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Calorimetric study of the nucleation of $La_xCo_4Sb_{12}$ prepared from modulated elemental reactants

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Abstract

A series of new compounds $La_xCo_4Sb_{12}$ with the skutterudite crystal structure, where $0 < x < 1$, was prepared using modulated elemental reactants. The evolution of the reaction was followed using calorimetry and X-ray diffraction. The modulated elemental reactants were found to inter-diffuse at temperatures below 150 °C forming an amorphous reaction intermediate. The crystallization temperature and nucleation energies for the transformation of the amorphous intermediate into the skutterudite crystal structure were both found to vary linearly with lanthanum content. The lattice parameter of the resulting skutterudite structures increased as the lanthanum filling was increased. The relative intensities of the Bragg reflections indicate that the lanthanum content in the skutterudite structure increases as the lanthanum content of the modulated elemental reactant increases. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

While calorimetry has been used to determine the thermodynamic stability of many extended inorganic solids, it has not often been used for the investigation of solid-state reaction kinetics. Most solid-state reactions occur at an appreciable rate only at high temperatures and even then they are typically diffusion limited and occur only at interfaces. Since the bulk of a sample is not at an interface, the heat produced by the reaction causes only a small temperature change due to the heat capacity of the remaining reactants. In 1986, Cotts et al. used calorimetry to understand the kinetics and thermodynamics of the reaction between thin Ni and Zr layers [1]. To optimize the signal, they deposited the alternating layers of Ni and Zr on a polished NaCl crystal and then dissolved the salt substrate in water, collecting the layered film via filtration. Approximately a milligram of this material was placed in a differential scanning calorimetry (DSC) pan and the resulting thermogram clearly showed two exothermic peaks. The first one corresponded to the inter-diffusion of the layers and the formation of an amorphous intermediate. The second, higher temperature exotherm corresponded to the nucleation and growth of a crystalline inter-metallic Ni–Zr compound from the amorphous intermediate.

We have used the calorimetry techniques originally developed by Cotts and Johnson during our studies of modulated elemental reactants. We used the design of the structure of the initially modulated reactant to control the subsequent inter-diffusion and nucleation of crystalline products. In this paper, we discuss the

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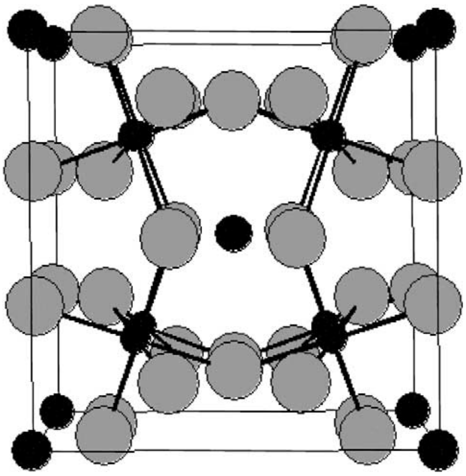

Fig. 1. The skutterudite crystal structure. The black circles represent the ternary atom, in this case lanthanum. The lightly shaded circles represent the antimony atoms and the medium shaded circles represent cobalt atoms.

formation of ternary La–Co–Sb compounds, $La_xCo_4Sb_{12}$, that forms the skutterudite crystal structure. Compounds with the skutterudite structure have been shown to be promising thermoelectric materials with a relatively high efficiency of transporting heat via the charge carriers [2]. In the binary skutterudite, $CoSb_3$, the high thermal conductivity of the lattice significantly reduces the temperature gradient resulting from a flow of current. Incorporation of a ternary cation in the void of the skutterudite structure, shown in Fig. 1, dramatically reduces the thermal conductivity. This reduction of the thermal conductivity is thought to result from the scattering of the lattice phonons by the ternary cation "rattling" in a high co-ordination number site that is too large for the co-ordination of the ternary cation [3]. The crystals maintain the large transport of charge from the conduction electrons, thus behaving as "electron crystals but phonon glasses" as suggested by Slack [4]. Previous studies using traditional high temperature solid-state synthesis techniques have reported that only samples of $La_xCo_4Sb_{12}$with $x < 0.2$ could be prepared. If $x > 0.2$, the samples contained multiple crystalline products when prepared using high temperature synthetic techniques. To prepare samples with $x > 0.2$, it was necessary to replace some of the cobalt with iron [2]. Here, we report the preparation of samples of $La_xCo_4Sb_{12}$, where $0 < x < 1$, that were single phase with respect to X-ray diffraction. DSC was used to determine the nucleation temperature of each composition and using the method first reported by Kissinger [5], we have determined the nucleation energies for each of these compositions.

2. Experimental

2.1. Sample preparation

The elementally modulated reactants are prepared by sequential deposition of the elements in a custom-built ultra-high vacuum deposition chamber described in detail elsewhere [6]. Each element is evaporated using Thermionics electron beam guns or, in the case of antimony, an effusion cell. Deposition rate is monitored using quartz crystal thickness monitors and the thickness of each elemental layer is controlled cycling shutters. Samples are simultaneously deposited on polished silicon wafers, silicon wafers spin coated with polymethylmethacrylate (PMMA) and on a polished mis-cut quartz zero-background plate. The samples deposited on the quartz plate are subsequently used for X-ray analysis as a function of annealing temperature. The sample deposited on the PMMA coated substrate is immersed in acetone, which dissolves the PMMA coating. The flakes of modulated reactant are collected by filtration through a Teflon filter and used in subsequent calorimetry experiments and composition analysis. Composition of the samples is determined using a Cameca SX-50 electron probe microanalysis system using 15 keV accelerating voltage, 10 nA of beam current and a 1 μm spot size.

2.2. Differential scanning calorimetry

Nucleation and growth events that liberate or absorb heat can be monitored using DSC. A TA instruments model 910 DSC cell was used. About a milligram of sample was sealed in a crimped aluminum DSC pan for each measurement. Two scans were collected on each sample and subtracted to obtain the irreversible heat flows resulting from the reaction of the multi-layered samples. To obtain information about the activation energy involved in the nucleation and growth of the products, data collected at different scan rates was analyzed using the method described by Kissinger [5].

2.3. X-ray diffraction

A Scintag model XDS 2000 theta–theta diffractometer and a Philips X'pert MRD diffractometer both using Cu Kα radiation were used to characterize the structure of the as deposited multi-layers as well as the crystalline products. The decay of the intensity of the low angle Bragg diffraction maxima, resulting from the layered nature of the initial reactant, was used to monitor the inter-diffusion of the elemental layers. Crystalline phase formation and lattice parameters were determined from the high angle diffraction data.

3. Results and discussion

Table 1 contains a summary of the samples prepared for this investigation. The layer thickness of the antimony and cobalt layers was calibrated to obtain the desired 3:1 atomic ratio of the elements. The thickness of the total repeating unit of the modulated reactant was kept below 20 Å to avoid interfacial nucleation of binary compounds. The layer thickness and composition of the samples varied as expected, with the lanthanum content increasing as the thickness of the lanthanum layer was increased.

Fig. 2 contains a typical DSC trace of one of these samples. A sharp exotherm is observed for all of the samples and the temperature of the exotherm increases as the lanthanum content of the samples increase as

Table 1
A summary of information on the samples prepared as part of this study

Sample	Intended La thickness	Intended Co thickness	Intended Sb thickness	Intend repeat thickness	Actual repeat thickness	Lattice parameter	DSC exotherm temperature (°C)
$La_{0.14}$	0.05	1.23	15.00	16.25	n.a.	9.03679	157.05
$La_{0.25}$	0.18	1.23	15.00	16.41	15.22	9.04560	163.75
$La_{0.5}$	0.45	1.23	15.00	16.73	n.a.	9.05277	175.95
$La_{0.65}$	0.60	1.23	15.00	16.85	15.63	9.06091	185.81
$La_{1.0}$	0.75	1.23	15.00	17.00	15.90	9.08023	203.73
$La_{1.3}$	1.00	1.23	15.00	17.20	16.12	9.08455	210.53
$La_{2.0}$	1.55	1.23	15.00	17.80	n.a.	9.09009	245.44

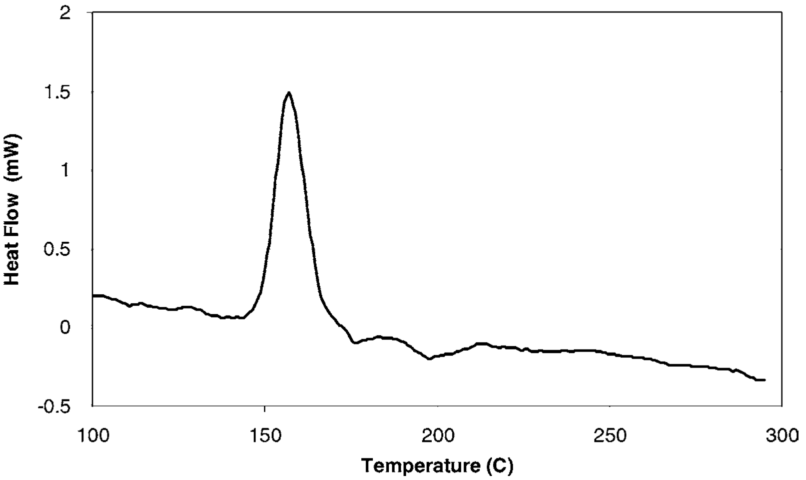

Fig. 2. A typical DSC trace of a sample prepared in this study. The exotherm at 157 °C results from the crystallization of the sample on heating. The small heat signals observed in the scan are due to contamination of the DSC cell.

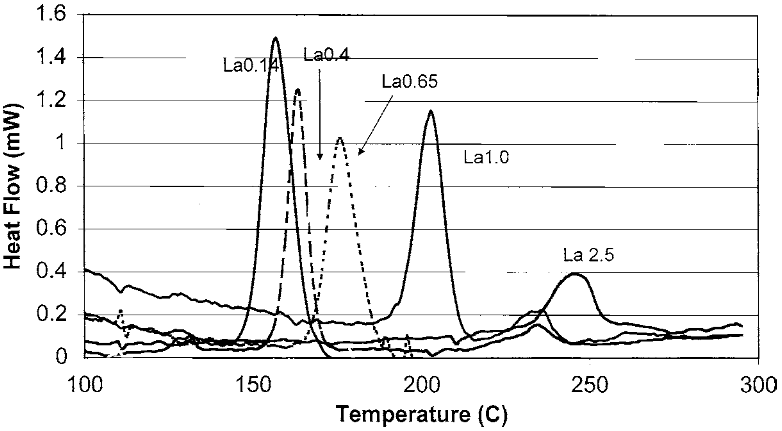

Fig. 3. Calorimetry traces for samples with varying lanthanum content. The exotherm temperature increases monotonically as the lanthanum content increases.

shown in Fig. 3. Diffraction patterns collected as a function of annealing temperatures show that the samples are initially amorphous on deposit with respect to X-ray diffraction. The amorphous nature of the as-deposited film is a result of significant inter-diffusion of the layers. This inter-diffusion is confirmed by low angle diffraction data studies of the as-deposited samples. The samples remain amorphous below the temperature corresponding to the exotherm observed in the DSC spectra. Low angle diffraction data shows that significant additional inter-diffusion occurs when annealing below the exotherm temperature. After the exotherm, the samples are crystalline, as shown in Fig. 4. Analysis of the rocking curves of the diffraction maxima shows that the film has no preferred orientation. The positions and intensities of the cubic diffraction pattern agree well with that expected from the skutterudite crystal structure. The diffraction data suggests that the exotherm is a result of the nucleation and growth of the crystalline skutterudite from an amorphous intermediate. As shown in Fig. 5, the temperature of the exotherm is observed to systematically increase as the lanthanum content increases. This may reflect an increase in the stability of the

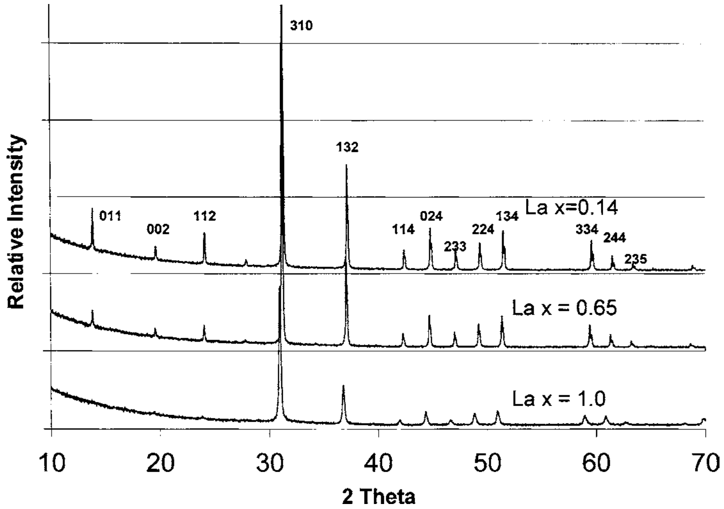

Fig. 4. A graph of the cubic diffraction patterns for several of the samples investigated in this study.

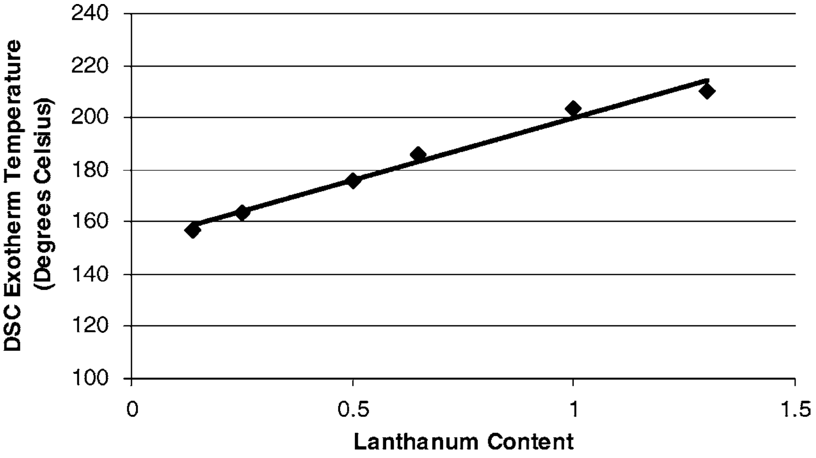

Fig. 5. A plot of exotherm temperature vs. lanthanum content for the samples studied.

amorphous state or a decrease in the stability of the skutterudite content with an increase in lanthanum content.

The diffraction patterns shown in Fig. 4 contain several systematic changes with increasing lanthanum content. The intensity of the first several diffraction maxima decreases as the lanthanum content increases and the lattice parameter increases as lanthanum content increases. Fig. 6 contains a simulation of the expected behavior of the (1 1 0), (2 1 1) and (2 0 0) diffraction peaks as a function of lanthanum content. This simulation agrees well with the observed diffraction patterns, shown in Fig. 6 showing that the decrease in the intensity of these Bragg diffraction maxima is a result of increasing lanthanum content in the skutterudite structure.

In Fig. 7, the change in the lattice parameter as a function of lanthanum composition in the initial reactant is plotted. There is a linear increase in lattice parameter with lanthanum composition up to a composition corresponding to complete filling of the available vacancy sites in the structure. This supports the observed increase in lanthanum occupancy with increasing lanthanum composition. For fillings $x > 1$, there is still a small increase in the lattice parameters, suggesting that there is a partitioning of the lanthanum between the grain boundaries and incorporation into the skutterudite structure. The increase in the diffraction line widths with increasing lanthanum content, suggesting a decrease in crystallite size, supports this idea. The reduced crystallite size results from the increase in the amount of lanthanum not incorporated in the structure as x increases. As the nucleated skutterudite crystallites grow, atoms not being incorporated into the structure must be pushed out in front of the growth front. Eventually, the composition of the growth front will be so depleted in the atoms required to grow the crystals that growth will stop. Since, the diffraction patterns in Fig. 4 contain no evidence for crystalline impurity phases, the impurities must be amorphous or nanocrystalline.

If there is a partitioning of the lanthanum between the skutterudite structure and the grain boundaries, one might also expect the activation energy to also be a function of lanthanum content in the initial reactants because lanthanum might de-stabilize nuclei of the skutterudite structure. Fig. 8 contains a plot of activation energy, determined using the method of Kissinger, as a function of lanthanum content. While these activation energies are associated with the nucleation and growth of the skutterudite compounds, their extraction from the non-isothermal DSC data is based on many assumptions. The derivation of the Kissinger analysis assumes that the nucleation and growth can be described by the Johnson–Mehl–Avrami equation, that the amorphous and the crystalline states have the same composition, and that the nucleation and growth rates are constant at constant temperature. A further approximation is made that both the nucleation rate and the growth rates may be

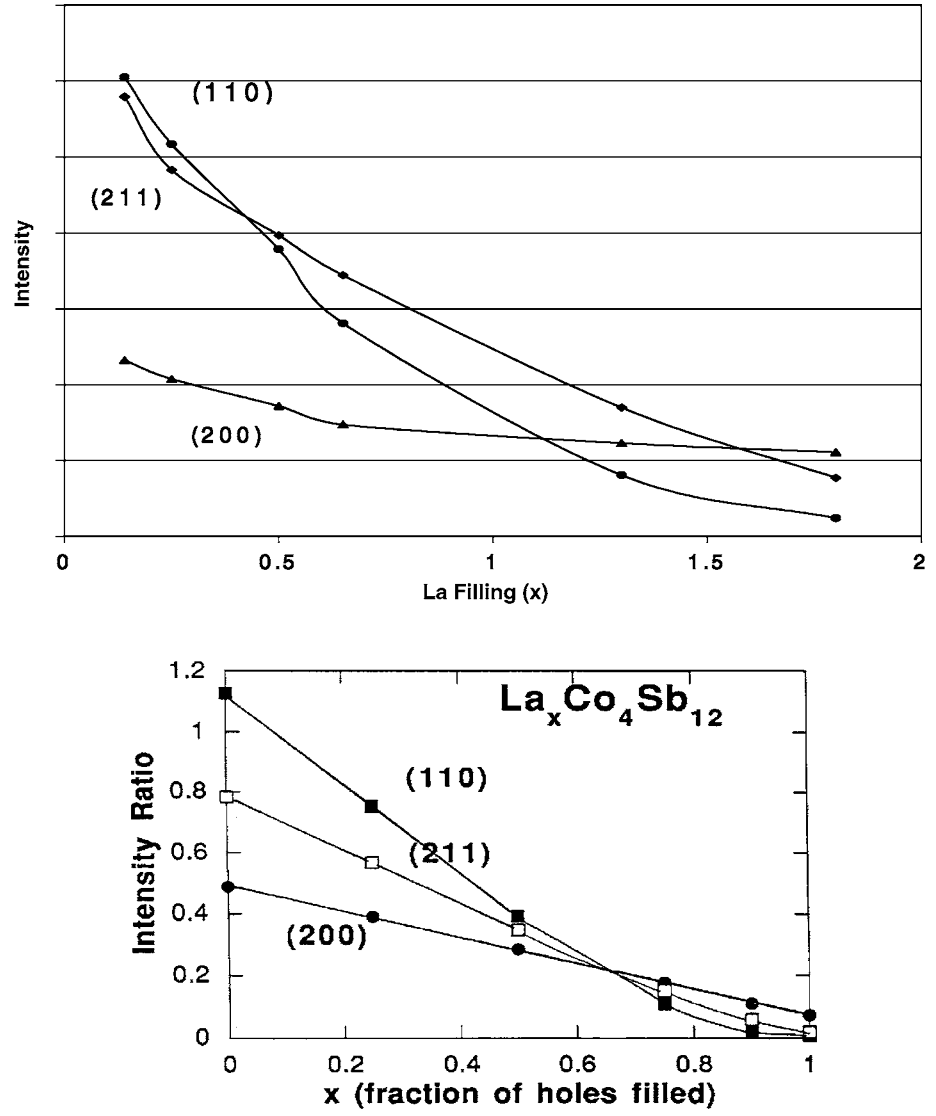

Fig. 6. A comparison of measured diffraction intensities vs. a simulation of the expected intensity changes in several of the Bragg diffraction maxima as a function of lanthanum content. The top graph shows the experimental data and the simulated data is displayed below.

described by Arrhenius expressions over the range of temperatures in which the peak temperature varies with scan rate. Examining Fig. 8, we observe a systematic increase in activation energy as lanthanum content increases. Since, previous researchers were unable to prepare samples with $x > 0.2$, we believe that this is the consequence of decreased thermodynamic stability of $La_xCo_4Sb_{12}$ as x increases. The lanthanum cations occupy a 12 co-ordinate site in the crystal structure, the size of which is determined by the atomic radii of antimony atoms. The size of this site is larger than that expected for a lanthanum cation, resulting in a large amplitude of thermal vibration of the lanthanum cations. The long antimony–lanthanum bond distances reflect the weak bonding of the lanthanum to the cobalt–antimony lattice. This may result in a decrease in the heat of formation of the lanthanum filled skutterudites as the lanthanum content is decreased. This would result in a decrease in the free energy change between the amorphous state and the

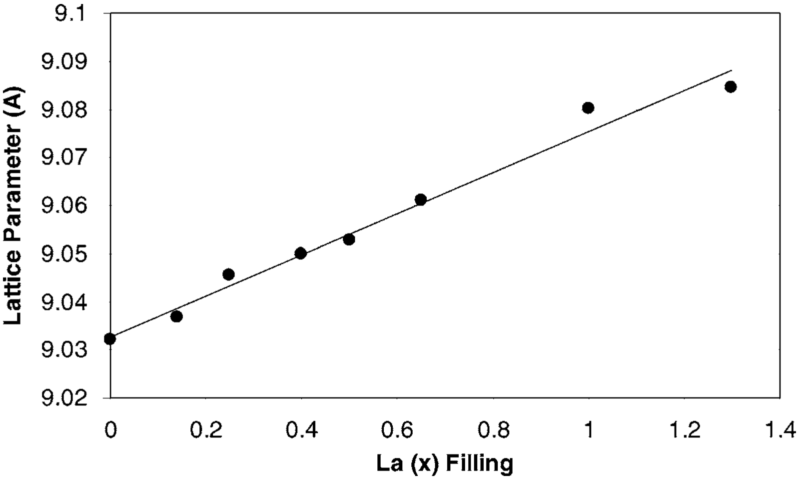

Fig. 7. The change in the measured lattice parameters as a function of lanthanum content for the samples prepared in this study.

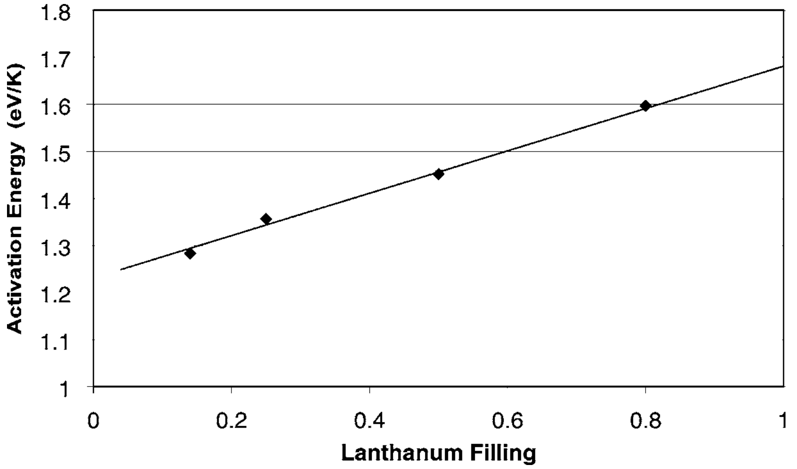

Fig. 8. The change in activation energy as a function of lanthanum content.

crystalline skutterudite, decreasing the driving force for nucleation.

4. Conclusions

A series on new compounds, $La_xCo_4Sb_{12}$, where $0 < x < 1$, were prepared using modulated elemental reactants. This synthesis technique permits the synthesis of these compounds with higher x-value than can be prepared using traditional synthetic approaches. Calorimetric investigation shows the compounds formed exothermically from the initial reactants below 200 °C, significantly below the temperatures required to form skutterudites using conventional synthetic approaches. The nucleation energies of the compounds were found to increase systematically as the lanthanum content increases. A systematic increase in unit cell size with increasing lanthanum content was observed.

Acknowledgements

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