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Interaction of the components in the systems Ce–Ag–Si at 500 °C and Eu–Ag–Si at 400 °C

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Abstract

Isothermal sections of the phase diagrams of the systems Ce–Ag–Si and Eu–Ag–Si were built at 500 and 400 °C, respectively. Three intermetallic compounds were found in the former system, two in the latter and their crystal structures and homogeneity regions were determined. The effective valence of europium in the $CeAl_2Ga_2$-type phase $EuAg_2Si_2$ was found to be 2+ over the whole homogeneity range, based on L_{III}-absorption spectroscopy. The temperature dependence of the electrical resistivity, thermoelectric power and magnetic susceptibility of this phase was also studied.

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Keywords: Silver-based systems; Phase diagram; Rare-earth compounds; Physical properties

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1. Introduction

The results presented in this paper continue a systematic research on silver-based ternary systems with rare-earth metals and main-group elements. The peculiar properties of cerium and europium distinguish these elements from the other rare-earth elements. The investigation of the interaction of cerium and europium with other elements, the conditions under which compounds are formed and the crystal structures and properties of these, makes it possible to establish relations between the properties of the elements and their place in the periodic system.

Several intermetallic compounds have been reported in R-Ag–Si systems [1], however, isothermal sections have only been built for the systems {La,Ce,Pr,Nd}–Ag–Si [2–5]. In the Ce–Ag–Si system studied at 850 °C three compounds have been identified: $CeAg_2Si_2$ ($CeAl_2Ga_2$-type structure), $Ce(Ag_xSi_{1-x})_{2-y}$ ($x = 0.35$–0.4, $y = 0$; AlB_2-type structure) and $CeAgSi_2$ (unknown structure) [3]. Our preliminary results of the investigation of the Eu–Ag–Si system have been reported in [6].

2. Experimental

The investigation of the phase equilibria was based on 92 and 120 alloys for the systems Ce–Ag–Si and Eu–Ag–Si, respectively. The samples were prepared by arc melting under high-purity argon on a water-cooled copper hearth. The starting materials were high-purity elements: cerium 99.89%, europium 98.8%, silver 99.9%, and silicon 99.9999%. The alloys were annealed for 2 weeks in evacuated quartz ampoules, at 500 °C for the system Ce–Ag–Si and at 400 °C for the system Eu–Ag–Si, and subsequently quenched in water.

The phase analysis was performed by X-ray powder diffraction (Debye-Scherrer method, RKD-57.3, Cr Kα radiation). The lattice parameters were determined using a powder diffractometer (DRON-2.0, Fe Kα radiation or DRON-3.0, Cu Kα radiation). The crystal structures of the compounds were studied by X-ray powder diffraction (automatic diffractometer HZG-4a, Cu Kα radiation).

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The microstructures of some alloys were studied visually using MIM8 and Neophot-30 microscopes.

The effective valence of europium was determined by L_{III}-absorption spectroscopy at room temperature. Electric resistance and thermoelectric power were measured with an accuracy of not worse than 5 and 10%, respectively. Magnetic susceptibility was measured by the Faraday method with 3% accuracy.

3. Results and discussion

The systems {Ce,Eu}–Ag–Si (Fig. 1, Table 1) are characterized by the formation of a few ternary compounds and solid solutions based on several binary compounds. According to the phase diagram of the Ce–Ag–Si system at 500 °C, the binary compounds of the systems Ce–Si and Ce–Ag dissolve no more than 5 at.% of the third component, except $CeSi_2$ with α-$ThSi_2$-type structure (space group $I4_1/amd$), which dissolves up to 18 at.% of silver (Fig. 2). The phase analysis shows that on increasing the amount of silver in this phase, the width of the homogeneity region gradually decreases from 3 to 1 at.% of cerium, without any significant decrease of the unit-cell volume. The increase of the cell volume observed on increasing the silver content along the isoconcentrate 33 at.% of cerium is explained by the formation of a solid solution where Si atoms ($r_{Si} = 0.134$ nm) are progressively replaced by larger Ag atoms ($r_{Ag} = 0.144$ nm). On the contrary, along the isoconcentrate with a constant silver content the lattice parameters remain practically unchanged, which corresponds to the formation of a solid solution where Si atoms are simply removed, and not replaced by the larger Ce atoms ($r_{Ce} = 0.183$ nm).

A previously unknown compound, $CeAg_{1.12}Si_{0.88}$, which crystallizes with a LaPtSi-type structure (space group $I4_1md$, $a = 0.42346(2)$, $c = 1.4712(1)$ nm), was found in the system Ce–Ag–Si. In addition, the existence of the compounds $CeAg_2Si_2$ [7] ($CeAl_2Ga_2$ structure type, space group $I4/mmm$) and CeAgSi [8] (AlB_2 structure type, space group $P6/mmm$) was confirmed. For the latter a significant homogeneity region was found, $CeAg_{0.90–1.10}Si_{1.10–0.90}$.

The binary compound $EuAg_2$ (KHg_2 structure type, space group $Imma$) dissolves up to 15 at.% of Si, with the lattice parameters changing from $a = 0.4772(3)$, $b = 0.7498(7)$, $c = 0.8187(7)$ to $a = 0.4706(8)$, $b = 0.7536(9)$, $c = 0.8167(8)$ nm within the homogeneity range (Fig. 3). It should be noted, that the binary compound Eu_2Si ($PbCl_2$ structure type, space group $Pnma$), which was found in an

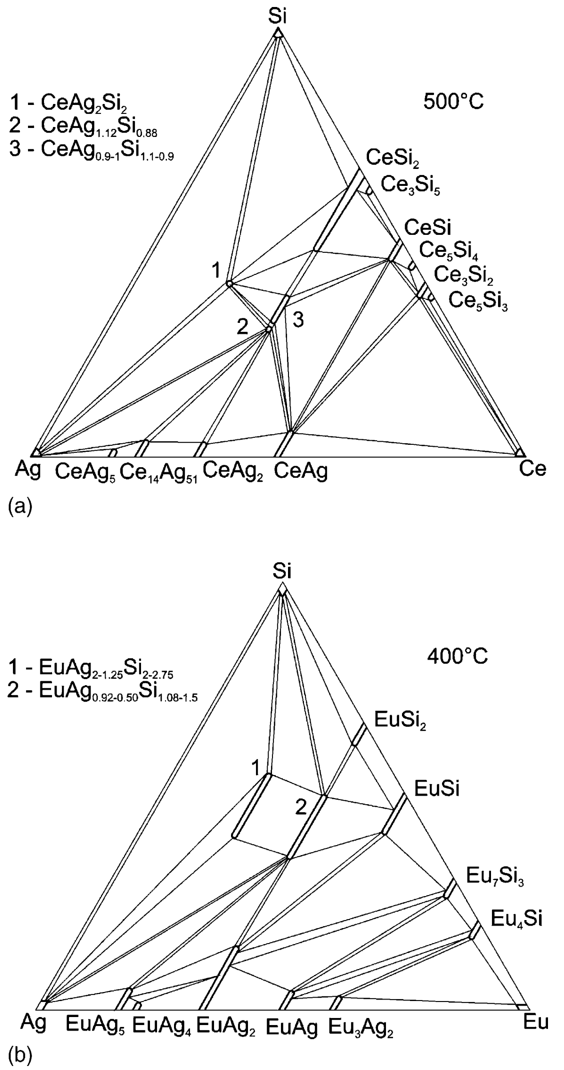

Fig. 1. Isothermal sections of the (a) Ce–Ag–Si system at 500 °C and of the (b) Eu–Ag–Si system at 400 °C.

Table 1
Crystallographic data of the ternary compounds in the systems {Ce,Eu}–Ag–Si

No.	Compound	Structure type	Space group	Lattice parameters (nm)	
				a	*c*
System Ce–Ag–Si					
1	$CeAg_2Si_2$	$CeAl_2Ga_2$	$I4/mmm$	0.4254(1)	1.0641(2)
2	$CeAg_{1.12}Si_{0.88}$	LaPtSi	$I4_1md$	0.42346(2)	1.4712(1)
3	$CeAg_{0.90–1.10}Si_{1.10–0.90}$	AlB_2	$P6/mmm$	0.4241(1) for composition CeAgSi	0.4203(1)
System Eu–Ag–Si					
1	$EuAg_{2.00–1.25}Si_{2.00–2.75}$	$CeAl_2Ga_2$	$I4/mmm$	0.4315(1)–0.4321(1)	1.0463(2)–1.0454(6)
2	$EuAg_{0.92–0.50}Si_{1.08–1.50}$	AlB_2	$P6/mmm$	0.4202(1)–0.4150(1)	0.4463(2)–0.4477(3)

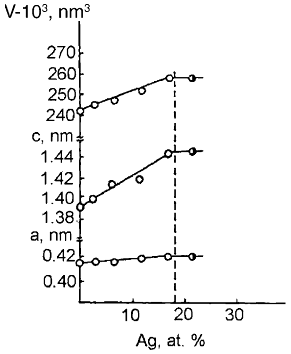

Fig. 2. Lattice parameters of the solid solution of Ag in $CeSi_2$.

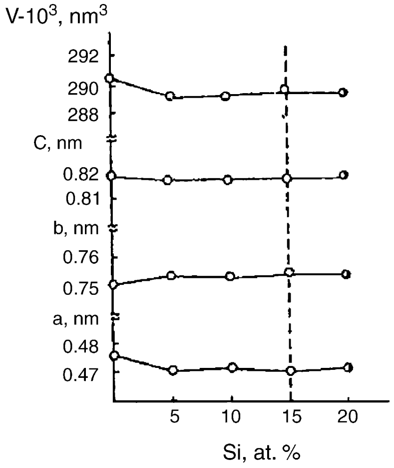

Fig. 3. Lattice parameters of the solid solution of Si in $EuAg_2$.

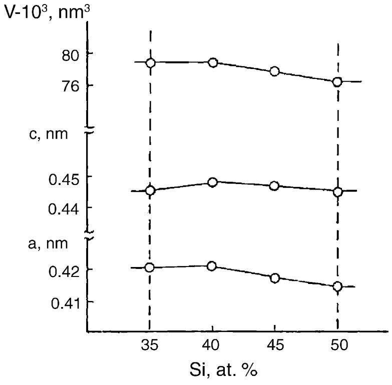

Fig. 5. Lattice parameters in the homogeneity region of the compound $EuAg_{0.92–0.50}Si_{1.08–1.50}$.

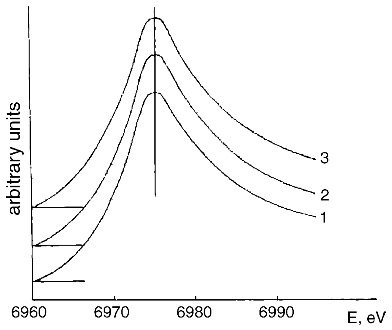

Fig. 6. L_{III}-absorption spectra of the samples: (1) $EuAg_{1.25}Si_{2.75}$; (2) $EuAg_{1.50}Si_{2.50}$ and (3) $EuAg_{1.75}Si_{2.25}$.

alloy annealed at 1000 °C and reported in [9], was not observed at 400 °C.

In the system Eu–Ag–Si at 400 °C, the existence of the compound $EuAg_2Si_2$ crystallizing with a $CeAl_2Ga_2$-type structure was confirmed. Its homogeneity region was found to be $EuAg_{2.00–1.25}Si_{2.00–2.75}$ (Fig. 4). The ternary AlB_2-type silicide in the Eu–Ag–Si system, already observed in earlier works [10], is also characterized by a variable content of silver and silicon, $EuAg_{0.92–0.50}Si_{1.08–1.50}$ (Fig. 5). The $Eu_4Ag_2Si_6$ compound, which was prepared at 1000 °C in a corundum crucible inside an evacuated quartz ampoule and reported in [11], was not found at 400 °C.

The results of X-ray L_{III}-absorption spectroscopy studies of the valence of Eu in the compound $EuAg_{2.00–1.25}Si_{2.00–2.75}$ (Fig. 6) allow us to conclude that Eu has a stable valence 2+ over the whole homogeneity region. The temperature dependence of the electrical resistance of $EuAg_2Si_2$ (Fig. 7) shows a typically metallic behavior, $\rho/\rho_{300\,K}$ increasing monotonically with increasing temperature. The thermoelectric power

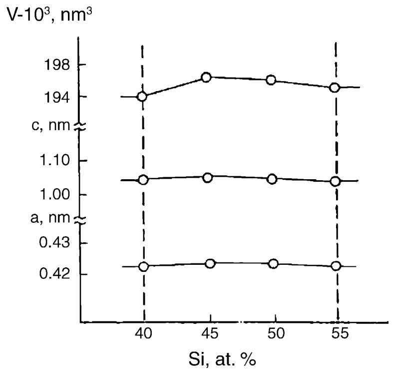

Fig. 4. Lattice parameters in the homogeneity region of the compound $EuAg_{2.00–1.25}Si_{2.00–2.75}$.

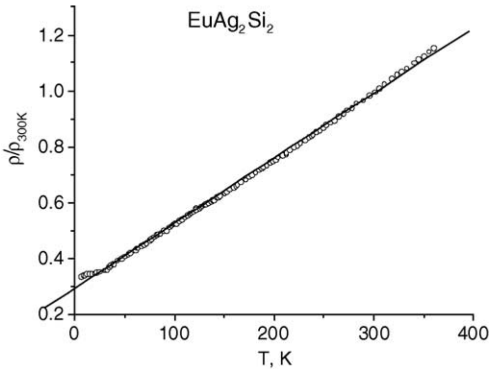

Fig. 7. Temperature dependence of the relative resistance $\rho/\rho_{300\,K}$ of $EuAg_2Si_2$.

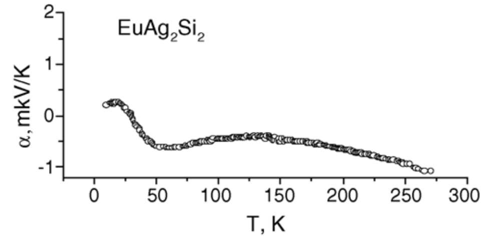

Fig. 8. Temperature dependence of the thermoelectric power of $EuAg_2Si_2$.

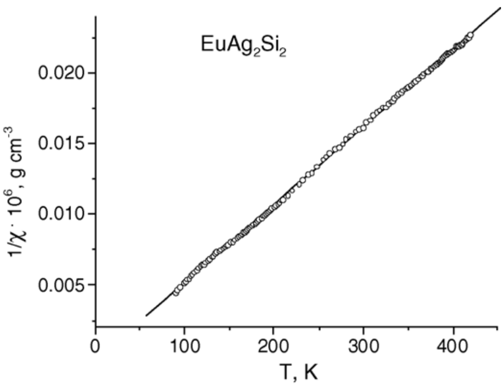

Fig. 9. Temperature dependence of the inverse magnetic susceptibility of $EuAg_2Si_2$.

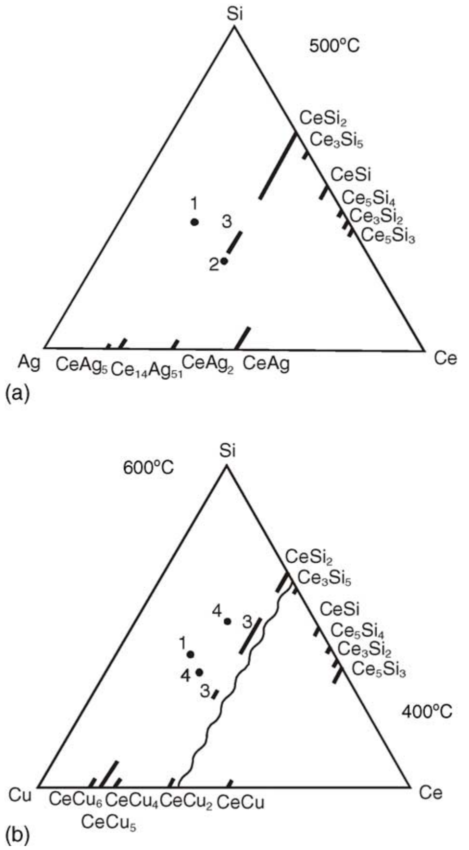

Fig. 10. Phases formed in the system: (a) Ce–Ag–Si and (b) Ce–Cu–Si; 1 – $CeGa_2Al_2$ type, 2 – LaPtSi type, 3 – AlB_2 type, 4 – $CeNiSi_2$ type.

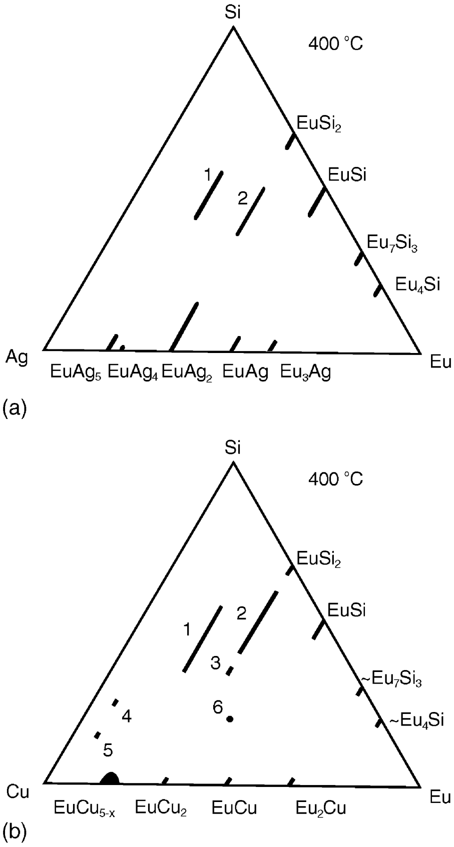

Fig. 11. Phases formed in the systems (a) Eu–Ag–Si and (b) Eu–Cu–Si; 1 – $CeGa_2Al_2$ type, 2 – AlB_2 type, 3,4,5, and 6 – unknown structure.

(Fig. 8) and the magnetic susceptibility (Fig. 9) have been determined for the same phase in the temperature region 77–450 K.

Among the chemical systems that are closely related to those investigated here, the most thoroughly studied are the systems Ce–Cu–Si [12] and Eu–Cu–Si [13]. A comparison of the corresponding copper and silver systems (Figs. 10 and 11) shows that by replacing copper by silver the number of phases is reduced, from 5 to 3 for the Ce-containing systems and from 6 to 2 for the Eu-containing systems.

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