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Production of $LaFe_{11.4}Si_{1.6}$ compound at high temperature with a very short annealing time

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In this work, $LaFe_{11.4}Si_{1.6}$ compound was prepared by arc-melting method and annealed at temperature of 1473 K for 5, 10, 30, 60, 180 and 7200 min. X-ray results indicated that as-cast compound mainly consists of α-Fe and LaFeSi phases. After 5 min annealing time at 1473 K, the mixture of α-Fe and LaFeSi was gradually transformed into cubic $NaZn_{13}$ type phase of $LaFe_{11.4}Si_{1.6}$. X-ray result indicated that the sample annealed for 30 min crystallized in a single phase with a cubic $NaZn_{13}$ structure. The magnetic characterizations of the samples were carried out at various temperatures and magnetic fields. The maximum magnetic entropy change ($|\Delta S_m|$) of the sample annealed at 1473 K for 30 min is 22.7 J/kg K at a magnetic field change of 5 T. It was shown that magnetic and magnetocaloric properties for short high temperature annealing of $LaFe_{11.4}Si_{1.6}$ compound are in a good agreement with previously reported values.

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1. Introduction

In recent years, due to the possibility of using magnetic materials as an active magnetic refrigerant in magnetic refrigeration technology, research on the magnetocaloric properties of magnetic materials has attracted considerable attention [1–4]. The magnetic refrigeration technology shows several advantages over the gas compression technique such as compactness, high effectiveness, low energy consumption and environmental safety. The room-temperature magnetic refrigeration, based on the magnetocaloric effect (MCE), has been demonstrated as a very promising alternative to conventional vapour-cycle refrigeration [5,6]. It has been reported that several important factors are required for the application of magnetic materials in magnetic refrigeration technology. The choice of the magnetic refrigerants plays a key role in magnetic refrigeration. First of all, the magnetic materials must be technologically viable in magnetic refrigeration technology. Therefore, the magnetic materials must exhibit large magnetocaloric effect (or large magnetic entropy change) especially at room temperature. Secondly, the preparation difficulties and time, the low cost of raw materials, toxicity, mechanical and chemical stability are also very important factors for using a material as an active magnetic refrigerant [7-11].

Nowadays, nearly all the studies on magnetocaloric effect and magnetic cooling have been focused on the search of the most suitable magnetic materials which have a large MCE, and are technologically viable in magnetic refrigeration technology. In order to obtain a large MCE, much attention has been paid to materials involving a first-order magnetic phase transition because the compounds undergoing a first-order magnetic phase transition exhibit larger values of the magnetocaloric parameters as compared with compound undergoing second-order magnetic phase transition [12-17]. Therefore, many materials with a so-called giant MCE have been found, such as $Gd_5Si_{4-x}Ge_x$ [12], MnAs [13] , $MnFeP_{1-x}As_x$ [14], $MnAs_{1-x}Sb_x$ [15], and $LaFe_{13-x}Si_x$ [16,17]. In all these materials, a first order magnetic phase transition occurs near or below room temperature that gives rise to an abrupt change of magnetization near the transition point. This, in turn, results in a large magnetic entropy change as large as 20-30 J/kg.K for a magnetic field change of 0-5 T.

Considering the above mentioned requirements, among these materials the $LaFe_{13-x}Si_x$ ($1.3 \leq x \leq 2.6$) compounds with cubic $NaZn_{13}$-type structure seem to be good candidate for magnetic refrigeration applications, especially due to the low cost of raw materials and no toxicity [7]. These compounds are known as soft magnetic materials, having a large magnetocaloric effect near room temperature. However, one technical problem is the preparation of a single phase $NaZn_{13}$ structure for these compounds [18-22]. The conventional preparation method involves arc melting or induction melting followed by annealing at 1073-1273 K for a very long homogenization treatment. Typical annealing times vary from ten days [20, 21] to over one or two months [22], which indicates a very slow diffusion-controlled transformation. Such a traditional preparing method obviously wastes a large amount of time and energy. It is thus quite necessary to develop an alternative technique, by which the formation of the $NaZn_{13}$-type phase could be significantly accelerated.

In many study, it has been reported that an alternative solidification technique with undercooling of melts by rapid solidification method, such as splat quenching, melt spinning, atomization, bulk undercooling, are efficient for the reducing of the time required for homogenization [23-

26]. Liu et al.[23] and Yan et al. [24] reported that the $NaZn_{13}$-type structure of $LaFe_{13-x}Si_x$ compounds could be obtained by melt-spinning and subsequent annealing at 1273 K for 20 min to 2 h. In particular, these techniques have found successful applications in quickly producing the $LaFe_{13-x}Si_x$ compounds. But it is important to note that, these techniques are difficult and very expensive which make these techniques disadvantageous. Therefore, in this study, the $NaZn_{13}$-type phase of $LaFe_{13-x}Si_x$ compound was prepared first time successfully by using the conventional preparation method involves arc melting followed by very short annealing times at 1473 K. It has been shown that sample quality is the same as that of the samples prepared with other previous expensive methods. As a magnetic refrigerant, the magnetic properties and magnetic entropy change of the short time annealed compounds was also discussed.

2. Experimental

$LaFe_{11.4}Si_{1.6}$ compounds were prepared by arc melting in an atmosphere of highly pure (99.99 %) argon gas. The highly pure (99.9+%) ingots were arc-melted four times and melting process was performed at 75 A current applied using a Miller Gold Star 402 arc-melting furnace. The buttons are being turned over each time to ensure samples homogeneity. The resulting buttons were sealed in a quartz tube of high vacuum, annealed at 1473 K for 5, 10, 30, 60, 180 and 7200 min, respectively, to homogenize the material. In all the heat treatments, sealed samples were directly placed into pre-heated furnace at 1473 K and after the annealing process, the samples were quenched in iced-water.

The structure of the samples was investigated by X-ray diffractometer (Rigaku-Radb) system. X-ray diffractograms were recorded with a power diffractometer at room temperature using CuKα radiation. Grain structures of the samples observed using a LEO-EVO-40 scanning electron microscope (SEM). The magnetic measurements were performed using a Q-3398 (Cryogenic) magnetometer in a temperature range from 50 to 250 K and 6 T maximum magnetic field was applied.

3. Results and discussion

Fig. 1 shows the room temperature X-ray diffraction patterns of as-cast and annealed between 5 min and 7200 min $LaFe_{11.4}Si_{1.6}$ samples. The results of the as-cast sample reveal the coexistence of α-Fe phase (peaks around 2θ = 44.7º) and LaFeSi phase (peaks around 2θ = 25º, 33º and 40º). The appearance of two minor peaks at 2θ = 38º, 44º and 46.8º in the sample annealed at 1473 K for 5 min indicates that a quite small amount of phases are crystallized in $NaZn_{13}$ type structure through peritectic reaction. The X-ray pattern of the short time annealed (5 min) sample shows that with increasing temperature, the mixture of α-Fe and LaFeSi are gradually transformed into cubic $NaZn_{13}$ type phase of $LaFe_{11.4}Si_{1.6}$. The rapid phase transformation is attributed to the accelerated diffusion of atoms during the period of high temperature annealing [27]. As can be seen from the X-ray pattern of the sample annealed for 10 min, the characteristic peaks of LaFeSi phase observed at 2θ = 25º, 33º and 40º nearly disappear and α-Fe phase observed at 44.7º is significantly reduced. The annealing at 1473 K for 10 min enhances the formation of the $NaZn_{13}$ type phase of $LaFe_{11.4}Si_{1.6}$. For the sample annealed for 30 min, α-Fe phase observed at 44.7º completely disappeared which fact indicates that the sample crystallized in a single phase with a cubic $NaZn_{13}$ structure. Liu et al. [28] prepared the $LaFe_{11.6}Si_{1.4}$ sample by arc-melting method and annealed at high temperatures of 1423, 1473 and 1573 K for an hour, respectively. They have showed that the main $NaZn_{13}$ phase increases with increasing annealing temperature, but traceable amount of α-Fe phase was observed in all their samples. As can be seen from X-ray pattern, the sample prepared in this study by arc-melting at 1473 K for 30 min has a high purity and no trace of α-Fe phase. The purity of the obtained phase in the short-time high temperature annealed samples is in agreement with those annealed at lower temperatures for several weeks (1073-1273 K for ten days to over one month) using arc melting method [20-22] or the samples prepared by rapid solidification methods [23-26]. Fig. 2 shows the typical SEM photographs for $LaFe_{11.4}Si_{1.6}$ samples annealed at 1473 K for 5, 10, 30 and 60 min, respectively. As, seen from Fig. 2, the grain size increases with increasing annealing time and more uniform structural forms.

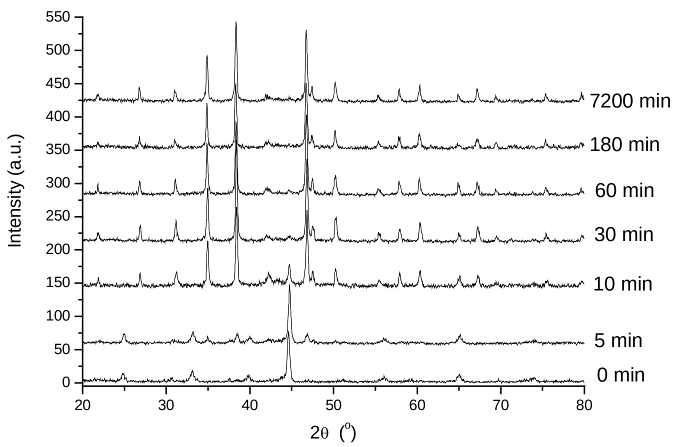

Fig. 1. XRD patterns of the as-cast and annealed $LaFe_{11.4}Si_{1.6}$ at 1473 K for 5, 10, 30, 60, 180, 7200 min.

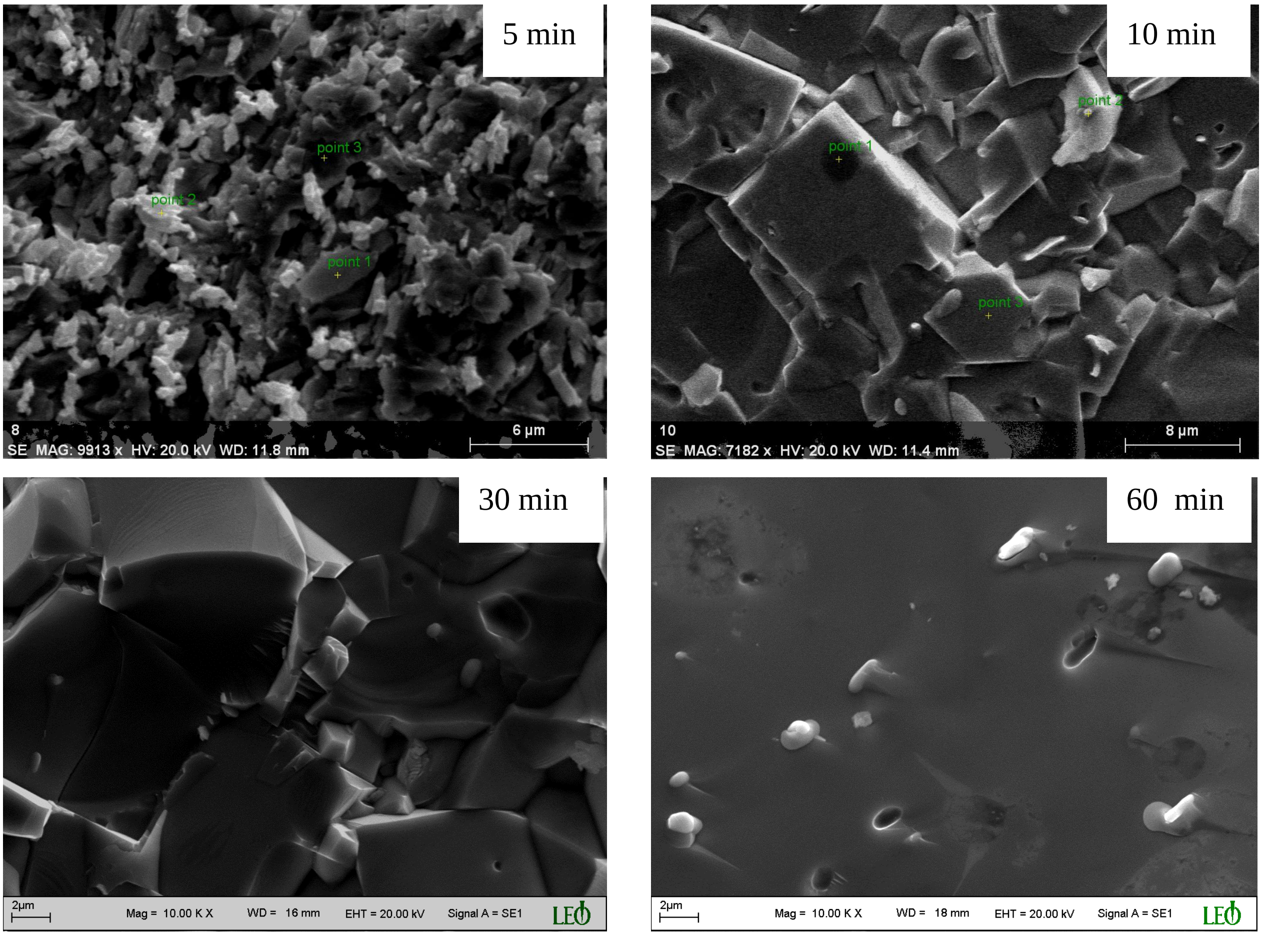

Fig. 2. SEM photographs for $LaFe_{11.4}Si_{1.6}$ samples annealed at 1473 K for 5, 10, 30 and 60 min respectively.

In order to gain more insight into the formation of $NaZn_{13}$ structure, differential thermal analysis (DTA) was performed. Fig. 3 displays an isothermal DTA curve for the $LaFe_{11.4}Si_{1.6}$ alloy annealed at 1473 K. An exothermal peak is clearly seen about 10 min for the arc melted sample, indicating the formation of a substantial amount of NaZn13 phase during the heating process. The isothermal DTA results confirm the fact that the formation of $NaZn_{13}$ phase in arc melted alloy annealed at 1473 K needs a very short annealing time.

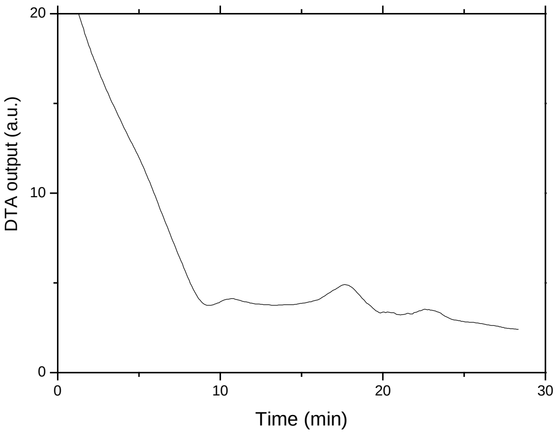

Fig. 3. Isothermal DTA curve for the $LaFe_{11.4}Si_{1.6}$ alloy annealed at 1473 K.

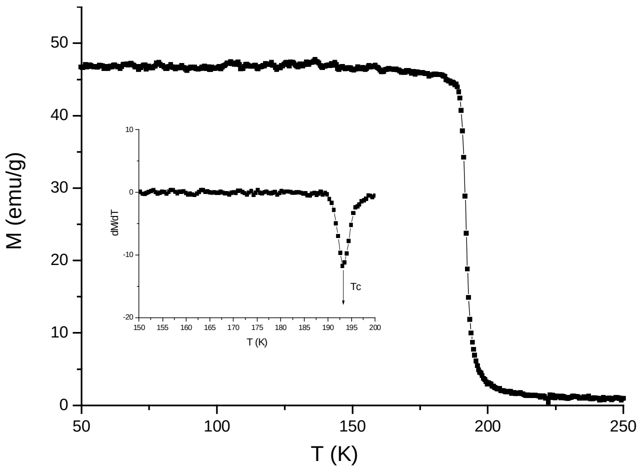

Fig. 4. The temperature dependence of magnetization for $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min. The inset presents the Tc.

Fig. 4 shows the temperature dependence of the magnetization of $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min in an applied magnetic field of 0.1 T. The Curie temperature (T_c) defined as the temperature of the maximum value in |dM/dT|, was found 193 K at 5 mT magnetic field. Fig.5 shows the variation of magnetization as a function of applied magnetic field at different temperatures for $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min. The sample shows ferromagnetic like behaviour below the Curie temperature. The saturation magnetization (M_s) of $LaFe_{11.4}Si_{1.6}$ determined from the magnetization curves is 140 emu/g, in agreement with the literature data [16-28].

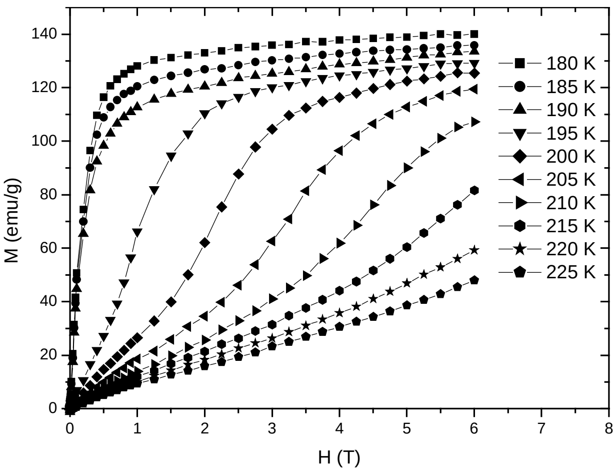

Fig. 5. Isothermal magnetization curves of $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min at various temperatures.

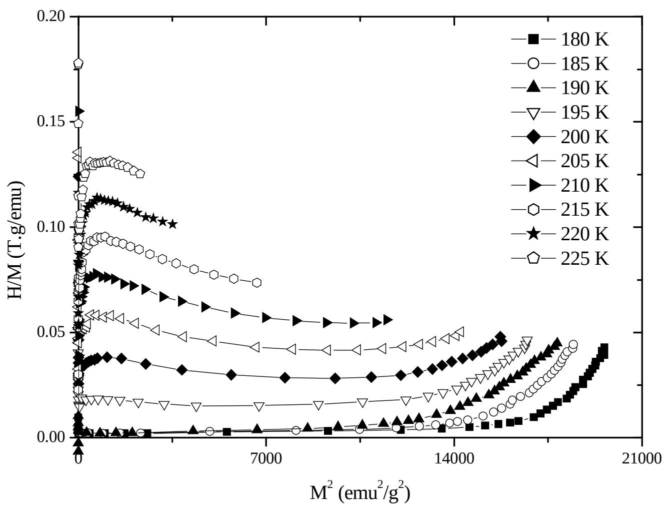

Fig. 6. Arrot plots of $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min.

Fig. 6 shows Arrot plots of $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min. A negative slope in the isotherm plots of H/M versus M^2 is a clear indication of a first-order phase transition from ferromagnetic to paramagnetic ordering.

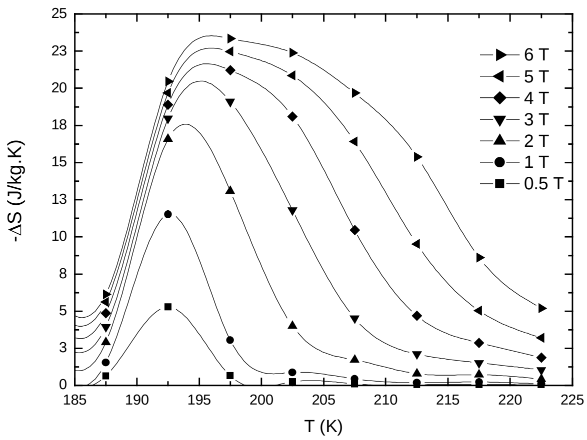

Fig. 7. Magnetic entropy change of $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min at various magnetic fields.

The magnetic entropy, which is associated with the MC effect, can be calculated from the isothermal magnetization curves (Fig.5) under the influence of a magnetic field. According to the classical thermodynamical theory, the magnetic entropy change ΔSm produced by the variation of a magnetic field from 0 to H_{max} is given by:

$$\Delta S_m(T,H) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (1)$$

To evaluate the magnetic entropy change ΔS_m numerical approximation of the integral in Eq. (1) is required. The usual method is to use isothermal magnetization measurement at small discrete field intervals and then ΔS_m can be approximated from Eq. (1) by:

$$\left|\Delta S_m\right| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i}\Delta H \qquad (2)$$

where M_i and M_{i+1} are the experimental values of the magnetization at T_i and T_{i+1}, respectively. Using Eq. (2) and the experimental M-H curves at various temperatures, the magnetic entropy change with the magnetic field variation can be calculated. Fig. 7 shows the magnetic entropy change at various magnetic fields for the $LaFe_{11.4}Si_{1.6}$ sample annealed at 1473 K for 30 min. The peak value of $|\Delta S_m|$ is 22.7 J/kg K at 5 T magnetic field, which is in a good agreement with 20.3 J/kgK of the $LaFe_{11.4}Si_{1.6}$ sample prepared by arc-melting method annealed at 1273 K for two weeks [23].

As a result, it has been shown that by increasing the annealing temperature from conventional 1273 K to 1473 K, the annealing time could decrease from a few weeks to a few minutes. While the conventional sample preparation methods obviously waste a large amount of time and energy, by using high annealing temperature the samples could be prepared more economically at very short time.

The more important is that there is no obvious difference in the structural, magnetic, magnetocaloric properties of samples prepared by high temperature annealing and other expensive methods.

4. Conclusions

$LaFe_{11.4}Si_{1.6}$ compound was prepared by arc-melting method and annealed at high temperature of 1473 K for 5, 10, 30, 60, 180 and 7200 min. X-ray results indicated that as-cast compound mainly consists of α-Fe and LaFeSi phases. X-ray results indicated that the sample annealed for 30 min nearly crystallized in a single phase with a cubic $NaZn_{13}$ structure. The SEM photographs are in agreement with the X-ray results. The isothermal DTA results conform to the fact that the formation of $NaZn_{13}$ phase in arc melted alloy annealed at 1473 K needs a very short annealing. The magnetic characterizations of the samples were defined at various temperatures and magnetic fields. The maximal magnetic entropy change ($|\Delta S_m|$) of the sample annealed at 1473 K for 30 min is 22.7 J/kg K at a magnetic field change of 5 T. It has been showed that magnetic and magnetocaloric properties of shortly high temperature annealing $LaFe_{11.4}Si_{1.6}$ compound are in a good agreement with that of the sample prepared by other methods.

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