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Phase transformation and microstructures of Ln_2S_3 (Ln = La, Sm) with different impurities content of oxygen and carbon

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Abstract

Although the reaction of Ln_2O_3 (where Ln = La and Sm) powders with CS_2 gas is a widely used method for preparing Ln_2S_3, the synthetic powders contain the impurities of oxygen and carbon. The behavior of these impurities in the sintering of Ln_2S_3 was studied using X-ray diffractometry and scanning electron microscopy. The sintering techniques used in this study were a pressure-assisted sintering and a pressureless sintering. While the β to γ phase transformation is dependent on the impurities content of oxygen and carbon, the α to γ phase transformation is not affected by the impurities content. Moreover, the grain size of sintered compact decreases with increasing carbon content. We confirmed that the carbon is removed from synthetic powder using NH_3 gas.

Keywords: Rare-earth sesquisulfides; Pressure-assisted sintering technique; Impurities content; Phase transformation; Grain size

1. Introduction

It is well known that Ln_2S_3 (where Ln = La and Sm) has three structure types: α, β, and γ [1]. The α-phase has an orthorhombic structure, and is exactly stoichiometric. At 1173 K, the α-phase transforms to the β-phase. The β-phase is actually $Ln_{10}S_{14}(O_xS_{1-x})$ with $0 \leq x \leq 1$, which has a tetragonal structure [2]. In its structure, the oxygen atom occupies a special position at the center of a regular tetrahedron of Ln atoms [2,3]. While the β-Ln_2S_3 ($x = 0$) transforms to the γ-phase at 1573 K, $Ln_{10}S_{14}O$ ($x = 1$) is stabilized in this phase over a wide range of temperatures [2]. The γ-phase has the cubic defect Th_3P_4 type structure with metal vacancies. Since the metal vacancies can be occupied by Ln atoms, the γ-phase exists in the compositional range from $LnS_{1.33}$ (Ln_3S_4) to $LnS_{1.50}$ (Ln_2S_3). The LnS_y with $1.33 \leq y \leq 1.50$ is attractive high-temperature thermoelectric materials because of its high melting point, low lattice thermal conductivity, and degenerate semiconducting behavior [4–9].

The usual preparation route for the Ln_2S_3 consists of the sulfurization of Ln_2O_3 using CS_2 or H_2S gas. The preparation of Ln_2S_3 using CS_2 gas became feasible at low temperature in comparison with the reaction with H_2S gas [10,11]. However, the Ln_2S_3 powder prepared using CS_2 gas contains the impurities of oxygen and carbon [12]. While the sintering technique is a widely used method for fabricating the thermoelectric elements of the LnS_y [13], the thermoelectric performance is affected by the microstructures.

In order to obtain thermoelectric elements of La_2S_3, it is important to form LnS_y (γ-phase) and control the microstructures. The microstructures of La_2S_3 prepared using H_2S gas have been characterized for IR window materials [14]. However, no results have ever been reported on the behavior of impurities in the sintering of Ln_2S_3. In present work, we report the influence of the impurities of oxygen and carbon on the phase transformation and the microstructures.

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2. Experimental

The formation behavior of Ln_2S_3 in the sulfurization of Ln_2O_3 powders using CS_2 gas was described elsewhere [10,12]. The starting powders were commercial La_2O_3 which had a particle size of 1.8 μm (Anan Kasei Co.) and commercial Sm_2O_3 which had a particle size of 3.0 μm (Shin-Etsu Chemical Co.). In order to obtain the single-phase powders, the sulfurization was carried out in temperature range from 1023 to 1323 K for 10.8–28.8 ks.

The synthetic powders were sintered by pressureless sintering technique and hot-pressing technique. Before the sintering, the tablets of 10–15 mm diameter and 2–4 mm thickness were fabricated by cold pressing under a uniaxial pressure of 30–50 MPa. For the pressureless sintering, the tablets, placed on a BN boat, were heated at 1773 K for 3.6 ks in 5×1.0^{-3} Pa vacuum. In the case of the hot-pressing, the tablets, placed in the die which was coated with BN, were heated at 1773 K for 3.6 ks under an uniaxial pressure of 30 MPa in 7×1.0^{-3} Pa vacuum. The both heating rates were $0.17\,K\,s^{-1}$.

Furthermore, the synthetic powders were sintered by a pressure-assisted pulsed electric current sintering (PECS) technique using spark plasma sintering apparatus (SPS-511S, Sumitomo Coal Mining Co.). The powders, placed in graphite die of 10 mm diameter, were introduced into PECS apparatus. The chamber was pumped down to 7×10^{-3} Pa. The powders were heated at rate of $0.42\,K\,s^{-1}$ up to 1573 K. After being held for 3.6 ks, the samples were cooled at rate of $0.84\,K\,s^{-1}$ to 873 K, followed by slow cooling to room temperature. An uniaxial pressure of 50 MPa in the die was applied during the heating and holding.

The synthetic powders and the sintered compacts were characterized by X-ray diffractometry (XRD; Rint-Ultima+, Rigaku Co.) using Cu Kα radiation and scanning electron microscopy (SEM; JSM-5310LV, JEOL). For the determination of lattice parameters, the XRD patterns were corrected using Si powder as an external standard.

3. Results and discussion

The synthetic powders which were prepared by the reaction of La_2O_3 with CS_2 consisted of the $La_{10}S_{14}(O_xS_{1-x})$ phase. Besançon found that the tetragonal lattice parameters are decreased by the substitution of oxygen atom for sulfur atom [2]. Our result agrees with that found in that paper. As shown in Fig. 1, the oxygen content determined by chemical analysis shows a sharp decrease at about 1200 K [12]. The tetragonal lattice constants a and c show a sharp increase in temperature range of 1150–1250 K, in agreement with the oxygen content data. It is evident that the unit cell is expanding as the oxygen content decreases; therefore, the result suggests that the substitutional oxygen content in $La_{10}S_{14}(O_xS_{1-x})$ decreases abruptly at about 1200 K.

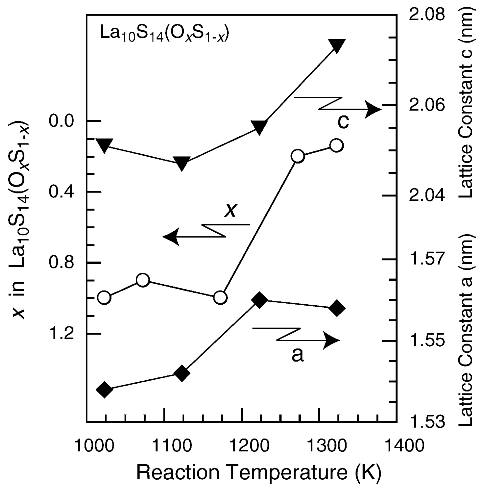

Fig. 1. Tetragonal lattice constants of the $La_{10}S_{14}(O_xS_{1-x})$ powders and the oxygen content in same powders [12] as a function of the reaction temperature.

As shown in Fig. 2, the carbon content in $La_{10}S_{14}(O_xS_{1-x})$ powders increases almost linearly with reaction temperature [12]. The carbon content was caused by the thermal dissociation reaction of a part of the CS_2 gas. Thus, the synthetic powders consist of $La_{10}S_{14}(O_xS_{1-x})$ and a few carbon. It is well known that the color of $La_{10}S_{14}(O_xS_{1-x})$ is a faint yellow; however, the color of synthetic powders changes from faint yellow to gray with increasing carbon content.

The single-phase α-Sm_2S_3 was confirmed by the sulfurization at 1023–1323 K. As reaction temperature increases, the oxygen content decreases from 0.52 to 0.24 wt.% while the carbon content increases from 0.03 to 0.06 wt.% [12]. The carbon was mixed by the thermal dissociation reaction of a part of the CS_2 gas, as mentioned above. In contrast, we were unsuccessful in finding origin of the oxygen content which was found by chemical analysis. For α-Sm_2S_3, there is no indication that the oxygen atom substitutes for the sulfur atom. A small amount of oxygen may remain as Sm_2O_3 or Sm_2O_2S.

Fig. 3 shows SEM micrographs of the La_2O_3 powder and the $La_{10}S_{14}(O_xS_{1-x})$ powders. As shown in Fig. 3(a), we

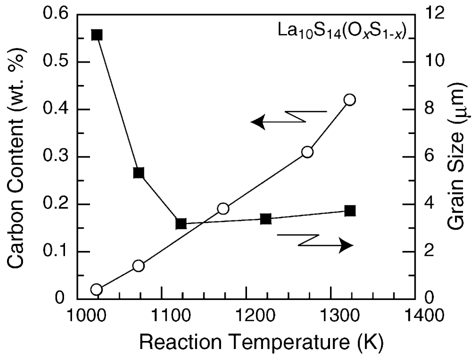

Fig. 2. Carbon content in the $La_{10}O_{14}(O_xS_{1-x})$ powders [12] and the grain size of $La_{10}O_{14}(O_xS_{1-x})$ after a pulsed electric current sintering at 1573 K as a function of the reaction temperature.

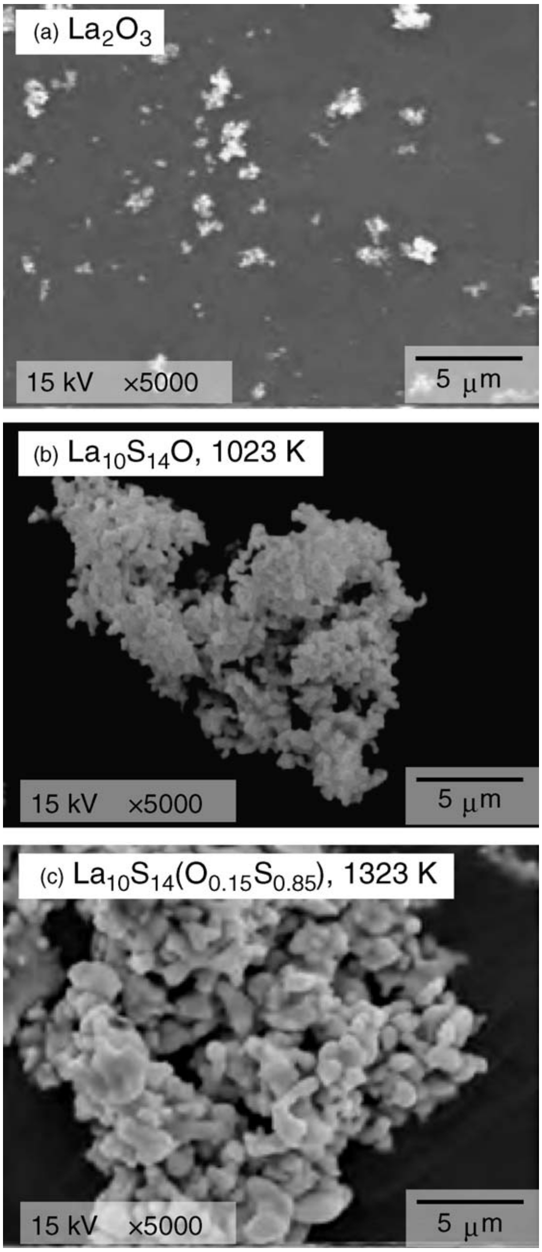

Fig. 3. SEM micrograph of (a) La_2O_3 powder, (b) $La_{10}S_{14}O$ powder prepared at 1023 K for 28.8 ks, and (c) $La_{10}S_{14}(O_{0.15}S_{0.85})$ powder prepared at 1323 K for 28.8 ks.

found the primary particles dispersing. In contrast, for the synthetic powder, Figs. 3(b) and (c) show the agglomeration of the primary particles. The SEM microscopy revealed that the agglomerate size increases with reaction temperature. The important point to note is increase in the size of primary particle with the reaction temperature increase.

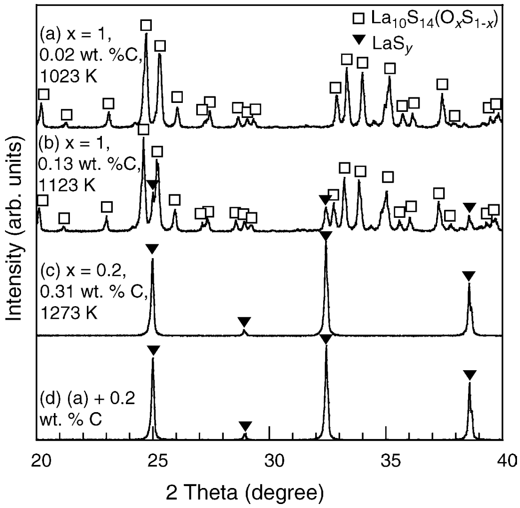

Fig. 4. XRD patterns of compacts obtained by pressureless sintering at 1773 K. The starting powders were: (a) the $La_{10}S_{14}O$ with 0.02 wt.% C prepared at 1023 K for 28.8 ks, (b) the $La_{10}S_{14}O$ with 0.13 wt.% C prepared at 1123 K for 28.8 ks, (c) the $La_{10}S_{14}(O_{0.2}S_{0.8})$ with 0.31 wt.% C prepared at 1273 K for 28.8 ks, and (d) the powder (a) with 0.20 wt.% carbon black.

The XRD patterns after pressureless sintering of $La_{10}S_{14}(O_xS_{1-x})$ are shown in Fig. 4. While the phase transformation from $La_{10}S_{14}(O_{0.2}S_{0.8})$ to LaS_y was observed at 1773 K and 0.31 wt.% C, the $La_{10}S_{14}O$ maintained in $La_{10}S_{14}(O_xS_{1-x})$ phase at 1773 K and 0.02 wt.% C. The results imply that the substitution of oxygen stabilizes the $La_{10}S_{14}(O_xS_{1-x})$ phase. Furthermore, one can find the influence of carbon on the phase transformation from Fig. 4(b) and (c). In Fig. 4(c), the formation of LaS_y due to carbon content of 0.13 wt.% was confirmed after the sintering of $La_{10}S_{14}O$ powder, unlike $La_{10}S_{14}O$ with 0.02 wt.% C shown in Fig. 4(b). In order to investigate the influence of the carbon content, the carbon black powder which has a particle size of 0.022 μm was added to the $La_{10}S_{14}O$ with 0.02 wt.% C powder. As shown in Fig. 4(d), the sintered compact consists of LaS_y; therefore, the result suggests that the phase transformation is accelerated by containing a large amount of carbon. Since the pressureless sintering caused a 25% decrease in the oxygen content and a 75% decrease in the carbon content, the acceleration is most likely attributed to the carbothermic reduction. Similarly, in the hot-pressing, we found that the impurities content of oxygen and carbon have influence on phase transformation from $La_{10}S_{14}(O_xS_{1-x})$ to LaS_y. The low temperature formation of LnS_y due to the carbon in the precursor like malonate has been already reported [15].

For a hot-pressing of α-Sm_2S_3 at 1773 K, the XRD patterns of compacts are shown in Fig. 5. While an increase in the reaction temperature was observed to decrease the oxygen content and increase the carbon content in the synthetic α-Sm_2S_3 powder, the all compacts consisted of the single-phase SmS_y. It is clear that the phase transformation from α-Sm_2S_3 to SmS_y was independent of the oxygen content less than 0.52 wt.% and the carbon less than 0.06 wt.%, unlike the phase transformation from $La_{10}S_{14}(O_xS_{1-x})$ to LaS_y shown in Fig. 4.

XRD analysis of compacts sintered by PECS at 1573 K shows that all samples consisted of the $La_{10}S_{14}(O_xS_{1-x})$ phase. The large linear shrinkage of the sample was observed in the temperature range of 1023–1473 K. As a result, the compacts close to the theoretical density were obtained by

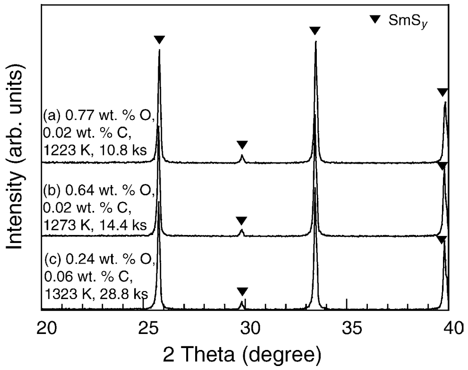

Fig. 5. XRD patterns of compacts obtained by hot-pressing at 1773 K. The starting powders were: (a) the α-Sm_2S_3 with 0.77 wt.% O and 0.02 wt.% C prepared at 1223 K for 10.8 ks, (b) the α-Sm_2S_3 with 0.64 wt.% O and 0.02 wt.% C prepared at 1273 K for 14.4 ks, and (c) the α-Sm_2S_3 with 0.24 wt.% O and 0.06 wt.% C prepared at 1323 K for 28.8 ks.

the sintering at temperatures above 1473 K. For cerium sulfide, the large linear shrinkage has been found in the same temperature range [11]. Vaughan-Forster and White have reported that the Ln_2S_3 powders sintered by pressureless sintering at 1623–1673 K in H_2S gas achieved relative densities of 92–98% [16].

Fig. 6 shows SEM micrographs of fracture surfaces of the $La_{10}S_{14}(O_xS_{1-x})$ sintered by PECS at 1573 K. We confirm that the $La_{10}S_{14}(O_xS_{1-x})$ have few pores. The grain size is plotted as a function of the reaction temperature of starting powder, as shown in Fig. 2. Although the primary particle size of starting powder increases with reaction temperature shown in Fig. 3, the grain size of compacts shows an abrupt decrease up to 1123 K and then a gradual increase. It appeared that the abrupt decrease up to 1123 K is due to the carbon content increase. We believe that the growth of the grain size is affected by the carbon content more than about 0.1 wt.%. However, since the oxygen content increase with reaction temperature, the effect of the carbon impurity is not fully understood. In order to investigate the effect of carbon content on grain size, the carbon black powder was added to the $La_{10}S_{14}O$ with 0.02 wt.% C powder. After being thoroughly mixed, the powders were sintered under the same PECS conditions. SEM micrographs revealed that the grain size shown in Fig. 6(d) is small compared to that shown in Fig. 6(a); therefore, we can conclude that the grain size is controlled by the carbon content. The carbon content from 0.1 to 0.2 wt.% has a dramatic effect on the growth of grain size. In contrast, the gradual increase in the grain size at temperatures above 1123 K is attributed to increase in the particle size of starting powder.

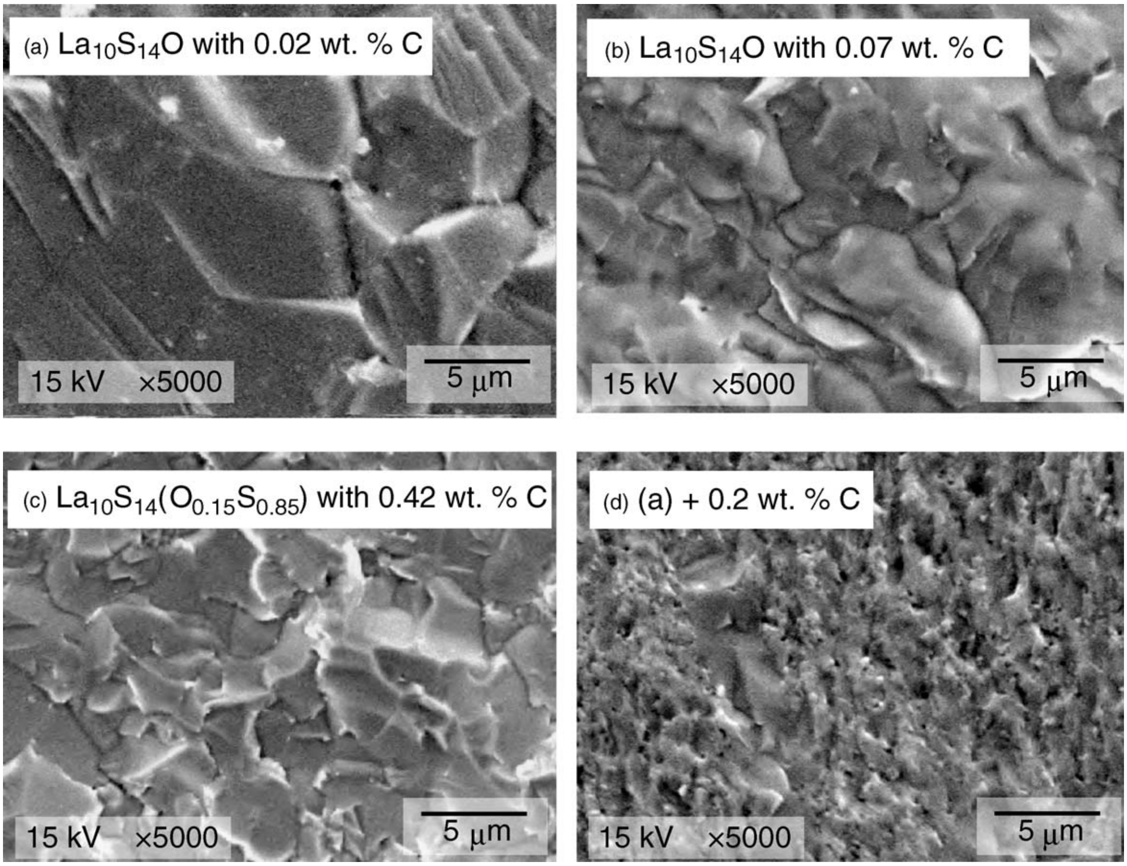

Fig. 6. SEM micrographs of fracture surfaces for the $La_{10}S_{14}(O_xS_{1-x})$ compacts obtained by a pulsed electric pulsed sintering at 1573 K. The starting powders were: (a) the $La_{10}S_{14}O$ with 0.02 wt.% C prepared at 1023 K for 28.8 ks, (b) the $La_{10}S_{14}O$ with 0.07 wt.% C prepared at 1173 K for 28.8 ks, (c) the $La_{10}S_{14}(O_{0.15}S_{0.85})$ with 0.42 wt.% C prepared at 1323 K for 28.8 ks, and (d) the powder (a) with 0.20 wt.% carbon black.

As the reaction temperature increases, the carbon content increases while the oxygen content decreases. Therefore, it is difficult to obtain the synthetic powder containing small amount of impurities. In particular, the carbon content has important influences on the phase transformation from $La_{10}S_{14}(O_xS_{1-x})$ to LaS_y and the microstructures. Sato et al. have proposed the reaction with NH_3 for removing the carbon impurity in Nd_2S_3 powder [17]. Using similarly technique, we investigated the decarburization of La_2S_3. NH_3 gas is used for the reaction:

$$4NH_3 + 3C = 2N_2 + 3CH_4 \quad (1)$$

The standard free-energy changes for the related reactions have been calculated from the thermodynamic data [18,19]. As a result, we conclude calculatedly that the carbon impurity is removed by the reaction in temperature above 500 K, without affecting La_2S_3. The synthetic $La_{10}S_{14}(O_xS_{1-x})$ powder, placed on a BN boat, was introduced into furnace with NH_3 atmosphere. After being heated at 1273 K for 3.6 ks, the carbon content decreased from 0.23 to 0.07 wt.%.

4. Conclusion

We conclude that the impurities of oxygen and carbon in the synthetic powder have influence on the phase transformation from $La_{10}S_{14}(O_xS_{1-x})$ to LaS_y. In contrast, the phase transformation from α-Sm_2S_3 to SmS_y is not affected by the impurities. While the compacts densities near theoretical density were achieved by the sintering at temperature above 1473 K, the grain size decreases as the carbon content increases. The carbon impurity in the synthetic powder is removed by the reaction with NH_3.

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