Journal of Crystal Growth 475 (2017) 10–20

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

Czochralski growth of $LaPd_2Al_2$ single crystals

P. Doležal [a,*], A. Rudajevová [a], K. Vlášková [a], D. Kriegner [a], K. Václavová [b], J. Prchal [a], P. Javorský [a]

[a] Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
[b] Charles University, Faculty of Mathematics and Physics, Department of Physics of Materials, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

ARTICLE INFO

Article history:
Received 13 February 2017
Received in revised form 5 May 2017
Accepted 16 May 2017
Available online 22 May 2017
Communicated by T.F. Kuech

Keywords:
B1. $LaPd_2Al_2$
B2. Unconventional superconductivity
A1. Differential scanning calorimetry (DSC)
A2. Czochralski method
A1. X-ray diffraction
A2. Single crystal growth

ABSTRACT

The present study is focused on the preparation of single crystalline $LaPd_2Al_2$ by the Czochralski method. Differential scanning calorimetry (DSC) and energy dispersive X-ray spectroscopy (EDX) analyses reveal that $LaPd_2Al_2$ is an incongruently melting phase which causes difficulties for the preparation of single crystalline $LaPd_2Al_2$ by the Czochralski method. Therefore several non-stoichiometric polycrystalline samples were studied for its preparation. Finally the successful growth of $LaPd_2Al_2$ without foreign phases has been achieved by using a non-stoichiometric precursor with atomic composition 22:39:39 (La:Pd:Al). X-ray powder diffraction, EDX analysis and DSC were used for the characterisation. A single crystalline sample was separated from the ingot prepared by the Czochralski method using the non-stoichiometric precursor. The presented procedure for the preparation of pure single phase $LaPd_2Al_2$ could be modified for other incongruently melting phases.

1. Introduction

$LaPd_2Al_2$ is a nonmagnetic compound which becomes superconducting when cooled below 1.88(3) K [1]. At room temperature, it crystallizes in tetragonal crystal system with the $CaBe_2Ge_2$ structural type, space group $P4/nmm$ (129), as illustrated in Fig. 1. Neutron diffraction revealed that it undergoes a structural phase transition from tetragonal to orthorhombic structure with the space group *Cmme* (67) below $T_{str} = 91.5$ K [2]. The structural instability of $LaPd_2Al_2$ at low temperatures is a frequently observed behaviour of materials crystallizing in the $CaBe_2Ge_2$ structural type. Distortions at low temperatures are also observed in $CeNi_2Sn_2$ [3], $CePt_2Ge_2$ [4], $CePd_2Ga_2$ [5] or $CePd_2Al_2$ [2] compounds. The stability of the tetragonal structure and the values of T_{str} in $LaPd_2Al_2$, $LaPd_2Ga_2$ and their Ce-based counterparts were also discussed in relation to the observation of magnetoelastic coupling in $CePd_2Al_2$ [2,6].

The superconducting properties of $LaPd_2Al_2$ and a broader series of $LaPd_2Al_{2-x}Ga_x$ compounds exhibit deviations from behaviour predicted by the Bardeen–Cooper–Schrieffer (BCS) theory [1]. Specific heat and electrical resistivity measurements revealed a non-exponential temperature dependence of the electronic contribution to specific heat below the T_{SC}, a positive curvature of $B_{c2}(T)$ and a value of $\frac{\Delta C_{el}}{\gamma T_{SC}} = 1.1$ which is below the value of 1.43 predicted by the BCS theory. This behaviour is similar to that which is typical for non-conventional or non-centrosymmetric superconductors and drives the interest in this class of materials even though the T_{SC} is rather moderate.

The existing experimental study of $LaPd_2Al_2$ referred as [2] was based on measurements on polycrystalline samples, which allows to draw only limited conclusions. Moreover, the presence of a certain amount of foreign unspecified phases was found in the studied samples [7]. High quality and phase pure single crystals would provide much deeper insight into the unusual physical properties of $LaPd_2Al_2$. The aim of the present study is thus the preparation of single crystalline bulk $LaPd_2Al_2$ and its detailed characterisation.

2. Experimental methods

Polycrystalline samples (mass ~ 1 g) were prepared by arc-melting of the pure elements in an argon protective atmosphere. The furnaces were baked during evacuation to decrease the oxidation of elements during melting. Samples were four times turned and remelted to achieve good homogenisation. Preparation of single crystalline samples was performed by the Czochralski method from ~ 6 g of polycrystalline precursor. The used elements were obtained from Alfa Aesar and certified to a purity of La 3N, Pd 4N5, Al 5N, where 4N5 refers to 99.995 % metals basis purity. The energy dispersive X-ray spectroscopy (EDX) analysis and imaging by back-scattered electrons (BSE) was performed by scanning electron microscope (SEM) TESCAN, type Mira I LMH. Figures

* Corresponding author.
E-mail address: petr284@seznam.cz (P. Doležal).

http://dx.doi.org/10.1016/j.jcrysgro.2017.05.016
0022-0248/

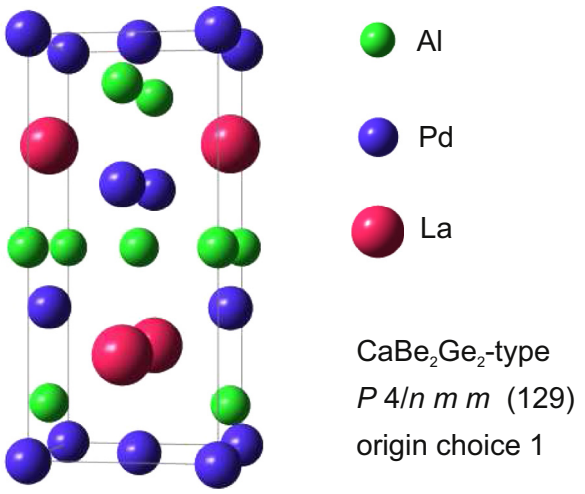

Fig. 1. Sketch of the crystal structure of $LaPd_2Al_2$ compound (phase f1).

showing channeling contrast were taken with a SEM Zeiss Auriga Compact equipped with a field emission gun emitter. The X-ray powder diffraction (XPD) technique was used for structural characterisation. Symmetrical $\omega - \theta$ scans were measured by a Bruker D8 Advance diffractometer in Bragg-Brentano geometry. Powder patterns were analysed by the Fullprof program [8] using the Rietveld method. Reciprocal space maps of a single crystalline grain were measured using a PANalytical X'Pert powder diffractometer. An X-ray mirror was used to produce a parallel beam and the diffracted signal was recorded with a linear detector allowing to map the shape of the Bragg peaks using a single sample rocking scan. Laue X-ray images were taken using a Laue X-ray Imaging System 20041209 SY Issue 8 (Photonic Science) with CCD camera (1220 × 1800 pixels) and air-cooled X-ray tube (40 kV, 300 μA). The neutron Laue technique was provided by OrientExpress diffractometer in Institut Laue-Langevin. The differential scanning calorimetry (DSC) analysis was carried out by a SETSYS Evolution 24 instrument from SETARAM Instrumentation.

3. $LaPd_2Al_2$ polycrystalline sample from the stoichiometric composition of the melt

We focus first on a polycrystalline sample, labelled as sample 1, prepared from stoichiometric composition of the melt with 20:40:40 La:Pd:Al atomic ratio (whenever we refer to stoichiometry of/in our samples we use this order of elements). The process used for preparation is the same as described in section experimental. Total sample mass was ∼ 1 g and the sample was cut to smaller pieces, which were consequently used for EDX, XPD, and DSC analysis. The BSE image shows five different phases obtained on this sample 1, which are labelled f1 to f4, and f9 (see Fig. 2). The composition of the phases is listed in Table 1 for each phase. The majority phase is clearly f1 with composition of 18:41:41. In part (a) and (c) of Fig. 2 we can see a stripe structure of phases f2, f3 which is probably a result of the fast cooling rate (similar to the quenching process) and only f4 phase forms a globular like grains (see Fig. 2(b)). We can deduce from this microstructure that the f4 phase is formed as first one from the melt. Subsequent

Table 1
Chemical composition (in atomic percent) of phases f1–f9 obtained as a result of EDX analysis. The error of analysis is between 1 and 2 % and the values are rounded to the nearest integer. The f9 phase contains more than 60 at.% O and since there are no La-O phases with more than 60 at.% O it is very probably that this phase is a hydroxide phase, which is formed due to the hygroscopicity of La_2O_3. Considering the higher error for detection of oxygen the f9 phase is likely $La(OH)_3$.

Phase	Ratio of elements (%)			
	La	Pd	Al	O
f1	18	41	41	–
f2	10	45	45	–
f3	20	52	28	–
f4	15	35	51	–
f5	15	52	33	–
f6	30	49	21	–
f7	29	56	15	–
f8	30	36	34	–
f9	18	–	–	82

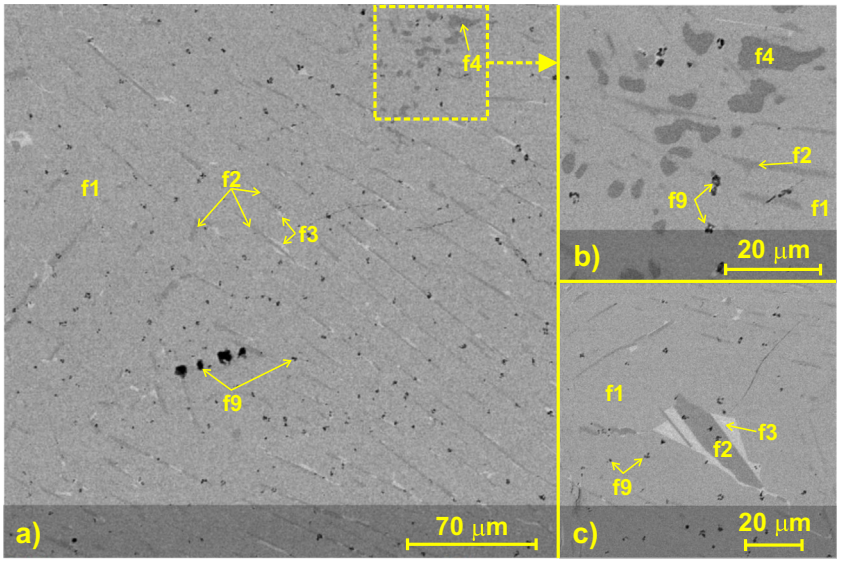

Fig. 2. Microstructure of the sample 1 (as cast): The BSE images – (a) Phases f2 and f3 have a stripe structure, (b) Detail of globular like grains of f4 structure, (c) Detail of f2 and f3 structure. For compositions of phases see Table 1.