# GROWTH AND SOME PROPERTIES OF $Cr_{11}Ge_{19}$

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## ABSTRACT

$Cr_{11}Ge_{19}$ belongs to a large family of materials known as the Nowotny chimney-ladder compounds, some of which were recently proposed as advanced thermoelectric materials particularly because of their low thermal conductivity related to their relatively complex crystal structure. in order to assess the potential of the compound $Cr_{11}Ge_{19}$ for thermoelectric applications, we grew large single crystals of this peritectic compound by a vertical gradient freeze technique and measured the thermoelectric properties of the crystals, $Cr_{11}Ge_{19}$ forms peritectically at 1201 K and crystals were grown from Ge-rich solutions. The conditions and the results of the crystal growth experiments are presented. The crystals were characterized by x-ray diffractometry, Laue technique, and electron probe microanalysis. The results of the thermoelectric properly measurements suggest that $Cr_{11}Ge_{19}$ has a metallic behavior and therefore presents little interest for thermoelectric applications.

## 1. INTRODUCTION

$TiSi_2$ is the prototype of a large family of materials known as Nowotny chimney-ladder compounds of composition $T_nX_m$ where 2>m/n> 1.25 (T= transition element, X= Si, Ge, Sn or Ga) [ 1 ]. These compounds are characterized by a long unit cell consisting of subcells of the transition elements, similar to the β-tin structure type, and a helical arrangement of the X elements. Some of the semiconducting compounds in this family, such as $Ru_2Si_3$, $Ru_2Ge_3$, and $Mn_{11}Ge_{19}$ [2-4], have been considered as advanced materials for thermoelectric applications because of their relatively low thermal conductivity which is favorable for achieving high thermoelectric figures of merit. Other compounds in this family, such as $TiSi_2$, have metallic conductivity [5]. It has been proposed by Nowotny that the chimney-ladder compounds having a number of 14 valence electrons (VEC) per metal atom should be semiconductors, and metals if the total is lower than 14 [6]. This rule has been remarkably followed for the compounds investigated up to now as pointed out by Jeitschko and Parthé [7].

$Cr_{11}Ge_{19}$ is one of these compounds and its structural data can be found in reference [8]. The phase diagram of the (Cr, Ge) system was recently re-investigated [9]. There are no congruently melting compounds in this system but a series of compounds decomposing peritectically starting with $C_3Ge$ through $Cr_5Ge_3$, $Cr_{11}Ge_8$, CrGe, and finally $Cr_{11}Ge_{19}$. The peritectic decomposition temperature of $Cr_{11}Ge_{19}$ is 1201 K. Because of its relatively complex structure, the thermal conductivity might be low, which is favorable for achieving high thermoelectric figures of merit. In addition, the semiconducting compound $CrSi_2$ (having a closely related structure to $TiSi_2$ -type compounds [10]) exhibits some interesting thermoelectric properties [11]. The possibility of forming solid solutions between $CrSi_2$ and $Cr_{11}Ge_{19}$ is potentially interesting because of the possible reduction of thermal conductivity for the alloys. However, information about the thermal properties of $Cr_{11}Ge_{19}$ is not available in the literature and only a few electrical property measurements were performed on polycrystalline bulk samples or films [12,13]. In particular, it is not clear if it is a semiconductor or a metal. According to the valence electron count rule proposed by Nowotny for these compounds, $Cr_{11}Ge_{19}$ should be metallic with a total of 12.9 electrons per atom of germanium. in order to verify the theoretical predictions and assess the usefulness of the compound $Cr_{11}Ge_{19}$ for thermoelectric applications, we grew large crystals of this chimney-ladder compound and measured some of its properties.

## 2. EXPERIMENTAL DETAILS

### 2.1. Crystal growth and analysis

The Cr-Ge phase diagram is redrawn in Fig. 1 and shows that the growth of $Cr_{11}Ge_{19}$ can only be **initiated from** Ge-rich **solutions** within 79 and 85 at.% of Ge. $Cr_{11}Ge_{19}$ crystals were grown from off-stoichiometric nominal melts with 80 at.% Ge (see Fig. 1). Ge pieces **(99.999% pure)** and Cr powder (99.996% pure) (total charge was about 12 g) were loaded in quartz ampoules subsequently sealed under vacuum. Quartz ampoules with pointed bottoms and a diameter of slightly less than 12.5 mm were used for the growth experiments. A vertical gradient freeze furnace was used to grow the crystals. The furnace was composed of a tubular SiC heater element for the upper zone of the furnace with a maximum working, temperature of 1700K and with a diameter of 45 mm. The lower zone was built with an ordinary wire heater suitable. for temperatures up to ~1300K. A thermal baffle made out of firebrick was introduced between the two zones to increase the temperature gradient at the liquid-solid interface and to avoid any air convection. An opening of 12.5 mm of diameter was made in the baffle to introduce the melt container. A differential thermocouple with a temperature programmer/controller was employed to control the temperature difference between the top and the bottom of the baffle so that the temperature gradient at the liquid-solid interface remained constant during the growth. The quartz ampoule remained stationary and the translation of the liquid-solid interface was achieved by lowering the temperature of the upper zone. other details about the furnace used for the growth can be found in reference [14]. During the runs, the temperature gradient was 42K/cm and the growth rate was about 1mm/day. Lowering the temperature of' the upper zone moved the liquid-solid interface from the bottom of the quartz ampoule up to the top. Samples were cut from the ingots using a diamond saw and used for microstructural anti various x-ray analyses. The microstructure of the grown ingots was investigated using a Nikon optical microscope. Some samples were ground for X-ray diffractometry (XRD) analyses which were performed on a Siemens D-500 diffractometer using Cu-$K_\alpha$ radiation with silicon as a standard. The Laue technique was also used to characterize the crystals. Electron probe microprobe analysis (EPMA) was performed on a JEOL JXA-733 superprobe. The density of several samples was measured by the immersion technique at room temperature using toluene as the displacement liquid.

### 2.2. Transport property measurements

Samples about 2 mm thick and between 5 and 10 mm in diameter were cut from the grown ingots perpendicular and parallel to the growth axis for transport property measurements. The transport properties arc indeed expected to be anisotropic for non-cubic structures such as $Cr_{11}Ge_{19}$. The high temperature resistivity, Hall effect, Seebeck coefficient., thermal diffusivity, and heat capacity measurements were conducted on selected samples between room temperature and about 11 OOK, The electrical resistivity (p) was measured using the van der Pauw technique with a current of 100 mA using a special high temperature apparatus [ 15]. The Hall coefficient ($R_H$) was measured in the same apparatus with a constant magnetic field value of - 10,400 Gauss. The errors were estimated at ± 0.50/0 and ± 20/0 for the resistivity and Hall coefficient measurements, respectively. The Seebeck coefficient of the samples was measured on the same samples used for resistivity and Hall coefficient measurements using a high temperature light pulse technique [16]. The error of the Seebeck coefficient measurement was estimated to be less than ± 3%. The heat capacity and thermal diffusivity were measured using a flash diffusivity technique [17] and the thermal conductivity was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall error in the thermal conductivity values was estimated at about ± 10O/..

## 3. RESULTS AND DISCUSSION

### 3.1. Crystal growth results

Several ingots were successfully grown and a typical ingot is shown in Fig. 2. As expected, the ingots were composed of two parts: the lower part corresponding to the $Cr_{11}Ge_{19}$ compound and the upper part corresponding to a Ge-rich eutectic. The interface between the two phases was always clearly seen on the ingots (see Fig. 2). One ingot was cut parallel to the growth axis to reveal the microstructure near the interface. Fig. 3 shows the cross-section and reveals the interface between the single-Jhase material and the eutectic type microstructure. Microprobe analysis showed that the material was single-phase below the interface with a composition corresponding to the 11:19 ratio. The same composition was found for the dark inclusions in the area above the interface while the brighter matrix corresponded to pure Ge. This interface was very flat, which indicates the uniformity of the temperature gradient in the furnace and in the melt as well as the temperature stability during the growth. Cracks tend 10 develop locally near the interface because of the difference in thermal expansion between the two type of phases which causes thermal stresses upon cooling. The lower part of the ingots was cut from the rest of the ingot and subjected to further analysis. The density of the entire lower portions of the ingots was found to be about 99.5 % of the theoretical density of $Cr_{11}Ge_{19}$ : 7.4 g $cm^{-3}$. XRD analysis of samples cut from the lower part of the ingots always showed that the samples were single phase with a composition corresponding 10 the $Cr_{11}Ge_{19}$ structure. Most the of the samples cut from the bottom portion of the ingots were single crystals as indicated by Laue patterns and microscopic examinations. Neither chemical etching nor electron microscopy revealed any grain boundaries and single crystals up to 10 x 10x 10 $mm^3$ were obtained. EPMA investigations of these samples also showed that they were single phase with a uniform composition close to 11:19.

3,2, **Transport properly** results

The electrical resistivity and Seebeck coefficient values measured for $Cr_{11}Ge_{19}$ single crystals are shown in Figs. 4 and 5, respectively. The Seebeck coefficients arc low, increase slightly with increasing temperature and vary little with the orientation. The electrical resistivity values arc also very low. Samples had p-type conductivity with typical values of 1 x $10^{22}$ $cm^{-3}$ for the carrier concentration and of 3 $cm^2$ V-' $s^{-1}$ for the Hall mobility. The room temperature electrical resistivity is about 0.17 mΩcm, in general agreement with the results obtained in two previous studies [ 12, 13]. The low electrical resistivity and Seebeck coefficient values, associated with the low carrier mobility and high carrier concentration tenet to indicate the metallic behavior of $Cr_{11}Ge_{19}$. Finally, Fig. 6 shows the thermal conductivity values as function of the temperature for two $Cr_{11}Ge_{19}$ single crystals. As for metals, the thermal conductivity increases with increasing temperature but the values arc rather low. The room temperature thermal conductivity is about 40 mW $cm^{-1}K^{-1}$ and is the sum of electronic and lattice components. The lattice component was estimated at about 17 mW cm-' K-l by subtracting the electronic component which was calculated using the Wiedemann-Franz law. This is a somewhat low lattice thermal conductivity for a metal but this might be explained by the complex crystal structure of $Cr_{11}Ge_{19}$ and also maybe with a high density of defects which was found in structural analogue compounds such as in the semi-l)lcta] $WSi_2$ [1 8]. All the properties measured suggest that $Cr_{11}Ge_{19}$ has a metallic behavior and further supports the rule proposed by Nowotny as we pointed out above. Therefore, the potential of the compound $Cr_{11}Ge_{19}$ for thermoelectric applications is limited, as is the case for all metallic compounds unless they possess Seebeck coefficient values of at least 120 μV K-l, which is not the case for $Cr_{11}Ge_{19}$ (see Fig. 5). Studies of the alloying of $Cr_{11}Ge_{19}$ with the semiconducting and structurally related compound $CrSi_2$ might, however, be of interest; since there is a possibility that a band gap would open in the band structure for these alloys, which should possess really low thermal conductivity values

## 4, SUMMARY

A two-zone vertical gradient freeze furnace was used to grow large single crystals of the peritectic Nowotny chimney-ladder compound $Cr_{11}Ge_{19}$. The crystals were characterized by x-ray diffractometry, Laue technique, density measurements, and electron microprobe analysis and the results showed the good quality of the grown samples. The thermoelectric properties of the crystals were measured and the results show that $Cr_{11}Ge_{19}$ has a metallic behavior and therefore presents little interest for thermoelectric applications. The metallic behavior of $Cr_{11}Ge_{19}$ is in agreement with theoretical predictions based on valence electrons for the Nowotny chimney-ladder compounds.

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**Figures captions**

Figure 1. Cr-Ge phase diagram redrawn from Ref. 9.

Figure 2. Single crystal of $Cr_{11}Ge_{19}$ grown by the gradient-ftcczc technique (scale in centimeters).

Figure 3. Cross section of one of the ingots near the boundary between the single phase material (gray area) and the eutectic microstructure (top part) (Magnification x 40).

Figure 4. Electrical resistivity as a function of inverse temperature for a $Cr_{11}Ge_{19}$ single crystal cut perpendicular to the growth direction.

Figure 5. Seebeck coefficient as a function of temperature for two $Cr_{11}Ge_{19}$ single crystals cut perpendicular and parallel to the growth direction,

Figure 6. Thermal conductivity as a function of temperature for two $Cr_{11}Ge_{19}$ single crystals cut perpendicular to the growth direction.

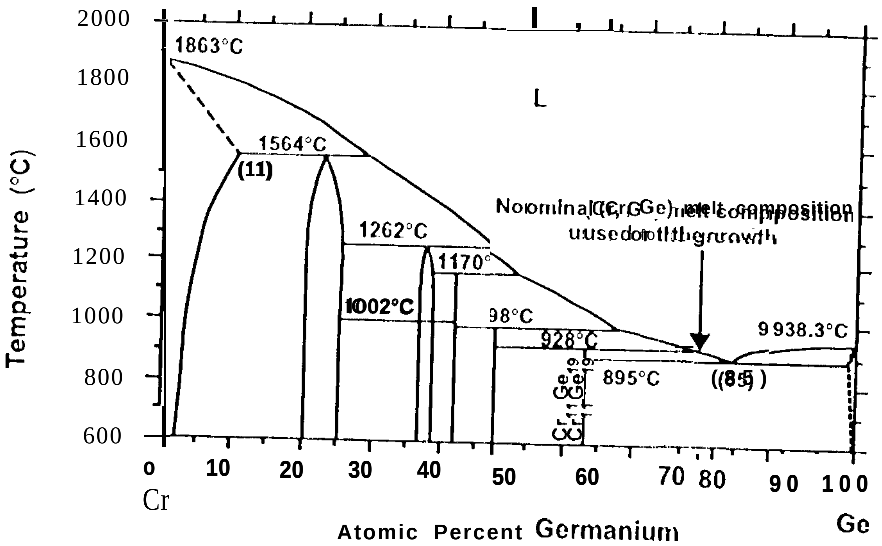

Temperature (°C)
2000
1800
1600
1400
1200
1000
800
600
1863°C
L
1564°C
(11)
1262°C
1170°
1002°C
928°C
895°C
(85)
938.3°C
Nominal (Cr,Ge) melt composition used for the growth
0
10
20
30
40
50
60
70
80
90
100
Cr
Ge
Atomic Percent Germanium

Fig (1)

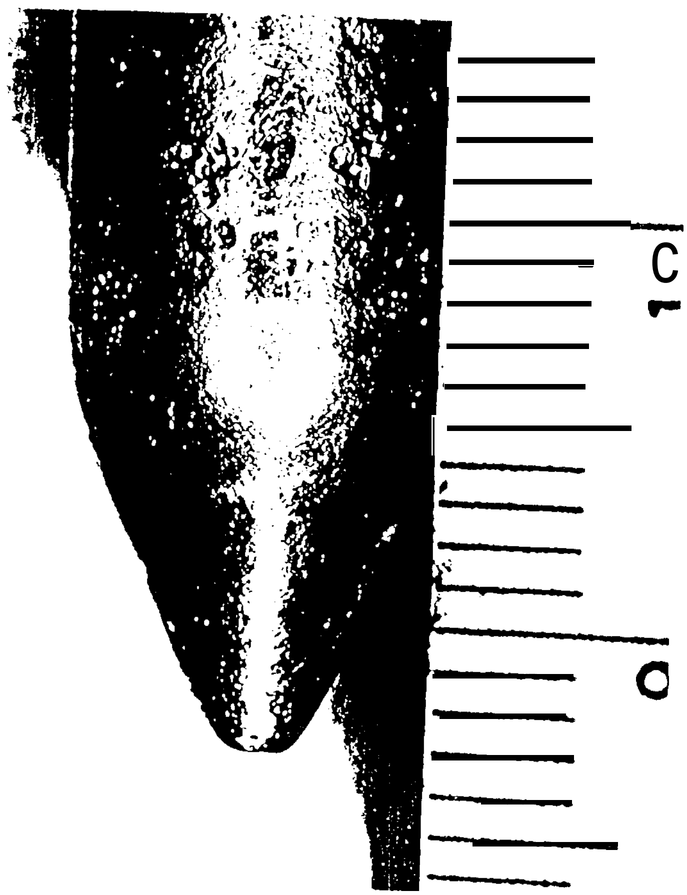
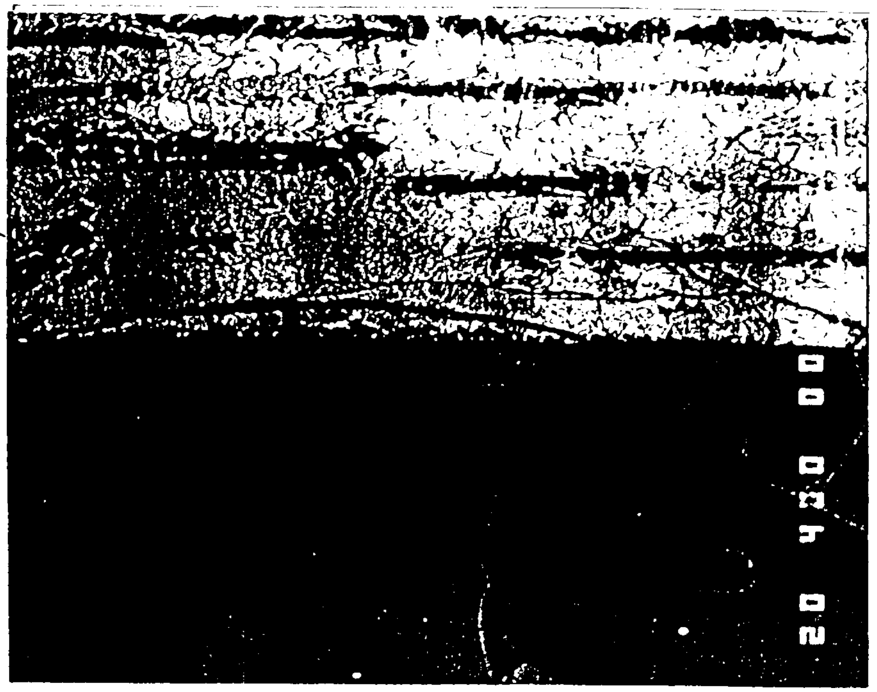
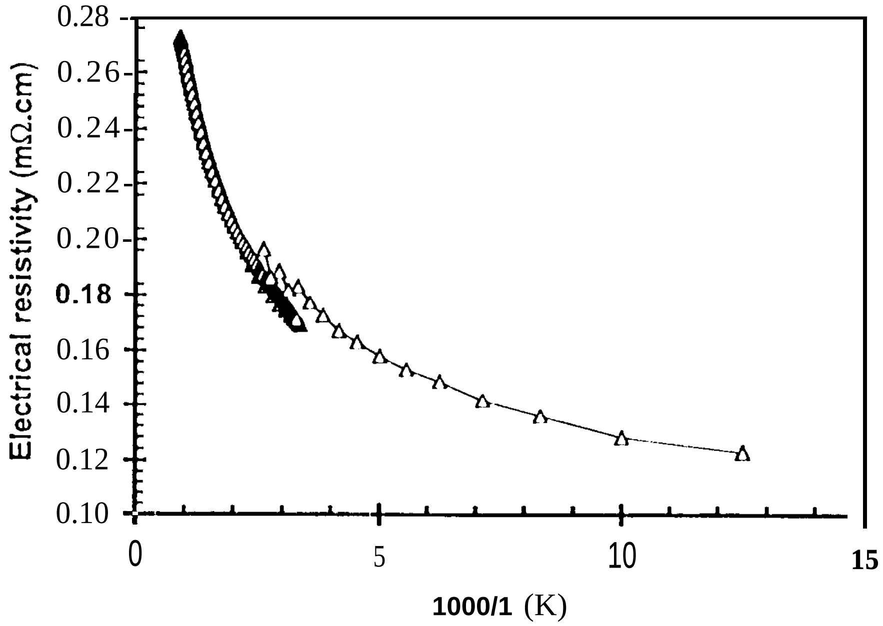


Fig 9

eutectic $Cr_{11}Ge_{19}$ + Ge

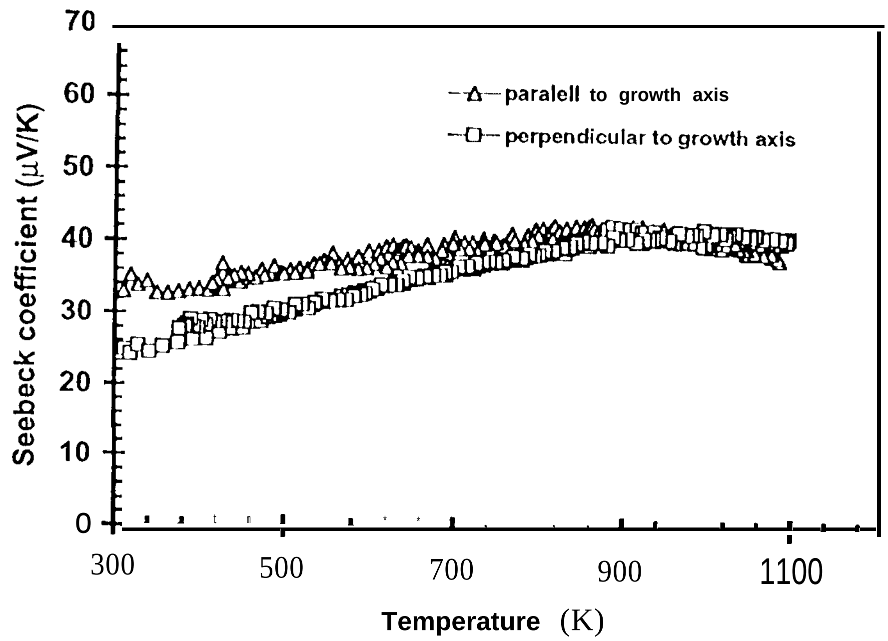


single phase, single crystalline $Cr_{11}Ge_{19}$
Some cracks are seen



0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
Electrical resistivity (mΩ.cm)
0
5
10
15
1000/1 (K)


Fig 6



70
60
50
40
30
20
10
0
Seebeck coefficient (μV/K)
—Δ— paralell to growth axis
—□— perpendicular to growth axis
300
500
700
900
1100
Temperature (K)


Fig 5

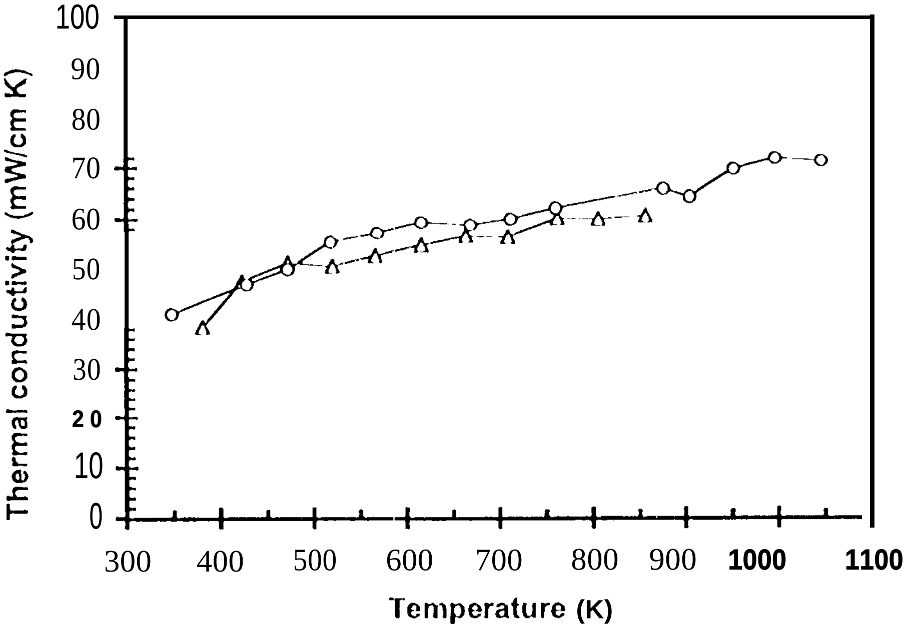

Thermal conductivity (mW/cm K)
100
90
80
70
60
50
40
30
20
10
0
300
400
500
600
700
800
900
1000
1100
Temperature (K)

Fig (6)