Crystal Growth of Rare Earth Pnictides and ZnSe in W and Mo Crucible closed by Electron Beam Welding†

Michio TOMIE*, Nobuyuki ABE*, Hiroshi SHIDA**, Yoshinori HAGA***, D. X. LI***, Akira OMINO**** and Takashi SUZUKI*****

Abstract

New results in both high temperature technology and crystal growth in closed systems are reported. The key problem to attain ultra high temperature in a vacuum furnace was resolved by applying new excellent radiation shield made of Pyrolytic BN. Improvement is carried out on the structure of welding part of metal crucibles to prevent leakage from the closed crucible during heating. New results of the crystal growth of ZnSe which is rapidly rising the possiblities of blue light emitting diode. Physical properties of CeP and CeAs are reported. As new materials which show heavy fermion state in extremely low carrier concentrations are also presented.

KEY WORDS: (Ultra High Temperature Radiation Shield) (ZnSe) (Blue Light Emitting Diode) (CeP) (CeAs) (Low Carrier Heavy Fermion) (Electron Beam Welding)

1. Introduction

Crystal growth in closed system is particularly important for volatile compounds such as chalcogenides and pnictides to keep its good stoichiometory. Quartz tubes are usually used as closed crucibles for low melting compounds below 1470K. However it is impossible to use for higher melting materials and there are a few suitable crucible materials to be able to get closed system except W, Mo and Ta. These are rather expensive and necessary to close the crucible by electron beam welding of which apparatus are also much more expensive. This is the reason why the searching for several properties and producing good single crystals were rather poor in the compounds of pnictides and chalcogenides with high melting temperature. Fortunately we could get the financial support of the Grant in aid for Scientific Research (Special Promoting Research) by Ministry of Education, Science and Culture in Japan from 1984 to 1986 and construct the series of the fundamental apparatus including electron beam welding system to be necessary to get crystals with melting points above 2730K and have already reported in this Transaction[1)]

2. Vacuum Furnace with Tungsten Heater

The vacuum furnace with tungsten heater is much more convenient to operate below 2270K and has great stability of the temperature within 1 degree/hr near 2270K and can control and programme of the heating process in crystal growth. The construction of this furnace is shown in **Fig. 1**. There are two kinds of W heater available as shown in **Fig. 2**, mesh heaters and plate heaters. The mesh heater is superior to the plate one in its thermal stability. The plate heater is rather easily deformed by the recrystalization of W especially in the operation near 2270K. The radiation shields are consisted of W, Mo and Ta thin plate. They are also deformed by heating up to 2270K for long time. So it is practically better to operate this type of furnace below 2270K for economical reason. The temperature is measured by W-Re thermocouple which is also very stable in vacuum below 2270K.

Typical temperature profile of this furnace is shown in **Fig. 3**. A crucible is vertically set on the top of long rod by screw which is vertically travelled by the external force in Bridgeman method. This rod is made of double pipe of stainless steel for water cooling, and a short rod of Mo is mounted between crucible and long rod to connect them

† Received on April, 1992

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Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka 567, Japan

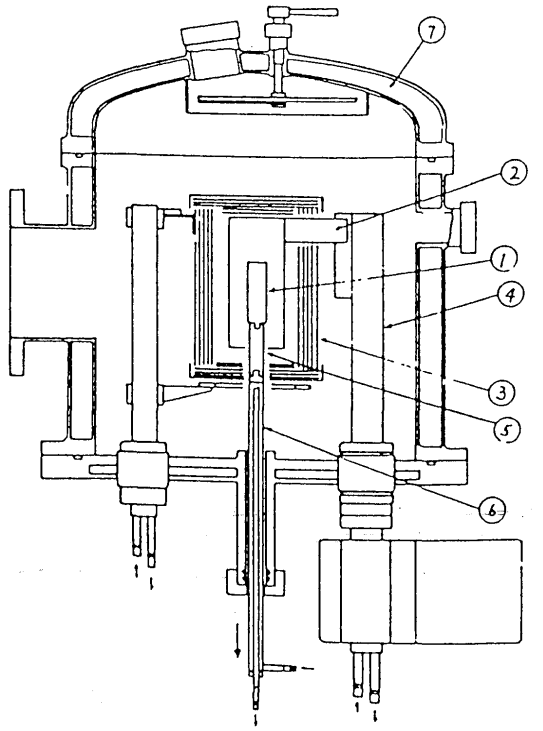


Fig. 1 Construction of the vacuum furnace with a tungsten heater. 1. Crucible 2. Tungsten heater 3. Radiation shield 4. Electrode 5. Mo rod 6. Water cooled rod 7. Water jaket

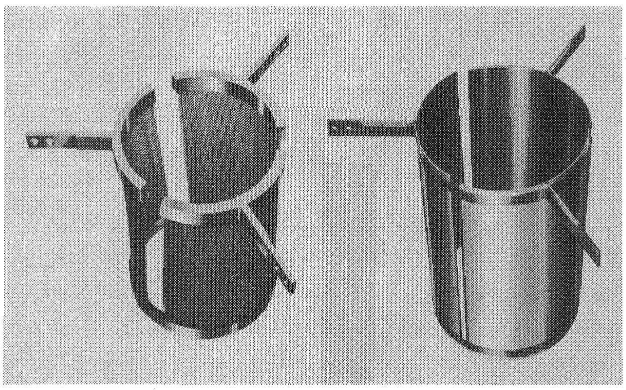


Fig. 2 A tungsten mesh heater and a tungsten plate heater

and prevent a stainless pipe flow destroying in high temperature. Additional BN rod is some times inserted in the case of the operation near 2270K and to reduce the temperature gradient at the bottom of the crucible as a thermal insulator. This furnace is quite useful to grow various crystals by Bridgemann method for congruent material or some kind of flux method for incongruent materials below 2270K. The details and results of the crystal growth used this furnace shall be described in the later chaper.

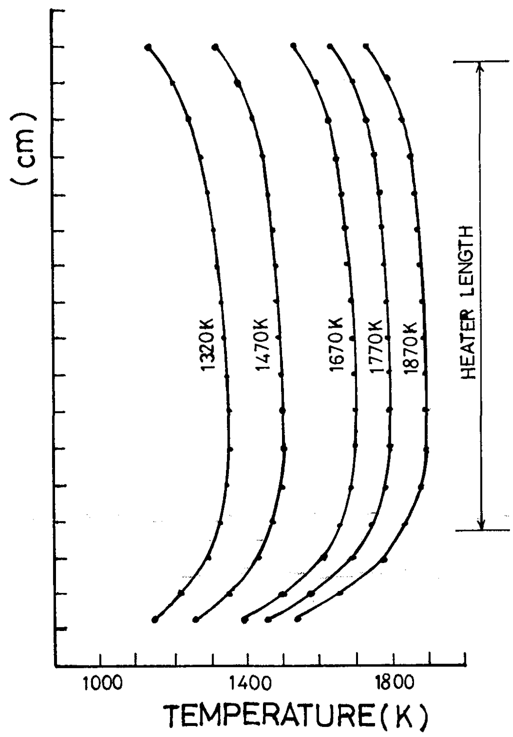


Fig. 3 Typical temperature profile of the vacuum furnace with a tungsten plate heater

3. Vacuum Furnace Heated by High Frequency (HF) Induction

Above 2270K we cannot practically use the W-heater type furnace as just mentioned above. So we developed the method of directly coupled with HF power and refractory metal crucible as shown in previous report[1]. However this furnace is possible to elevate up to the maximum temperature to be 2670K.

Because the strong radiation loss coming from the surface of crucible cannot stored the supplied HF power, the larger supplied power results larger radiation loss. It is desirable to shield this radiation. We have tried several kind of carbon fiber and oxide ceramics as a radiation shield materials and found all material to be destroied in such high temperature. However we discovered fortunately that pyrolytic BN is very preferable for the radiation shield in ultra high temperature if a suitable treatments would be done. Pyrolytic BN is transparent in itself for such radiation but not perfect and partly reflect by diffuse scattering due to its random mosaic structure. Our idea is to stick a thin tungsten layer on the inner surface of the cylindrical BN by evaporation from tungsten crucible in vacuum heating. It stand as perfect radiation shield. The radiation coming from the surface of the crucible reflect by this thin layer but much lower frequency HF power can easily pass through this thin layer for its large penetration depth.

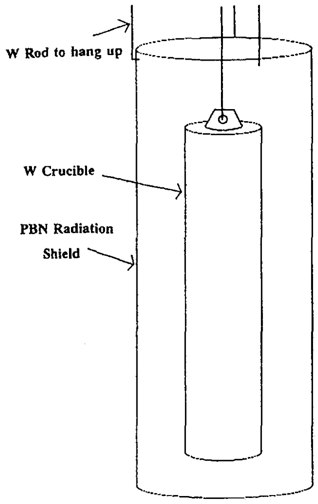


Fig. 4 Pyrolitic BN radiation shield

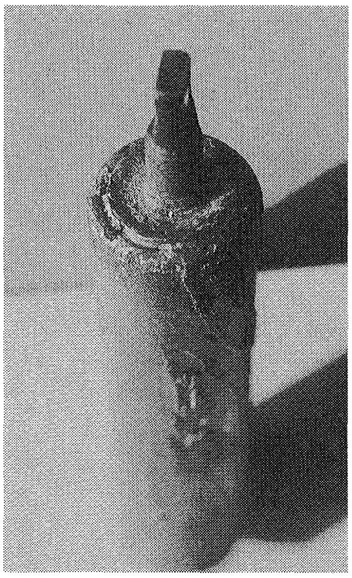


Fig. 5 Leakage occurred on welding part of W crucible

Furthermore several advantages are obtained; 1) The temperature gradient on the horizontal plane inside the crucible is remarkably improved. 2). It is to enable us to operate the furnace by rather small input HF power in very stable condition. 3) It is disappeared the adhesion of the thin W layer on the inner surface of silica tube and then goes out the fine boiling phenomena in the cooling water through the double wall the silica tube. The example of excellent BN radiation shield is shown in **Fig. 4**.

Our vacuum furnace heated by HF induction is very simple but enable us to get very stable ultra high temperature even up to 3270K and has a good advantage of cost performance.

4. Improvement of the Welding Part of the Crucible

We can challenge to prepare the single crystal of ultra high melting point matrial of YbP of YbN etc for the sake of new discovering the superior radiation shield of pyrolitic BN. However these compounds have high vapor pressure even in the 2530K and occurred a rapture in the welding part as shown in **Fig. 5**. We thought that there are some structure problem in the cup of the crucible adapted in the past as shown in **Fig. 6a**. The highest part of the W cylinder was a little bit higher than the cup, then this higher part melt at first by electron beam and melting part may cover the cup. Outside of viewing is good as if the welding is completed. This may be the reason why it has not strongly weld between cup and crucible. We improve the structure of the welding part to avoid the problem mentioned above as shown in **Fig. 6b**. It is possible to melt

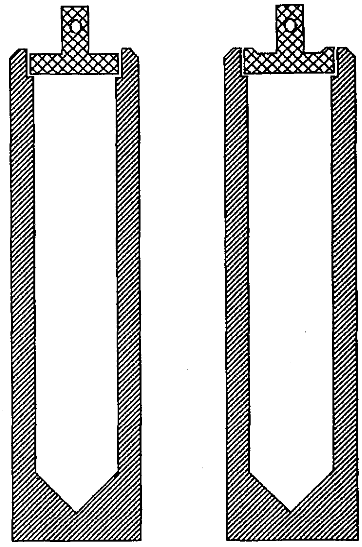


Fig. 6 a) The structure of the welding part of crucible adapted previously.
b) Improved one

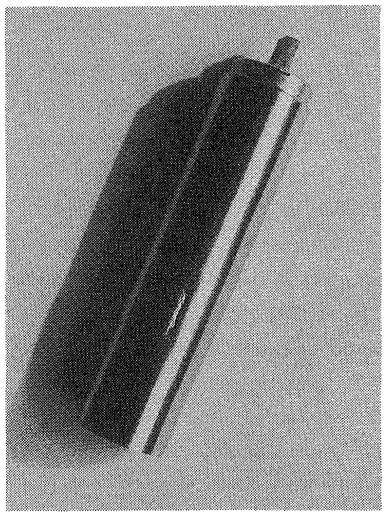


Fig. 7 Crack and swelling near the center on the W crucible due to strong internal pressure in high temperature.

at the same time in both cup and the top of the crucible and confirm by external appearance. Adoption of this improved type was certainly succeeded and no leakage occurred in this part but another trouble was happened. It broke out by crack near the center part of the crucible and swell a little bit due to large internal pressure of the vapor of the compound as shown in **Fig. 7**. If some small fault come into crucible during the machine process, this may be enlarged into the crack in severe condition such as high temperature and high pressure. We are now trying to crystal growth in lower temperature taking a lot of time due to lower the growth rate of crystal, although it still remains to be solved the problem mentioned above.

5. Crystal Growth in Vacuum Furnace with Tungsten Heater

An advantage to adopt the closed system for crystal growth is to be able to prevent the evaporation and escape of the volatile element and to keep the stoichiometory of the compunds. It is essentially important for chalcogenide and pnictides. Recently the needs for suitable good quality and size of ZnSe single crystals are rapidly increased due to be near at hand the realization of the blue luminessence light emitting diode. However the growth of single crystals of ZnSe from a stoichiometric melt was difficult because the compound has high dissociation pressure of 1.8 atm at 1790K[2,3]. Up to now, the crystals have been grown by the Bridgeman method in high pressure autoclave[4] or what is called "soft ampoule" method[5]. In the former method the compound could be melted by retarding the decomposition with high inert gas pressure more than 100 atm, however, graphite crucibles were more or less porous and not gas-tight, therefore the method could not restrain the melt from evaporation and deviation from the stoichiometory[6]. The latter method is simpler, in which the compound was melted in a fused quartz ampoule supported by a graphite crucible, and crystals were grown in a sealed hot walled system. However, rising internal pressure during the initial heating, as well as devitrification of the quartz during soaking, led to ampoule failures[5]. In this situation we studied the growth of single crystals of ZnSe from the melts by the Bridgeman method with molybdenum (Mo) crucibles[7]. The direct use of Mo crucibles for the crystal growth was possible, but the grown crystals stuck with the wall of the metal crucibles. Therefore in this study, an inner crucible made of pyrolitic boron nitride (PBN) which is not wettable with the melt of ZnSe was inserted to the metal crucible as shown in **Fig. 8**[7] and seal of which was performed by an electron beam welder.

As the starting materials for the crystal growth, nominal 5N ZnSe powders manufactured by Rare Metallic Co. Ltd (Japan) were used. A polycrystal seed or single crystal seed which was obtained in previous experiments, was insert at the bottom of the PBN crucible. Obtained single crystal is shown in **Fig. 9**. The twin boundaries is observed in macroscopically, but there are a few microscopical twin in the case of using seed crystal. On the other hand, the grown crystals without seed have typical micro twinning parallel to the grown axis. The photoluminescence spectrum of the single crystal grown on a seed is shown in **Fig. 10**. The deep level emission such as Cu-red around 1.95 eV, Cu-green around 2.31 eV were not observed. On the other hand, rather distinct bound-exiton emission band can be seen which is observed only on pure vapor growth ZnSe. It is to be considered that the quality of our single crystals of ZnSe grown by the present method is comparable to the vapor grown one, and the size of this crystals are satisfactory big enough to use for a substrate of the blue light emitting diode.

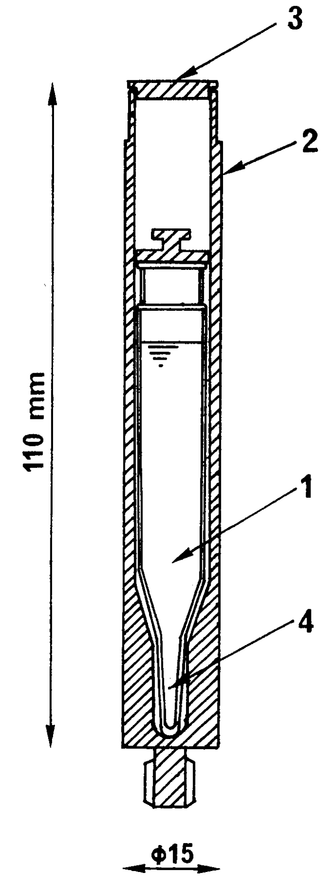
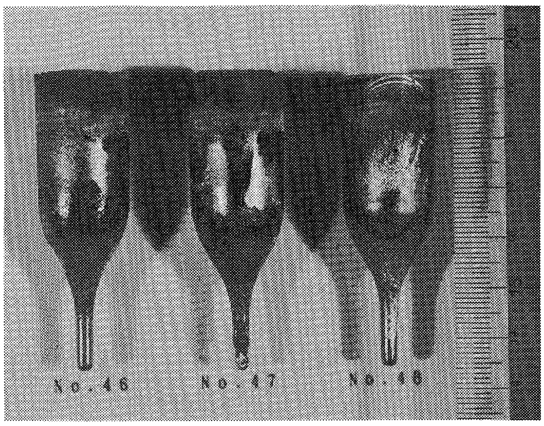
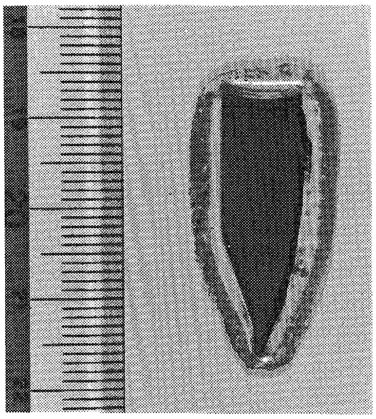


Fig. 8 Assemble of the double crucible; 1. Lid of crucible, 2. Mo crucible contain inner PBN crucible, 3. Portion for seed crystal, 4. Single crystal of ZnSe



(a)



(b)

Fig. 9 Section of ZnSe single crystal ingot

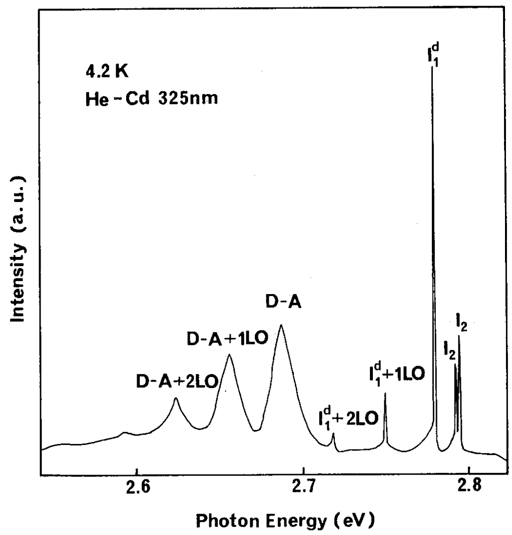


Fig. 10 Photoluminescence spectrum measured on the single crystal of ZnSe

6. Crystal Growth of Rare Earth Pnictides in Ultra High Temperature

Nevertheless we have encountered many trouble in preparation of Yb monopnictides as described in the chapter 4, we could get good single crystal CeP and CeAs due to our new discovered excellent radiation shield. The difficulty to obtain reliable results on these compounds have been reported by F. Hulliger[8] in which the sample dependences were extremely large. Why are there such large unusual sample dependence? It suggests that the systems are low carrier semimetals. In fact, in the series of Ce-monopnictides, CeP and CeAs are expected to be semiconductor or semimetals with very small overlap between conduction band and valence bands from theoretical works by A. Hasegawa[9]. So we thought that these compounds have possibility to be typical example of Kondo systems with extremely low carrier concentration. Then we started to obtain good single crystal. Most important work is how to control and establish the stoichiometory. After many tries and errors, we get very good and pure single crystal of CeP and CeAs. It should be necessary that the ratio of Ce and P of starting material are not just 1:1 (Sample 1) but nearly 10% excess of P (Sample 2). Most clear evidence to be pure crystal would be able to detect the Schubnikov dHvA effect or large positive magnetoresistance in high magnetic field. We could detect these effect only on the sample 2 with 10% excess P of starting materials as shown in **Fig. 11** and **Fig. 12**[10]. The magnetoresistance and Shubnikov dHvA for CeAs effect are also given in **Fig. 13** and **Fig. 14**. After Fourier analysis of these oscillation vers to inverse magnetic field, we could exactly determined the carrier concentration as 0.2% for CeAs and 0.25% for CeP[11].

Kondo behavior in high temperature region can be seen in **Fig. 15** and **Fig. 16** respectively. We have claimed that there are several compounds showed the Kondo behavior

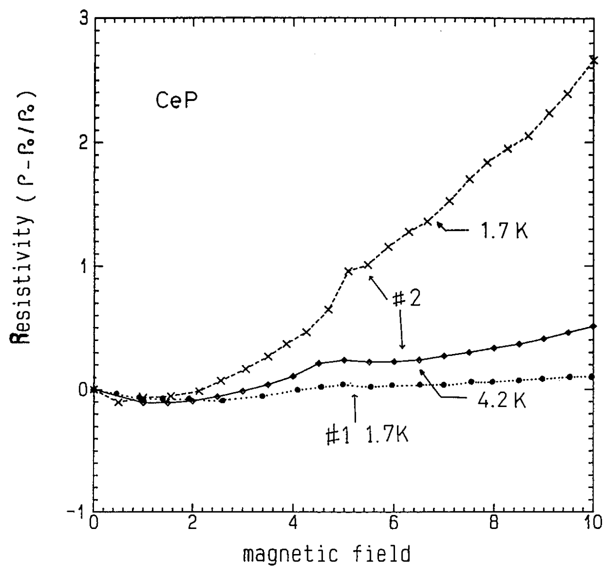


Fig. 11 Magnetoresistance for sample 1 and 2 of CeP

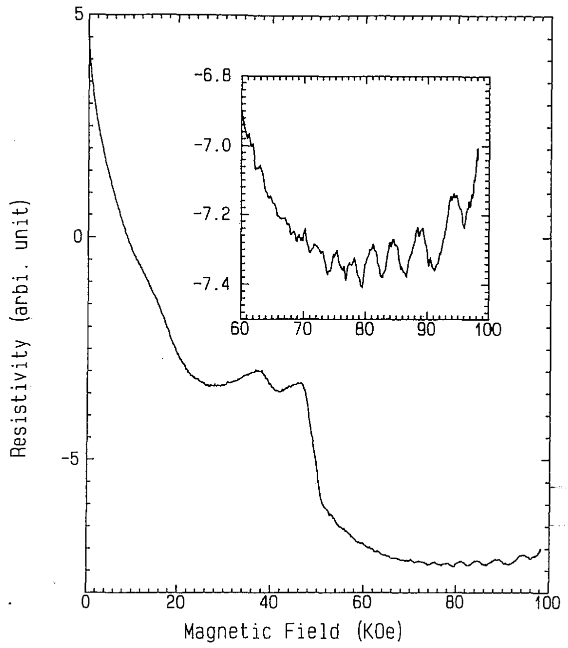


Fig. 12 Schubnikov dHvA oscillations for sample 2 of CeP

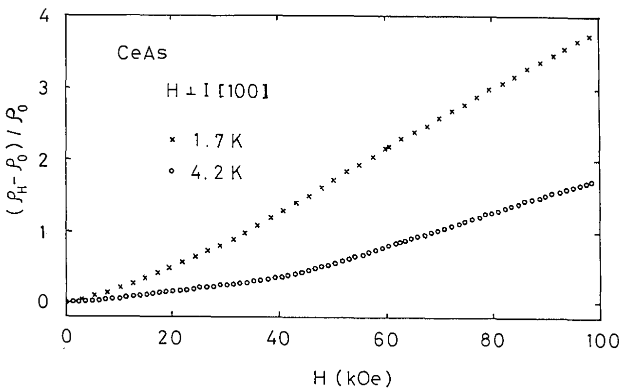


Fig. 13 Magnetoresistance for CeAs

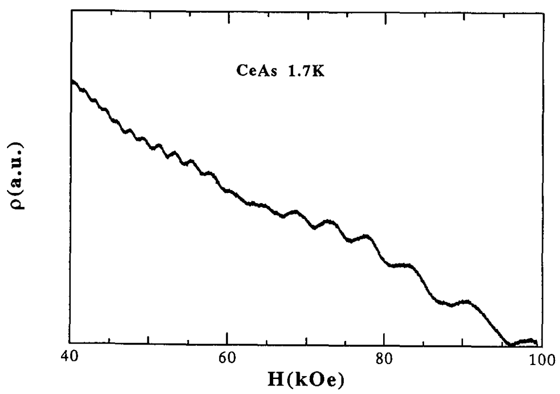


Fig. 14 Schubnikov dHvA oscillations for CeAs

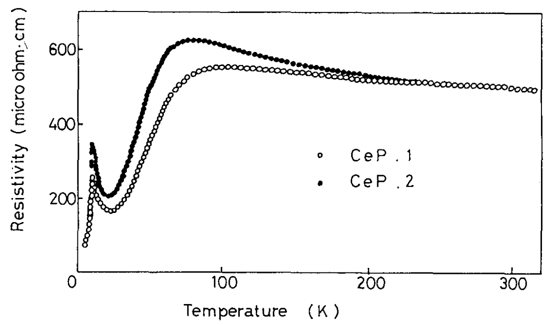


Fig. 15 Temperature dependence of electrical resistivity for CeP

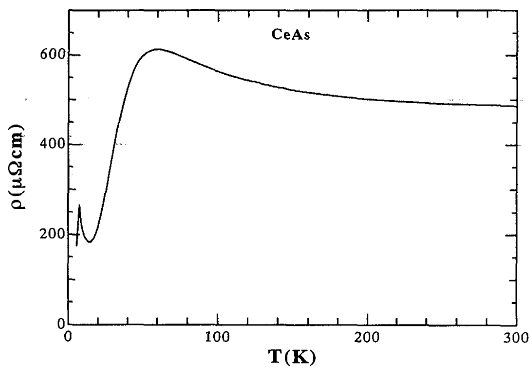


Fig. 16 Temperature dependence of electrical resistivity for CeAs

or heavy fermion state in the low carrier concentration systems[12]. However it is serious problem because simple picture of Kondo state is necessary a lot of carrier to kill the localized spin and to get singlet state. So it was hard to get a consensus by usual researchers. Now we have another example of Kondo state in extremely low concentration system in CeP and CeAs and several collaborations are proceeding such as magnetization process in ultra high magnetic field with Prof. M. Date group in Osaka Univ. and physical properties under high pressure with Prof. N. Mori group in ISSP of Tokyo Univ. etc.

The interesting problem in heavy fermion state for low carrier systems are getting the sound foundation due to successive appearrence of new material and now in progress.

7. Conclusion

PBN cylinder with thin layer of tungsten on its surface was found as excellent radiation shield material to realize ultra high temperature in HF furnace. The problem of leakage in the welding part of W crucible was resolved by improvement of the structure of the cruible. We succeeded in growing reasonable good single crystal in both quality and size and promised to be able to use for the base crystal of blue light emitting diode of ZnSe which was recently paid much attention for the inductrial apllication. The new compounds of CeP and CeAs were synthesized and studied for several physical properties and found the very low carrier systems with localized spin which is show various anormalous properties.

The authors would like to express their sincere thanks to Prof. Y. Arata for his continuous encouragement. This work is partially suported by the grand in Aid for Scientific Research from the Ministry of Education, Science and Culture (Grt. No. 03452027).

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