Journal of Alloys and Compounds 460 (2008) 155–159

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Crystal structure determination of CoGeTe from powder diffraction data

F. Laufek [a,*], J. Navrátil [b], J. Plášil [c], T. Plecháček [b]

[a] Czech Geological Survey, Geologická 6, 15200 Praha 5, Czech Republic
[b] Joint Laboratory of Solid State Chemistry of IMC AS ČR and University of Pardubice, Studentská 84, 53210 Pardubice, Czech Republic
[c] Faculty of Science, Charles University, Albertov 6, 12843 Praha 2, Czech Republic

Received 24 April 2007; received in revised form 8 June 2007; accepted 13 June 2007

Abstract

The crystal structure of cobalt germanium telluride CoGeTe has been determined by direct methods using integrate intensities of conventional X-ray powder diffraction data and subsequently refined with the Rietveld method. The title compound was prepared by heating of stoichiometric amount of Co, Ge and Te in silica glass tube at 670 °C.

CoGeTe adopts orthorhombic symmetry, space group *Pbca* with unit cell parameters $a = 6.1892(4)$ Å, $b = 6.2285(4)$ Å, $c = 11.1240(6)$ Å, $V = 428.8(1)$ Å^3 and $Z = 8$. Its crystal structure is formed by [$CoGe_3Te_3$] octahedra sharing both edges and corners. CoGeTe represents a ternary ordered variant of α-$NiAs_2$ type structure. An important feature present in CoGeTe is an occurrence of short Co–Co distance across the shared edge of [$CoGe_3Te_3$] octahedra. Differential thermal analysis (DTA) has revealed that CoGeTe melts incongruently at about 725 °C; CoGeTe decomposes into GeTe, CoGe and $CoTe_2$. Temperature dependence of the electrical conductivity and value of Seebeck coefficient at 300 K are also reported.

Keywords: CoGeTe; Crystal structure; X-ray powder diffraction; Direct methods; Rietveld refinement

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1. Introduction

The present paper is a part of systematic investigations on the crystal structures of the MXCh compounds of cobalt-group metals (M = Co, Ir and Rh) and main groups IV and VI elements (X = Si, Ge and Sn; Ch = S, Se and Te). With regard to ternary cobalt bearing germanide chalcogenides (Ch = S, Se and Te), the examples encountered so far are $CoGe_{1.5}S_{1.5}$, $CoGe_{1.5}Se_{1.5}$ [1,2] and $CoGe_{1.5}Te_{1.5}$ [3]. The crystal structures of these compounds can be viewed as a modification of skutterudite structure MX_3 (M = Co, Rh or Ir; X = P, As or Sb), where Ge and Ch atoms exhibit long-range ordering, which results in a lowering of the symmetry from original cubic to rhombohedral [2]. These phases are of interest in materials science because of their possible thermoelectric applications.

In this work, we present a detailed study of the crystal structure of the new ternary compound CoGeTe, which is a distorted variant of α-$NiAs_2$, using conventional powder X-ray diffraction. Data obtained by differential thermal analysis are also reported. In spite of the relatively intensive research effort on the Co–Ge–Te system [3–5], it is surprising that this compound has not been previously reported.

2. Experimental

2.1. Synthesis, chemical composition and differential thermal analysis

The CoGeTe ternary compound was synthesised from the elements by high temperature solid-state reactions. Co powder was first heated at 900 °C for 2 h in H_2/Ar (15:85) atmosphere to remove possible oxides. Stoichiometric amounts of Co (99.99%), Ge (99.99%) and Te (99.99%) were sealed in evacuated quartz tubes and heated at 1150 °C for 4 h. Following this, the sample was ground in argon atmosphere using the agate mortar and pestle, and cold pressed into cylindrical pellet. The pellet was then sealed into evacuated quartz tube and heated at 550 °C for 3 days. The resultant material was once again ground and heated at 670 °C for 6 days. After annealing, the sample was quenched in cold water.

The chemical composition of the CoGeTe was characterised in the polished section by an energy-dispersive system Oxford Link ISIS 300 connected to the CamScan IV scanning electron microscope. The accelerating voltage was set to 20 kV and the sample current to 2.5 nA. Data were collected from several spots on several different crystals and then averaged. As measured, the ratio of the

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[*] Corresponding author. Fax: +420 251 818 748.
E-mail address: laufek@cgu.cz (F. Laufek).

doi:10.1016/j.jallcom.2007.06.048

elements Co:Ge:Te was 1:0.98:1.04 (32.9(2)% Co, 32.5(2)% Ge and 34.49(3)% Te) which is extremely close to our final crystal structure solution of 1:1:1.

The differential thermal analysis (DTA) was carried out using the instrument R.M.I.-DTA 003 (Electronic Measuring Instruments, Czech Republic) at a non-isothermal regime in the temperature range 25–800 °C. Small quartz ampoule with powdered sample (about 40 mg weight) was evacuated down to 10^{-3} Pa and heated with rate of 5 K min^{-1}. The calibration was made with the help of In, Al, Zn, Pb and Sn in order to eliminate the differences between the temperature of the thermocouples in the furnace and in the vicinity of the sample. Pure Al_2O_3 was used as a standard.

2.2. Structure determination and refinement

Preliminary scanning-electron observations showed that the crystals have plate-like habit, typically up to 5 μm, rarely up to 15 μm. Therefore, a single-crystal study was impracticable, and the crystal structure of CoGeTe was solved and refined from powder data ab initio.

The X-ray diffraction pattern used for the structure determination was collected in Bragg–Brentano geometry on X’Pert Pro PANalytical diffractometer, equipped with X’Celerator detector using CuKα radiation. The sample was found to be phase pure; no other compounds were detected. To minimize background, the sample was placed on a flat low-background silicon wafer. The data were collected in the range between 13 and 109° 2θ. The details of the data collection and basic crystallographic facts are given in Table 1.

The indexing of the X-ray powder pattern was performed using the DICLVOL04 program [6]. The first 20 lines, with an absolute error of 0.03° 2θ on peak positions, were indexed on the basis of the orthorhombic cell listed in Table 1. The figures of merit M_{20} [7] and F_{20} [8] for assessing the quality of the solution were $M_{20} = 69$ and $F_{20} = 79.9$ (0.0037 and 68). The analysis of systematic absences pointed to the space group *Pbca*. The extraction of the integral intensities as well as the structure solution by direct methods was accomplished using the EXPO2004 program [9]. After the subtraction of the background scattering, the integral intensities up to $2\theta = 62°$ were extracted with the Pearson VII function using the modified LeBail method. All three atoms were found from the first four peaks generated from an E-map with the highest figure of merit. All of them are in a general Wyckoff position 8c of the space group *Pbca*; no special positions are occupied.

The structural model found by EXPO2004 [9] was introduced into the FullProf program [10] for a Rietveld analysis. The Rietveld refinement was carried out in the angular range 13–109° 2θ containing 268 reflections. A pseudo-Voight function was selected to describe individual line profiles, with a variation of the mixing factor η defining the Lorentzian and the Gaussian character of the peaks’ shape. The corrections taking into account the asymmetry of the peaks caused by axial divergence were used according to [11]. The angular variation of the line width was accounted for by using the Cagliotti function [12]. Intensities within 15 times the full width at half maximum of a peak were considered to contribute to the central reflection. The background was determined by the linear interpolation between consecutive breakpoints in the pattern. The convergence criterion, ε, forcing the termination of the refinement when the parameter shifts $<\varepsilon \times \sigma$, was set to 0.1. The refinement involved the following parameters: 12 atomic parameters (including 3 isotropic atomic displacement parameters), 1 scale factor, 1 zero-point, 3 cell parameters, 3 half-widths, 2 asymmetry parameters, 2 variables for the angular variation of η and parameter G1 linked to the preferred orientation along [0 0 1] according to the March–Dollase [13] function. The refinement converged to satisfactory residual factors $R_{\text{Bragg}} = 0.065$ and $R_{\text{wp}} = 0.082$. The details of the refinement are reported in Table 1; Fig. 1 shows the final Rietveld plot. Atomic coordinates and isotropic displacement parameters are listed inTable 2.

Table 1
Data collection and Rietveld analysis

Data collection	
Radiation type, source	X-ray, CuKα
Generator settings	40 kV, 30 mA
Data collection temperature	Room temperature
Range in 2θ (°)	13–109
Step size (°)	0.0167273
Crystal data	
Space group	*Pbca* (no. 61)
Unit cell content	CoGeTe, $Z = 8$
Unit cell parameters (Å)	$a = 6.1892(4)$ $b = 6.2285(4)$ $c = 11.1240(6)$
Rietveld analysis	
No. of reflections	268
No. of structural parameters	12
No. of profile parameters	7
R_F	0.051
R_B	0.065
R_p	0.065
R_{wp}	0.083
χ^2	2.42
Weighting scheme	$1/y_0$

R agreement factors defined according to McCuster et al. [23].

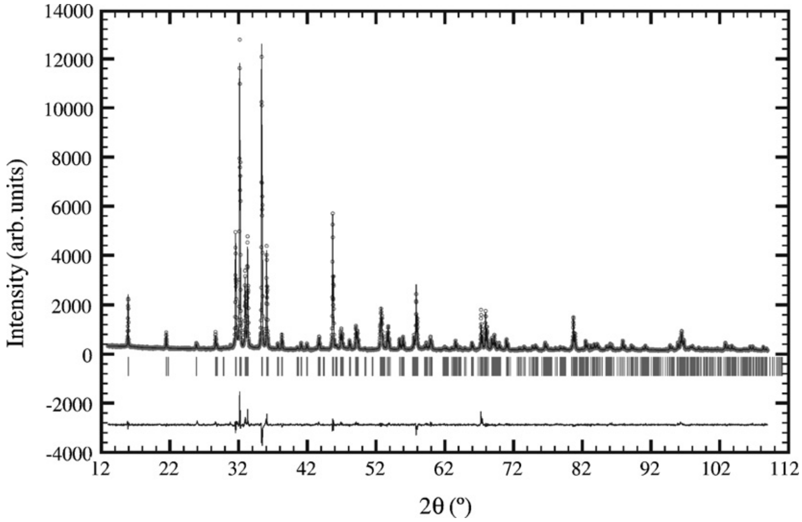

Fig. 1. The Rietveld plot of CoGeTe. The upper trace shows the observed data as dots and the calculated pattern is shown by solid line. The lower trace is a plot of the difference: observed − calculated. The vertical bars indicate the positions of Bragg peaks.

Table 2
Atomic coordinates and isotropic displacement parameters for the CoGeTe compound

Atom	x	y	z	B_{iso} (Å^2)
Co	0.0055(6)	0.6069(6)	0.1119(3)	1.41(6)
Ge	0.6633(4)	0.7698(6)	0.0710(2)	1.57(5)
Te	0.1157(2)	0.9887(3)	0.1740(3)	1.23(3)

2.3. *Electrical conductivity*

Electrical conductivity was measured with four-probe method using Lock-In Amplifier (EG&G model 5209). The Seebeck coefficient was determined using temperature gradient on the samples not exceeding 10 K at the temperature 300 K.

Table 3
Selected bond distances (Å) for CoGeTe and CoAsSe [21]

	CoGeTe	CoAsSe
Co–Ch(i)	2.552(4)	2.358(7)
Co–Ch	2.568(4)	2.375(6)
Co–Ch(ii)	2.602(3)	2.37(1)
Mean Co–Ch	2.574	2.367
Co–X(iii)	2.385(3)	2.34(1)
Co–X(iv)	2.388(5)	2.348(6)
Co–X	2.392(5)	2.331(6)
Mean Co–X	2.388	2.339
Co–Co(v)	2.825(4)	3.50(1)

Symmetry codes: (i) $1/2-x$, $y-1/2$, z; (ii) $-x$, $y-1/2$, $1/2-z$; (iii) $x-1/2$, $1/2-y$, $-z$; (iv) $1/2-x$, $y-1/2$, z; (v) $-x$, $-y$, $-z$.

3. Results and discussion

3.1. *Crystal structure*

CoGeTe is the second cobalt germanide telluride discovered in the Co–Ge–Te system, where 11 phases were known before. The crystal structure of CoGeTe is depicted in Fig. 2. Each cobalt atom is octahedrally coordinated by three germanium and three tellurium atoms, with Co–Ge and Co–Te distances of 2.385(3)–2.392(5) Å and 2.552(4)–2.602(3) Å (see Table 3), respectively, comparable to those observed in cobalt binary tellurides [14] and germanides [15]. X–M–X (X = Te and Ge) angles in CoGeTe, ranging from 79.8(1)° to 107.5(1)°, exhibit a significant deviation from the ideal octahedral geometry. When compared with the octahedra in binary tellurides such as $Co_{0.63}Te$ [16], the octahedra in CoGeTe are more distorted. In CoGeTe structure, one Ge–Ge edge of [$CoGe_3Te_3$] octahedron is shared with an adjacent [$CoGe_3Te_3$] octahedron, and all corners are shared with two other [$CoGe_3Te_3$] octahedra. The Co atoms across the shared Ge–Ge and shared corners are separated by of 2.823(4) Å and by 4.361(4) Å, respectively. The structure of the CoGeTe compound displays the presence of Ge–Te anion pairs with the distance of 2.713(3) Å, so a Ge–Te single bond can be supposed. Apart from this Ge–Te bond, each Ge and Te anion is also surrounded by three Co atoms showing distorted tetrahedral coordination.

The crystal structure of CoGeTe can be directly compared to that of PtSiSb which has been recently described by Wang et al. [17]. As suggested by Wang et al. [17], these structures can be derived from that of α-$NiAs_2$, which is also known as a mineral pararammelsbergite [18]. All compounds have the same space group (*Pbca*) and display a very similar structural arrangement. Fig. 2b depicts the linking of [$CoGe_3Te_3$] octahedra along the *c*-axis. Analogically to the PtSiSb, CoGeTe can be viewed as a ternary ordered variant of α-$NiAs_2$, which is transitional between the marcasite-type and the pyrite-type structures. The major difference displayed by these three structures is the way the octahedra are connected together. Whereas, in pyrite struc-

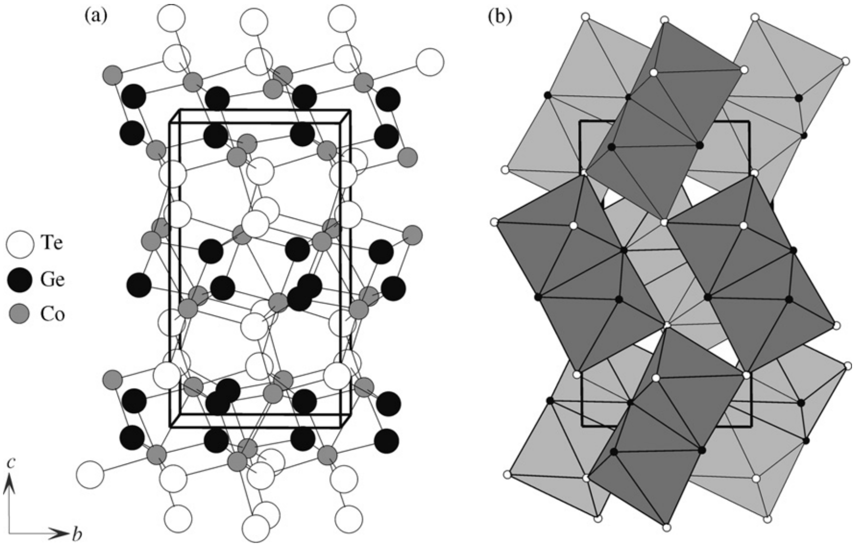

Fig. 2. Two representations of the CoGeTe structure: (a) ball and stick representation; (b) polyhedral representation showing the [$CoGe_3Te_3$] octahedra.

Table 4
Selected distortion parameters and Co–Co distance (Å) for CoGeTe compared with those for CoAsSe [21], CoSbS [19], CoPSe [21] and α-$NiAs_2$ [21]

	QE	OAV	Co–Co distance
CoGeTe	1.022	75.59	2.825(4)
CoAsSe	1.008	28.68	3.50(1)
CoSbS	1.010	26.46	3.350(2)
CoPSe	1.009	28.58	3.448(3)
α-$NiAs_2$	1.008	26.54	3.531(9)

OAV (octahedral angle variance) (°) = $\sum_{i=1}^{11}(\theta_i - 90)^2/11$ [22]; QE (quadratic elongation):=$\sum_{i=1}^{6}(d_i - d_0)^2/6$ (d_0 is the centre-to-vertex distance of a regular octahedron of the same volume) [22].

ture the octahedra share only corners, in marcasite structure they share both edges and corners, forming chains of linked octahedra. The CoGeTe structure is composed of layers of atoms perpendicular to the *c*-axis with stacking alternating between pyrite- and marcasite-type of blocks, as shown in Fig. 2b. In the CoGeTe structure, these alternating layers have every second marcasite-type layer in the reverse orientation. This arrangement has been described for the structure of PtSiSb and CoSbS by Wang et al. [17] and by Rowland et al. [19], respectively. Similarly to the PtSiSb, the centres of Co–Co pairs form a face centred cubic type arrangement elongated along *c*-axis.

An important feature present in CoGeTe is a short Co–Co distance across the shared edge of [$CoGe_3Te_3$] octahedra. The Co atoms are displaced from the centre of the octahedra towards each other, reducing the Co–Co distance to the value of 2.825(4) Å. This distance is somewhat longer than the Co–Co distance of 2.506 Å observed in elementary Co [20], but can be compared with the Pt–Pt distance of 2.8565(8) Å found in PtSiSb [17], which adopts also α-$NiAs_2$ type structure. The metal–metal distance of other α-$NiAs_2$-type compounds containing Co is significantly longer (see Table 4); the difference between the Co–Co distance in CoGeTe and that in CoAsSe [21] is more than 0.6 Å.

To assess the displacement of the metal atom from the centres of octahedra, we applied an approach of the so-called distortion parameters. Such distortion indices as octahedral angle variance and quadratic elongation [22] are commonly used to characterise the departure of an irregular octahedron from the ideal regular geometry. Table 4 shows octahedral angle variance, quadratic elongation and Co–Co distance of Co-bearing $NiAs_2$-type compounds. It is obvious that the [$CoGe_3Te_3$] octahedra are more deviated from their ideal geometry than octahedra in CoAsSe, CoSbS and CoPSe. This corresponds to the shortening of the Co–Co distance in CoGeTe, which, as a consequence, deforms the [$CoGe_3Te_3$] octahedron (more specifically, it lowers one of the angles of X–Co–X (X = Ge, As, Sb and P). Fig. 3 depicts both the contraction of the Co–Co distance and the deformation of the X–Co–X angle; moreover, it shows a comparison with CoAsSe and α-$NiAs_2$.

3.2. Differential thermal analysis

The DTA curve is reproduced in Fig. 4. The sharp endothermic peak at about 725 °C represents the incongruent melting of CoGeTe; it decomposes into GeTe (which is present in a liquid form), CoGe and $CoTe_2$. These phases were identified by XRD after heating the sample of CoGeTe in an evacuated silica glass tube at 750 °C and consequently rapid quenching to the room temperature.

3.3. Electrical conductivity

Very weak temperature dependence of the electrical conductivity of CoGeTe sample (see Fig. 5) and quite high value of the Seebeck coefficient at 300 K ($S_{300} \sim -180\,\mu V\,K^{-1}$) suggests semiconducting behaviour of the CoGeTe sample. The

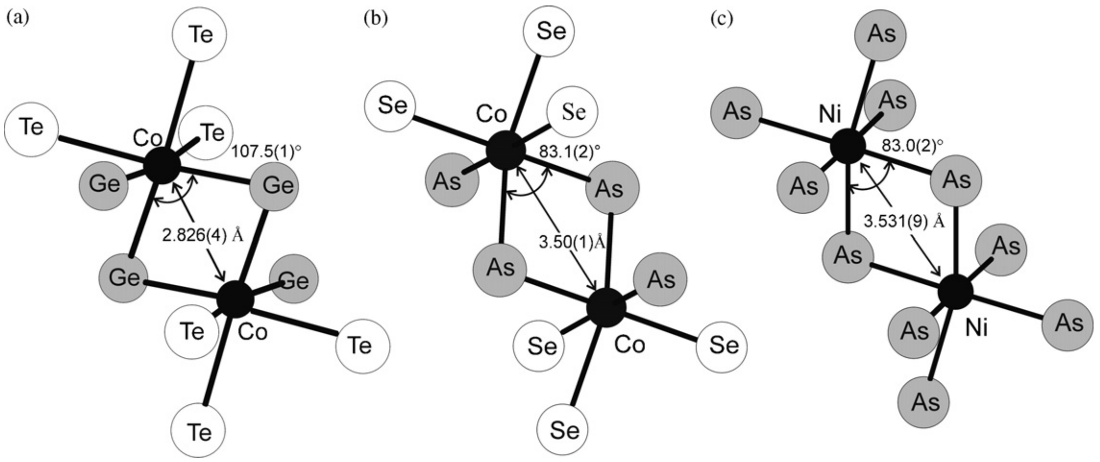

Fig. 3. Comparison of the edge-sharing octahedra in (a) CoGeTe; (b) CoAsSe [21]; (c) α-$NiAs_2$ [21].

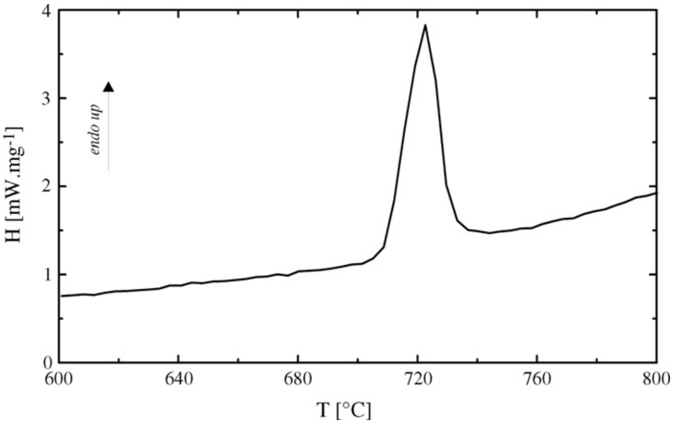

Fig. 4. Differential thermal curve for CoGeTe compound.

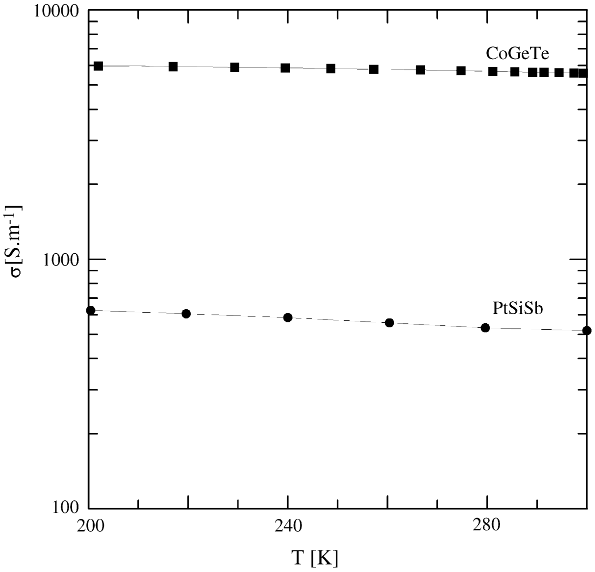

Fig. 5. Temperature dependence of the electrical conductivity of CoGeTe sample compared with the electrical conductivity of PtSiSb [17].

opinion is supported by comparing the above-mentioned dependence with the one for isostructural compound PtSiSb [17], which was considered also as semiconductor with small band gap ($E_g \sim 0.6$ eV).

4. Conclusion

To conclude, CoGeTe represents a ternary ordered variant of α-$NiAs_2$ structure, the most striking difference being the presence of metal–metal bonded pairs. As discussed in [17], with the exception of PtSiSb, all hitherto known α-$NiAs_2$ type compounds have 20 valence electrons per formula unit. As opposed to that, PtSiSb and CoGeTe have 19 valence electrons per formula unit. This change in number of electrons per formula unit is accompanied by creating one Co–Co bond formed to each Co atom. It might be revealing to study the development of metal–metal interaction depending on the continual change of the electron count, for instance, in the solid solution $Co_xNi_{1-x}GeTe$. This investigation is currently in progress. Other solid solutions derived from a different α-$NiAs_2$-type could be an interesting subject to further analyses.

Acknowledgements

This work was supported by the internal project of Czech Geological Survey (project number 3230) and by the Czech Science Foundation (project number 203/07/0267).

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