32/9-18-90JS ②

CONF-8709426--1

IS-M 635

A STUDY OF THE THERMOELECTRIC PROPERTIES OF Ca, Sr AND Hg SUBSTITUTED LANTHANUM SULFIDES

J. F. Nakahara, T. Takeshita*, M. J. Tschetter,
B. J. Beaudry, and K. A. Gschneidner, Jr.**

IS-M--635

DE90 016713

Ames Laboratory+, Iowa State University,
Ames, IA 50011, U.S.A.

*Present address: Mitsubishi Metal Corp. Ltd., 1-297 Kitabukuro-cho, Ohmiya, Saitama, Japan

**Also Department of Materials Science and Engineering

+Ames Laboratory is supported by the U.S. Department of Energy, Office of Defense Energy Projects and Special Applications, Office of Nuclear Energy, under contract no. W-7405-ENG-82.

ABSTRACT

Compounds of the type $La_{3-x}M_xS_4$, where M is Ca, Sr or Hg and x ranges from 0.1 to 0.9, were prepared by the pressure assisted reaction sintering (PARS) method. These compounds have the Th_3P_4-type structure. Results of the measurements of the Seebeck coefficient and electrical conductivity from room temperature to 1000°C showed these compounds to be n-type semiconductors and have electrical power factors near 11 $\mu W\ cm^{-1}\ °C^{-2}$ for $x < 0.3$. However, if estimates of the thermal conductivity based on the binary LaS_y series are taken into consideration, the optimum figure-of-merit shifts to higher values of x. In this study, the maximum value of

First European Conference on Thermoelectrics
September 15-17. 1987
University of South Wales Cardiff, Wales, United Kingdom

---

the figure-of-merit was 0.4 x 10^{-3} °C^{-1} for x = 0.6. Studies of the stability of these Th_3P_4-type ternary compounds showed the formation of a second phase at 1100°C over a period of 2000 hours.

INTRODUCTION

In a previous paper[1] the temperature and composition dependence of the Seebeck coefficients and electrical conductivity of the ternary compounds $La_{3-x}M_xS_4$ with M = Sm, Eu or Yb and for x = 0.1 to 0.9 with the Th_3P_4-type structure were reported. It was found that these ternary materials were n-type semiconductors whose thermoelectric figure-of-merit at 1000°C was better than for the binary lanthanum sulfides. The figure-of-merit for $La_{2.3}M_{0.7}S_4$ (M = Eu, Yb) was 0.6 x 10^{-3} °C^{-1} compared to 0.45 x 10^{-3} °C^{-1} for $La_{1.45}$[2]. In the present paper divalent Ca, Sr or Hg are substituted for trivalent La in La_3S_4. The Seebeck coefficient and electrical conductivity have been measured from room temperature up to 1000°C and the long term phase stability at 1100°C has also been examined.

EXPERIMENTAL

The compounds used in this study were prepared by the pressure assisted reaction sintering (PARS) method.[3] A mixture of finely divided powders of La_2S_3, MS (M = Ca, Sr or Hg) and LaH_3 were thoroughly mixed in stoichiometric amounts according to the balanced reaction

$$\tfrac{1}{3}(4-x)La_2S_3 + \tfrac{1}{3}(1-x)LaH_3 + xMS \longrightarrow La_{3-x}M_xS_4 + \tfrac{1}{2}(1-x)H_2\uparrow .$$

The powders of La_2S_3 and CaS or SrS were first prepared by reacting the metal (prepared at the Materials Preparation Center of the Ames Laboratory) and sulfur (purchased from ASARCO, 99.999 at.% pure) at low temperature in sealed ampoules. The mercuric sulfide was purchased from Fisher Scientific Company. The lanthanum hydride was prepared by reacting zero grade hydrogen gas with a piece of electropolished lanthanum in a stainless steel reaction tube at room temperature. The powders were all handled in a helium environment to minimize contamination by oxygen.

The mixture of powders was compacted into a graphite die and vacuum hot pressed in a double action compaction die at 31 MPa (4500 psi) for 2 hours at 1450°C. The sample was allowed to cool slowly to room temperature before being removed from the die. X-ray powder diffraction patterns were obtained for the hot pressed compacts using a Scintag Pad V[4] automatic diffractometer.

The Seebeck coefficient (S) and electrical conductivity (σ) were measured simultaneously as a function of temperature using the experimental setup and procedure reported previously.[1] Those Ca and Sr ternary samples which possessed an electrical power factor ($S^2\sigma$) greater than 8 $\mu W\ cm^{-1}\ {}^{\circ}C^{-2}$ were subsequently put on a long term stability test at 1100°C for over 2000 hours in vacuum. X-ray diffraction and metallographic analyses were performed on these heat treated samples.

RESULTS AND DISCUSSION

The x-ray powder diffraction patterns of the reaction sintered Ca, Sr and Hg ternary compounds, $La_{3-x}M_xS_4$, exhibited diffraction peaks characteristics of the Th_3P_4-type structure. The cubic lattice parameter of the Ca and Hg ternaries decreased while those of the Sr ternaries increased with increasing values of x (Fig. 1). This observation is in agreement with the variation of the Shannon-Prewitt ionic radius of the constituent metal atoms: La^{3+} (1.045

Å)[5], Ca^{2+} (1.00 Å)[6], Sr^{2+} (1.13 Å)[5] and Hg^{2+} (1.02 Å)[6].

Figures 2 and 3 display the composition dependence of the Seebeck coefficient at 25°C and 1000°C, respectively, for binary LaS_y and the Ca, Sr and Hg ternaries. The calculated value of the electron concentration is assumed to be independent of temperature and was calculated from the experimental value of the lattice parameter and composition. The data for the Ca, Sr and Hg substituted La_3S_4 generally lie along a line which has a steeper slope than the binary lanthanum sulfides.[2,3] The curves would be expected to coincide at $LaS_{1.333}$ when $x = 0$ (i.e. $n^{-2/3} = 3.02 \times 10^{-15}$) and this is observed at T = 25°C, Fig. 2. However, at T = 1000°C, Fig. 3, there is a definite offset. We are not able to offer a good explanation for this observation, but it is possible that there are some differences in the impurity levels of the Wood *et al.* samples relative to ours. It should be noted, however, that our results[5] for the LaS_y alloys are in excellent agreement with the Wood *et al.* data at room temperature. Additional work is needed to resolve the observed offset.

The corresponding electrical conductivity data are shown in Figures 4 and 5. The data for the ternary sulfides, in contrast to the binary results, lie on two straight line segments with a break at an electron concentration of about 3.5×10^{21} cm^{-3}. In all cases the conductivity increases with increasing electron concentration. At 25°C and 1000°C and for the same value of n, the conductivity of the ternaries are lower than for LaS_y, indicating that the carrier mobilities of the former are smaller than the latter. However, at high electron concentrations the electrical conductivity of the ternaries tend to approach that of the binary LaS_y alloys. It is also noticed that the conductivity and hence carrier mobility decrease with increasing temperature opposite to that which is desired in high temperature thermoelectric applications. It is interesting to note that at n = 0, the conductivity is nonzero and one can infer that substituting a divalent ion for trivalent La changes the electrical nature (i.e., bandgap or Fermi effect) of these ternary compounds.

The electrical power factor $S^2\sigma$ at 1000°C was computed for each sample and is plotted as a function of composition in Figure 6. It is interesting to note that the data points for the ternary lanthanum sulfides occur along a common curve and are essentially equal to those of the binary lanthanum sulfide between $n = 2.5 \times 10^{21}$ and 4×10^{21} cm^{-3}. Below 2.5×10^{21} cm^{-3} the power factor of the binaries is better than the ternaries while the opposite is true above 4×10^{21} cm^{-3}. From this plot, the optimum composition is for x between 0.1 and 0.3 in which the electrical power factor at 1000°C is near 11 $\mu W\ cm^{-1}\ °C^{-2}$. A similar value was obtained for the Sm, Eu and Yb substituted La_3S_4.[1]

If the thermal conductivity is taken into consideration then the composition which possesses the optimum thermoelectric properties shifts towards larger x values. The thermal conductivity values were obtained from a study by Wood, et al.[2] on binary LaS_y and they are assumed to be the same for the ternaries at a given electron concentration, see Table I. For small values of x the electron concentrations are high, and the thermal conductivity values are large and hence the figure-of-merit is small. As x approaches 0.5 or

0.6, the thermal thermal conductivity is half as large and the figure-of-merit is a maximum with a value of 0.4 x 10^{-3} °C^{-1}. This value is 1.5 times smaller than that obtained for the Eu and Yb ternaries ($x = 0.7$, $Z = 0.6 \times 10^{-3}$ °C^{-1}).

The results of the long term phase stability of the Ca and Sr samples indicate that the high temperature Th_3P_4-type structure is not stable below 1100°C after an extended period exceeding 2000 hours in vacuum. The x-ray diffraction pattern and metallography results indicate the formation of a second phase which was identified as β-La_2S_3 (actually $La_{10}S_{14}O$) and whose presence degrades the thermoelectric performance. Figure 7 shows typical data of the growth of diffraction peaks due to the second phase. This result is identical to that observed in heat treated binary LaS_y[7] and the Sm and Eu ternaries.[1]

SUMMARY

The ternary lanthanum sulfides $La_{3-x}M_xS_4$ for M = Ca, Sr and Hg and x = 0.1 to 0.9 were prepared by the presure assisted reaction sintering method and had the high temperature Th_3P_4-type structure. The compounds with x = 0.1 to 0.3 possessed the best electrical power factor at 1000°C, but the figure-of-merit was best for x = 0.6. These materials which contained traces of oxygen are not suitable after long term anneals at 1100°C since they slowly transform from the high temperature γ-form to the lower temperature β-form ($La_{10}S_{14}O$) which destroys their ability to perform as thermoelectric materials.

REFERENCES

1. J. F. Nakahara, T. Takeshita, M. J. Tschetter, B. J. Beaudry and K. A. Gschneidner, Jr., to be published.

2. C. Wood, A. Lockwood, J. Parker, A. Zoltan, D. Zoltan, L. R. Danielson and V. Raag, J. Appl. Phys. 58, 1542 (1985).

3. T. Takeshita, K. A. Gschneidner, Jr. and B. J. Beaudry, J. Appl. Phys. 57, 4633 (1985).

4. Scintag, Inc., 3350 Scott Boulevard, Building 28, Santa Clara, CA 95054.

5. R. D. Shannon and C. T. Prewitt, Acta Cryst. B26, 1046 (1970).

6. R. D. Shannon and C. T. Prewitt, Acta Cryst. B25, 925 (1969).

7. B. J. Beaudry, M. J. Tschetter, J. F. Nakahara, T. Takeshita and K. A. Gschneidner, Jr., in Proceedings 6th International Conference on Thermoelectric Energy Conversion, Arlington, TX, March 12-14, 1986, edited by K. R. Rao (University of Texas, Arlington, TX, 1986), p. 20.

TABLE I. Electrical power factor, thermal conductivity and figure-of-merit at 1000°C for $La_{3-x}M_xS_4$ (M= Ca, Sr, Hg and x = 0.1 to 0.9).

x	$S^2\sigma$ (μWcm^{-1}°C^{-2})[a]	κ[b] (mWcm^{-1}°C^{-1})	$Z = S^2\sigma/\kappa$ (x 10^{-3}°C^{-1})
0.1	11.0	39.0	0.28
0.2	11.4	33.8	0.34
0.3	10.8	29.0	0.37
0.4	7.9	24.7	0.32
0.5	7.5	21.0	0.36
0.6	6.8	17.8	0.38
0.7	4.9	15.0	0.33
0.8	3.7	13.0	0.28
0.9	3.1	11.5	0.27

[a] This study

[b] Wood, *et al*.[2], for binary LaS_y $1.33 < y < 1.50$.

FIGURE CAPTIONS

Fig. 1. Lattice parameters as a function of x for $La_{3-x}M_xS_4$ (M = Ca, Sr, Hg).

Fig. 2. Seebeck coefficient versus the negative two-thirds power of the electron concentration at 25°C for binary LaS_y (Takeshita, _et al._[3]) and the ternary lanthanum sulfides.

Fig. 3. Seebeck coefficient versus the negative two-thirds power of the electron concentration at 1000°C for binary LaS_y (Wood, _et al._[2]) and the ternary lanthanum sulfides.

Fig. 4. Electrical conductivity versus electron concentration at 25°C for binary LaS_y (Takeshita, _et al._[3]) and the ternary lanthanum sulfides.

Fig. 5. Electrical conductivity versus electron concentration at 1000°C for binary LaS_y (Wood, _et al._[2]) and the ternary lanthanum sulfides.

Fig. 6. Electrical power factor versus composition at 1000°C for binary LaS_y (Wood, _et al._[2]) and the ternary lanthanum sulfides.

Fig. 7. X-ray powder diffraction pattern of $La_{2.8}Ca_{0.2}S_4$ before and after 2500 hours at 1100°C in vacuum. The peaks due to the second phase can be seen between 33 and 38 degrees 2-theta.

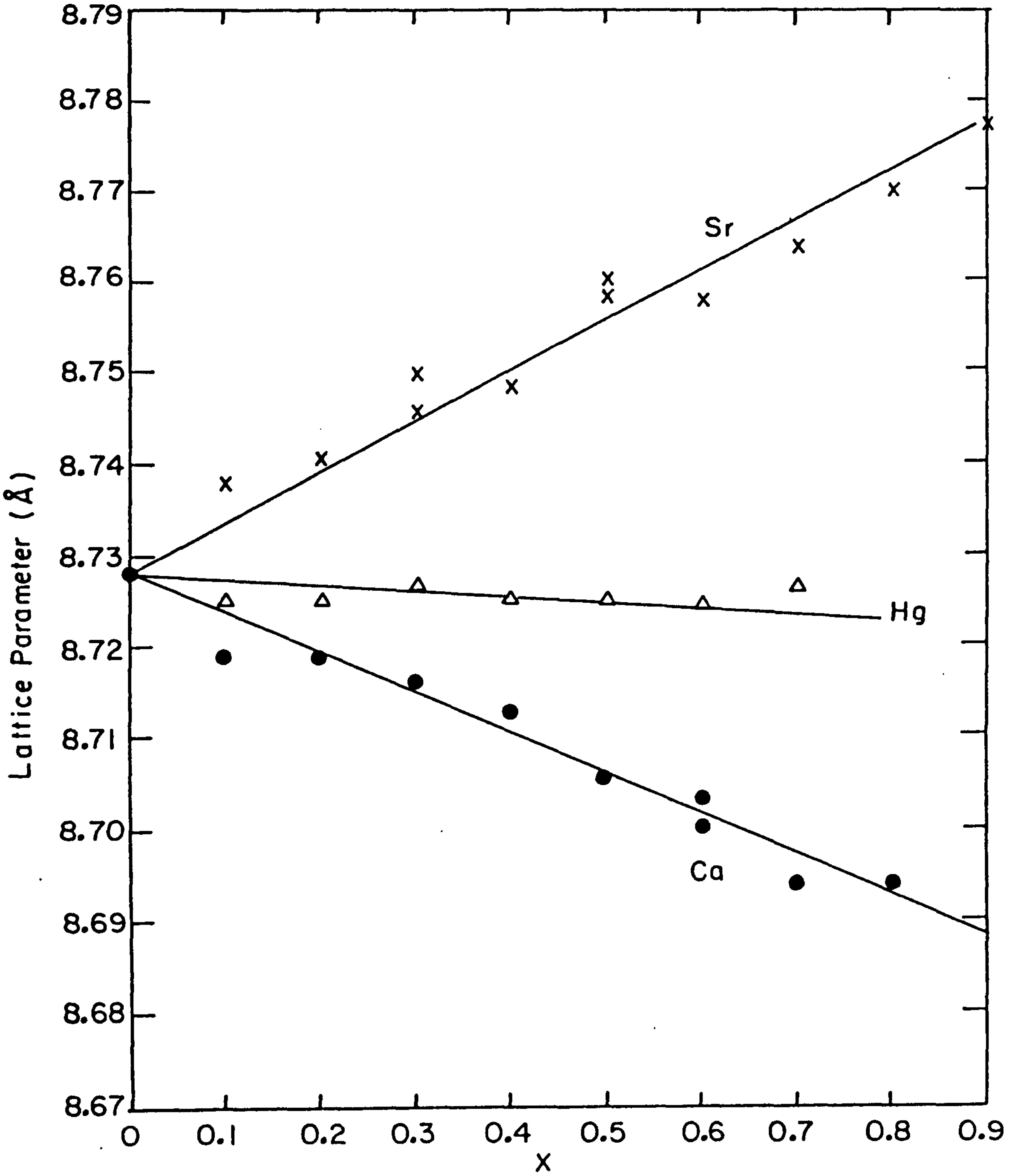

Fig. 1. Lattice parameters as a function of x for $La_{3-x}M_xS_4$ (M = Ca, Sr, Hg).

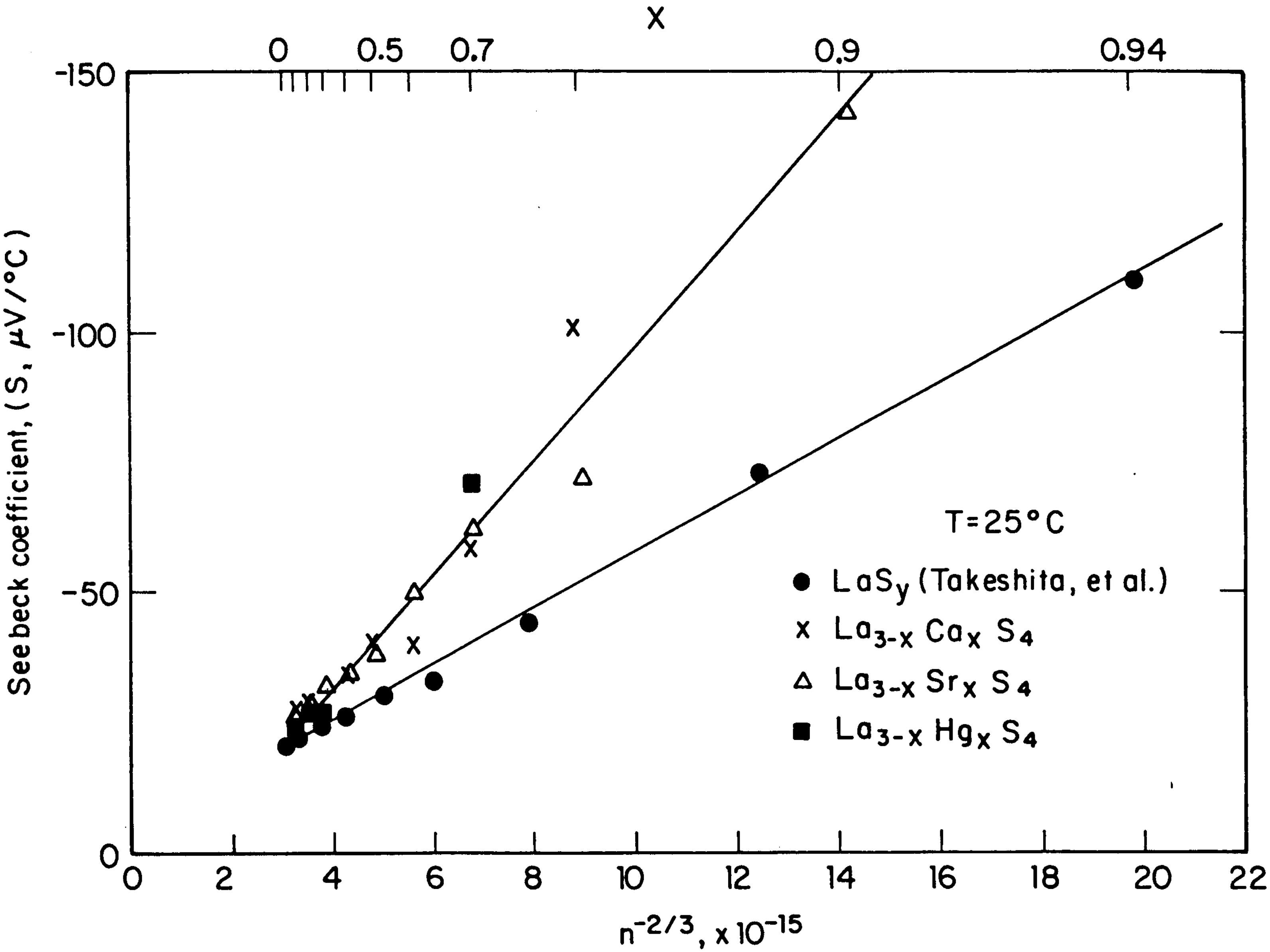

Fig. 2. Seebeck coefficient versus the negative two-thirds power of the electron concentration at 25°C for binary LaS_y (Takeshita, et al.[3]) and the ternary lanthanum sulfides.

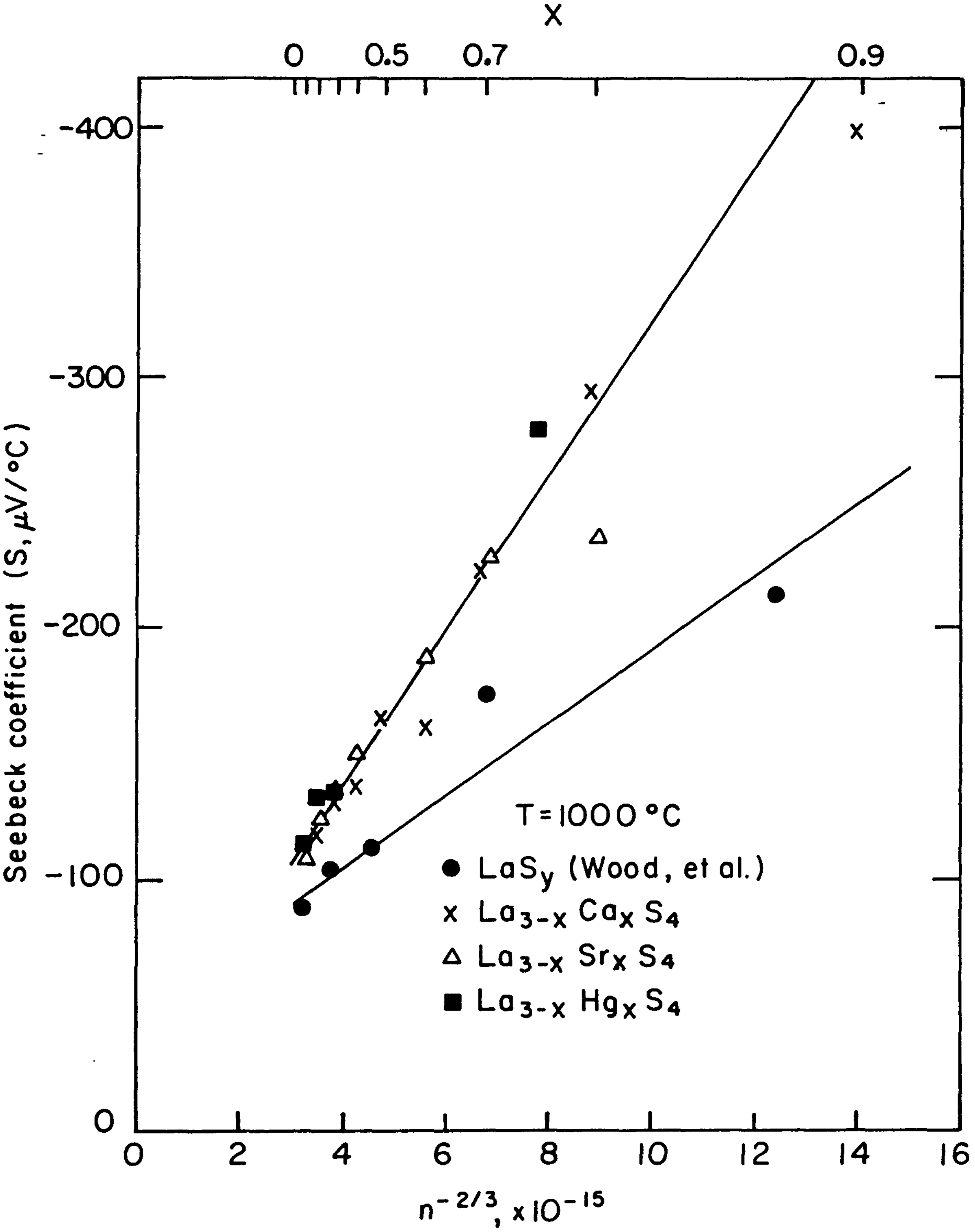

Fig. 3. Seebeck coefficient versus the negative two-thirds power of the electron concentration at 1000°C for binary LaS_y (Wood, *et al.*[2]) and the ternary lanthanum sulfides.

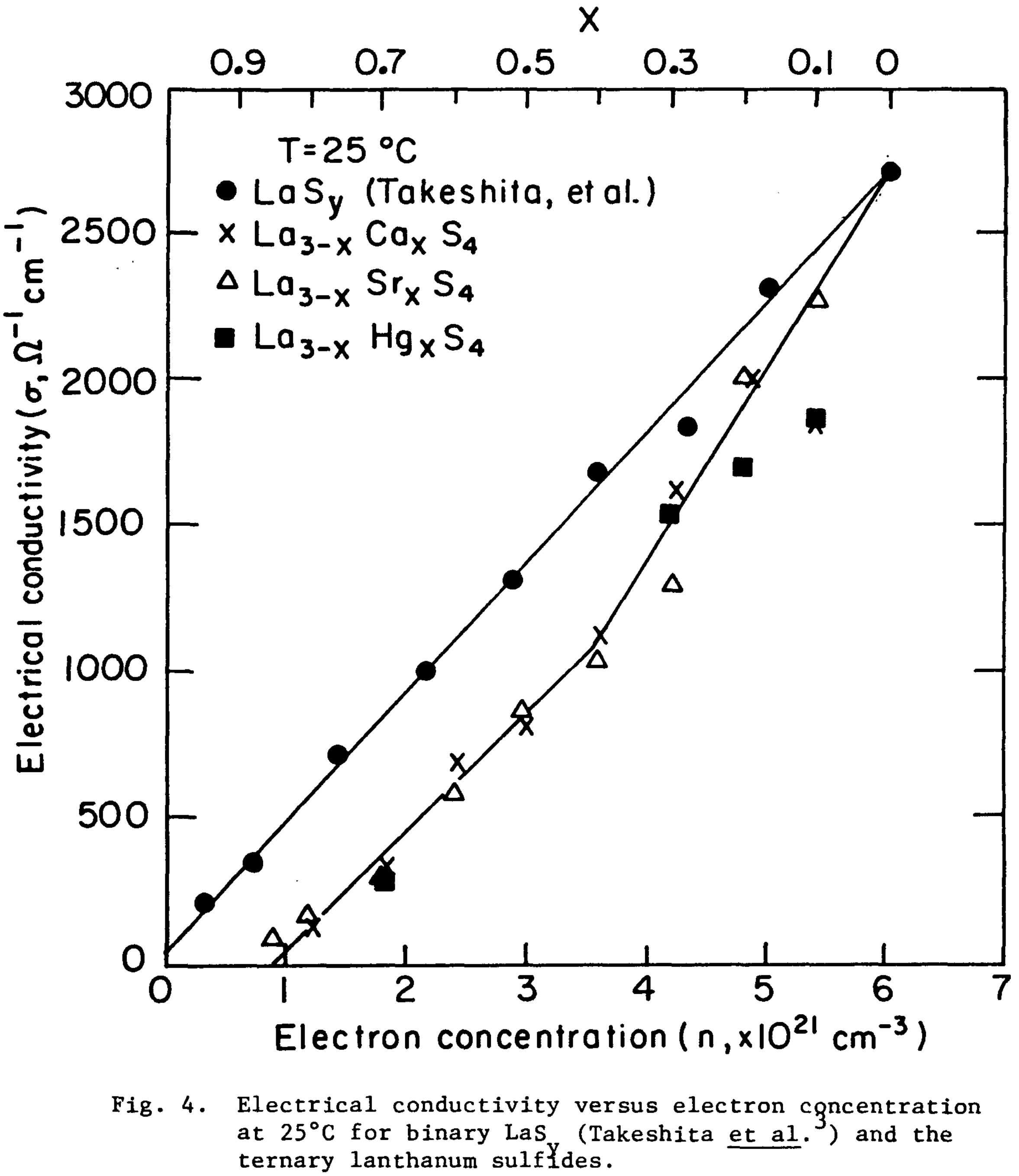

Fig. 4. Electrical conductivity versus electron concentration at 25°C for binary LaS$_y$ (Takeshita et al.[3]) and the ternary lanthanum sulfides.

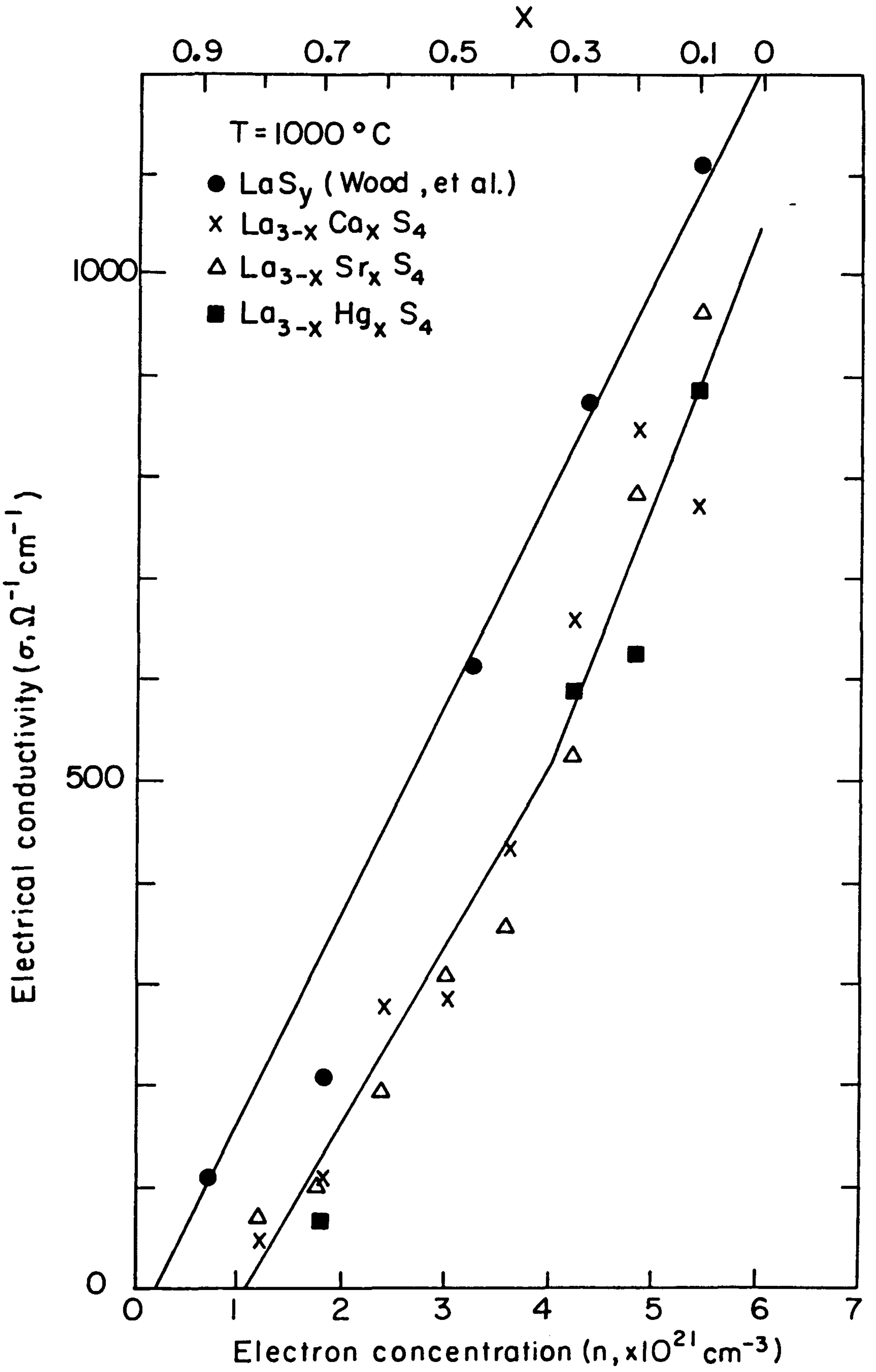

Fig. 5. Electrical conductivity versus electron concentration at 1000°C for binary LaS_y (Wood, et al.[2]) and the ternary lanthanum sulfides.

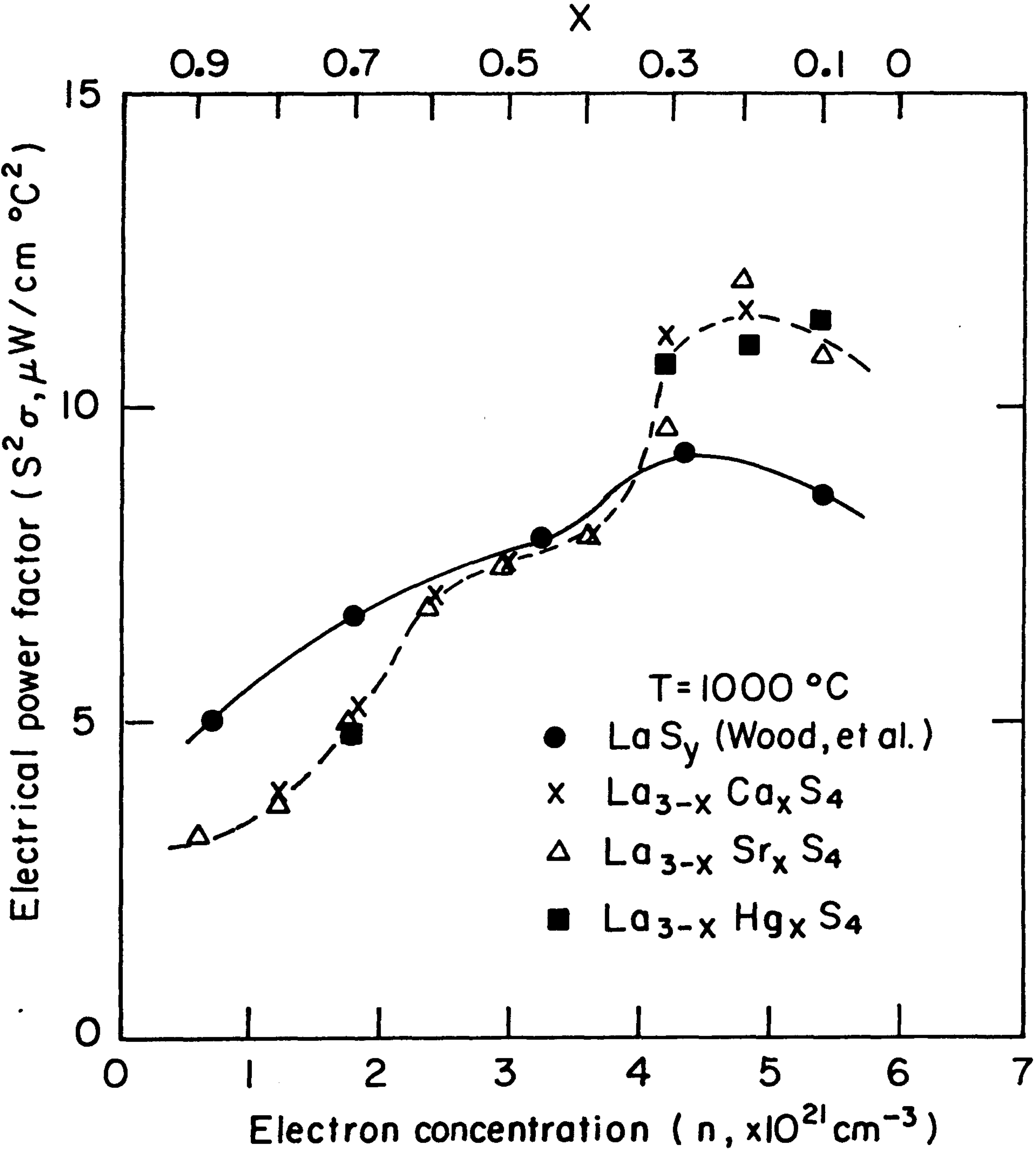

Fig. 6. Electrical power factor versus composition at 1000°C for binary LaS_y (Wood, et al.[2]) and the ternary lanthanum sulfides.

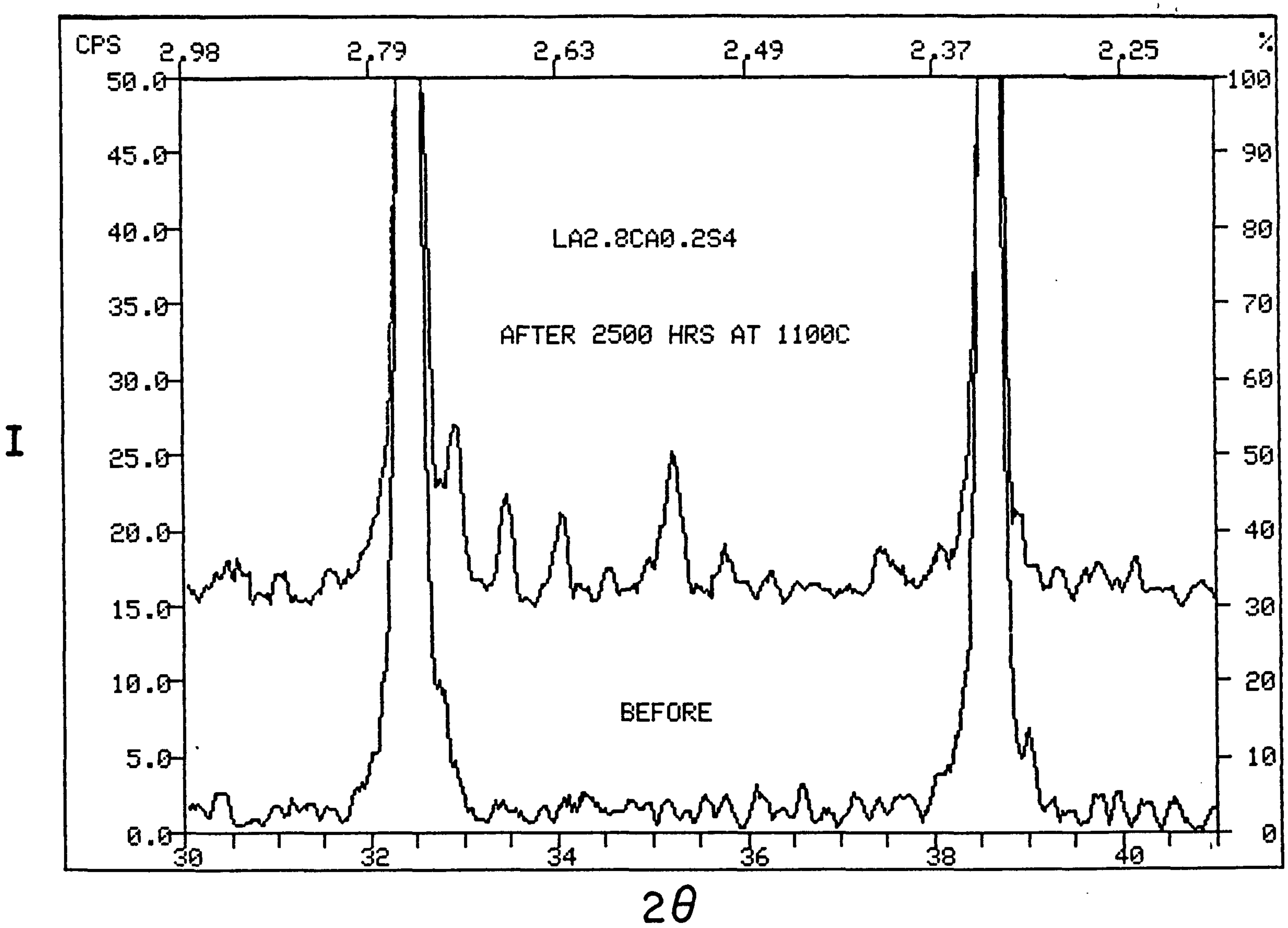

Fig. 7. X-ray powder diffraction pattern of $La_{2.8}Ca_{0.2}S_4$ before and after 2500 hours at 1100°C in vacuum. The peaks due to the second phase can be seen between 33 and 38 degrees 2-theta.