 11Na \rightarrow NdSi_2 + 12NaF + 3NaCl \quad (1)$$

2. Experimental

All the manipulations were carried out in a dry glove box filled with N_2. Typically, 0.01 mol anhydrous $NdCl_3$ and 0.02 mol Na_2SiF_6 were placed in a quartz inner-liner tube.

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Then about 0.11 mol metallic sodium was added in the tube. After that, the liner tube was put into a stainless steel autoclave and sealed under argon atmosphere. The autoclave was heated at 650 °C for 10 h, followed by cooling to room temperature in the furnace. The obtained products from the tube were washed several times with dilute alkali solution, distilled water and absolute ethanol to remove impurities. The final product was vacuum-dried at 60 °C for 12 h.

The powder product was analyzed by powder X-ray diffraction (XRD) on an X-ray differactiometer (Rigaku rA) using Cu Kα radiation (wavelength $\lambda = 1.54178$ Å) and transmission electron microscopy (TEM) on a Hitachi 800 transmission electron microscope. The thermogravimetric analysis was performed on a thermal analyzer (Model: TA-50) below 1000 °C in air at a rate of 10 °C min^{-1} to study its oxidation behavior.

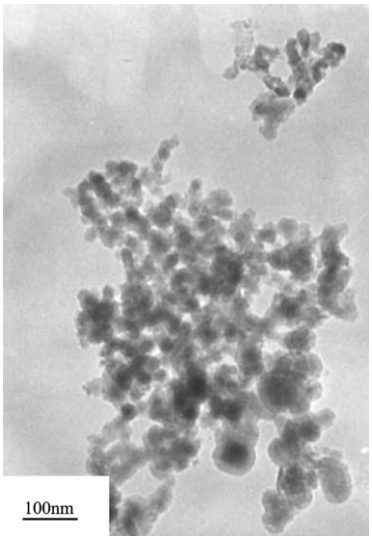

Fig. 2. TEM image of the neodymium disilicide prepared via a co-reduction route.

3. Results and discussion

Fig. 1 shows the XRD pattern of the as-prepared neodymium disilicide sample. All the ten diffraction peaks at the different d-spacing can be indexed as tetragonal phase of neodymium disilicide ((101), (004), (103), (112), (105), (200), (211), (116), (204 and 107) and (213)). After refinement, the lattice parameters are calculated to be $a = 4.104$ Å, $c = 13.49$ Å, which are in good agreement with the values ($a = 4.111$ Å, $c = 13.56$ Å) found in the literature [9]. No evidences of impurities such as Nd, Si, Nd_2O_3 and SiO_2, can be found in the XRD pattern.

Fig. 2 shows the transmission electron microscope (TEM) image of as-prepared neodymium disilicide. From the image, we can find the sample consists of particles with an average size of 25 nm in diameter. But it exhibits slightly agglomerated particle morphology.

The oxidation behavior of the as-prepared nanocrystalline $NdSi_2$ was studied below 1000 °C by TGA, as shown in Fig. 3. Below 550 °C, the weight of the sample decreases slightly. This is because the sample adsorbs some water on the surface of the particles. Meanwhile hydration phenomenon might take place on the surface due to the activity of $NdSi_2$. This can also be confirmed by the TEM image in Fig. 2. The image shows that the particles have out layers due to the hydration of neodymium disilicide. So, on the TGA curve, dehydration of absorbed water occurs around 100 °C

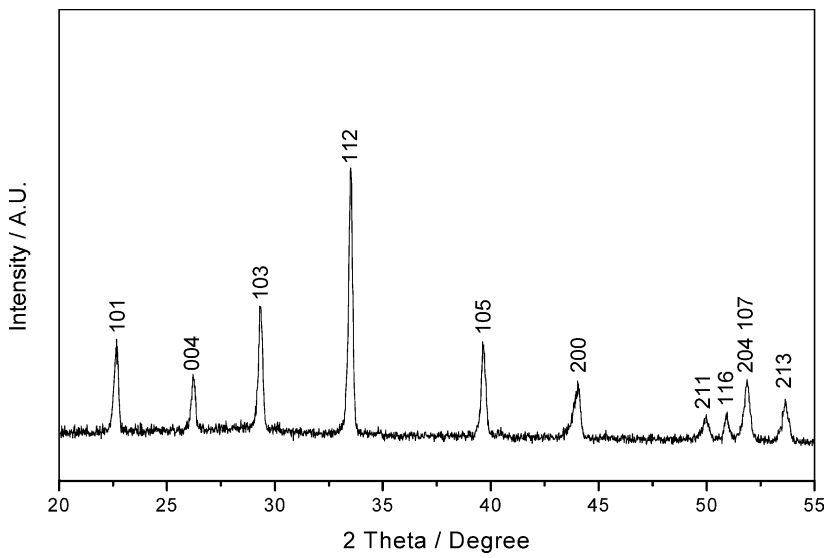

Fig. 1. XRD pattern of the neodymium disilicide prepared via a co-reduction route.

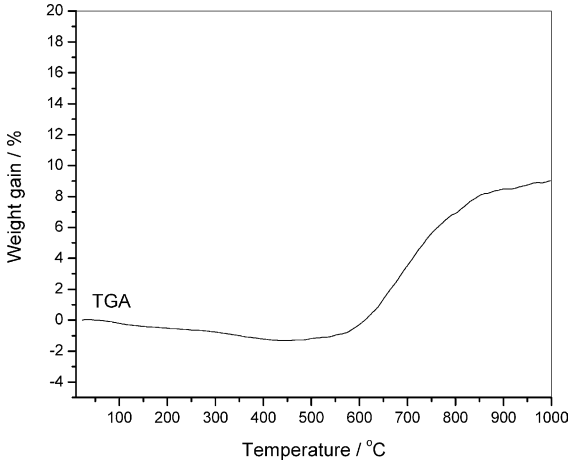

Fig. 3. TGA curves heated in flowing air for the neodymium disilicide.

and dehydration of hydration-water occurs at 300 °C. From 550 to 800 °C, the weight of the powders increases rapidly which means that the oxidation of the sample begins at 550 °C. So from this curve, we can conclude that the as-prepared nanocrystalline neodymium disilicide has good oxidation resistance below 550 °C.

In this route, sodium fluorosilicate can decompose into sodium fluoride and gaseous silicon tetrafluoride above 400 °C. So it is believed that the synthetic reaction of neodymium disilicide is based on the co-reduction of anhydrous neodymium trichloride and silicon tetrafluoride by metallic sodium. The formation process of neodymium disilicide can be described as follows:

$$Na_2SiF_6 \rightarrow 2NaF + SiF_4 \quad (2)$$

$$SiF_4 + 4Na \rightarrow Si^* + 4NaF \quad (3)$$

$$NdCl_3 + 3Na \rightarrow Nd^* + 3NaCl \quad (4)$$

$$Nd^* + 2Si^* \rightarrow NdSi_2 \quad (5)$$

NaF, NaCl can be formed as by-products. When the reaction takes place, the formed heat can make the system in liquid. So the reaction (5), in which nascent neodymium (Nd^*) combines with nascent silicon (Si^*) to form neodymium disilicide, can be carried out in this molten salt system. The molten salt helps to form the nanocrystalline neodymium disilicide. So we can conclude that the formation steps of nanocrystalline neodymium disilicide are as follows: decomposition of the sodium fluorosilicate, co-reduction of silicon tetrafluoride and anhydrous neodymium trichloride and formation of nanocrystalline neodymium disilicide in molten salt system.

4. Conclusion

In summary, nanocrystalline tetragonal neodymium disilicide has been successfully prepared via a co-reduction route by the reaction of metallic sodium with neodymium trichloride and sodium fluorosilicate in an autoclave at 650 °C. The molten salt system serves as reaction medium to control the reaction speed and particle size. The particles have an average size of 25 nm in diameter. The TGA curve shows that the oxidation begins at 550 °C. So the sample has good oxidation resistance below 550 °C.

Acknowledgements

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