Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 981–989

PHASE EQUILIBRIA IN THE CdI_2–Bi_2O_3 SYSTEM

V. Vassilev[*], *V. Parvanova and L. Aljihmani*

University of Chemical Technology and Metallurgy, 8 Kliment Ohridski blvd.,1756 Sofia, Bulgaria

(Received December 9, 2003; in revised form June 1, 2004)

Abstract

The phase diagram of the system CdI_2–Bi_2O_3 is studied by means of X-ray diffraction, differential thermal analysis and measurements of the density of the material. As a result of the synthetic and peritectic interactions, two incongruently melting intermediate phases i.e. phase A – $CdI_2\cdot 2Bi_2O_3$ and phase B – $CdI_2\cdot 4Bi_2O_3$ (stable in the temperature interval 370–850°C) are formed.

The phase A exists in two polymorphic forms with a temperature of the phase transition $T_{\alpha\leftrightarrow\beta}$=320–370°C. The unit cell parameters at low temperature modification of α-$CdI_2\cdot 2Bi_2O_3$ were determined. (a=1.032 nm, b=1.046 nm, c=1.046 nm, α=115.02°, β=109.11° and γ=82.04°). The phases A and B have fields of homogeneity.

Keywords: phase diagram, phase equilibria, unit cell parameters

Introduction

The system CdI_2–Bi_2O_3 has not been studied in relation with the phases equilibria in it and with the possible formation of new crystalline or glassy phases. It is of scientific and practical interest because its building components CdI_2 and Bi_2O_3 (together or single) are included in the composition of the oxide, oxyhalide, chalco halide and oxyhalco halide glasses. The stability and the characteristics of these glasses depend to a great extent of the characters of the initial building and new (intermediate) compounds, which could be formed on their base.

The crystalline CdI_2 has a laminar structure [1] and depending on the used method three polymorphic forms exist, each of which has a hexagonal unit cell. For example, at the crystallization of water solutions at pressure 400 N m^{-2} unit cell parameters are a=0.424 nm and c=0.6835 nm [2].

Bi_2O_3 crystallizes in some polymorphic forms, two of which α (monoclinic) and δ (cubic-face centered) are stable and three, β (tetragonal), γ (cubic-body centered) and C-phase (cubic-primitive) are metastable [3]. The unit cell parameters in α-phase are a=0.58486 nm, b=0.8166 nm, c=0.75097 nm and β=113, in δ-phase – a=0.56595 nm.

---

[*] Author for correspondence: E-mail: venciv@uctm.edu.

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

CdI_2 and Bi_2O_3 introduced into the composition of different glasses affect their properties: physical, optical, thermal, electrical, etc. [4, 5]. CdI_2 is in the composition of solid electrolytes and ion-selective membranes [6], and Bi_2O_3 and Bi_2O_3-based crystals find application in the acousto-optics [7–9].

The main goal of this work is the investigation of the phase equilibria in the system CdI_2–Bi_2O_3 by means of the conventional differential thermal analysis (DTA) [10, 11], and X-ray powder diffraction (XRD) [12–14] as well as determining the limits of the solid solutions and the compositions of the intermediate phases (if such exist), thus building a base for a further complex investigation.

Experimental

The phase diagram of the system CdI_2–Bi_2O_3 has been studied by means of 17 compositions synthesized every 5 or 10 mol% Bi_2O_3 in a concentration interval from 0 to 100 mol% Bi_2O_3. CdI_2 and Bi_2O_3 of the Merck Company at a commercial product of p.a. grade purity have been used as initial components. Samples of the studied system have been obtained by a direct mono-temperature synthesis [15] at 500–850°C throughout 0.5–2.0 h depending on the Bi_2O_3 contents whereupon the melts were cooled to a room temperature in a furnace switched off regime. The samples were heat-treated under vacuum 0.133 Pa in quartz ampullas at 280±5° in the course of 240 h. XRD characteristics were used as a criterion for thermodynamic equilibrium reaching. The obtained samples were crystalline.

The phase transformations in the samples were investigated by means of several methods as follows: DTA (equipment of the system Paulik–Paulik–Erdey made by MOM, Hungary) at heating rate of 10°C min^{-1}; reference substance (calcinated γ-Al_2O_3) and the studied substance weighed 0.3 g and was placed in evacuated and sealed quartz ampoules at pressure equal to 0.1 Pa; XRD (equipment TUR-M61) with CuK_α radiation and Ni-filter, θ=5–40° and measurements of the density of the samples (hydrostatic technique with toluene as reference liquid [27]).

Results

The data obtained from the X-ray analyses of the sample in the system $(CdI_2)_{100-x}(Bi_2O_3)_x$, where $0\leq x\leq 100$ are summarized in the schematic diagram in Fig. 1. The X-ray data of the initial compounds CdI_2 and Bi_2O_3 coincide with that mentioned in literature, respectively [16] and [17].

Derivatograms were made of the samples of the studied systems in a heating regime. The DTA data are shown in Table 1.

The results of measuring the system $(CdI_2)_{100-x}\cdot(Bi_2O_3)_x$ samples at equilibrium density (the preciseness of d is ±5%) are shown in Fig. 2. The density values of the initial components CdI_2 and Bi_2O_3 are in appropriate correspondence with the literature values of 5.3 and 8.5 g cm^{-3}, respectively [6].

Table 1 Endothermal effect extremums during heating the samples of the CdI_2–Bi_2O_3 system

No.	Composition/mol%		Endothermal effect extremums/°C									
	CdI_2	Bi_2O_3	1	2	3	4	5	6	7	8	9	10
1	100	0										385
2	95	5	330									380
3	90	10	330									
4	80	20	325	380								535
5	75	25	330	375								600
6	70	30	325	380								680
7	66.7	33.3		375								720
8	60	40	330	380								750
9	50	50	330	375								795
10	40	60	330	380							855	855
11	33.3	66.7		370	370						860	920
12	30	70		350	350					845	860	955
13	25	75			320					845	860	945
14	20	80			320	375		815				935
15	10	90			320	375		770	835	845	860	860
16	5	95			320		720	790	835			835
17	0	100					720					830

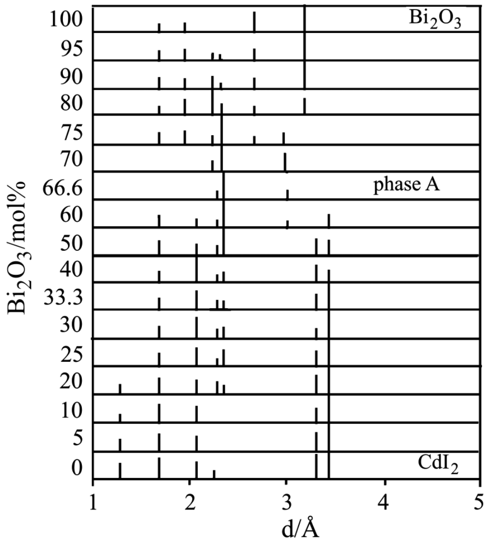

Fig. 1 A strich-diagram of the $(CdI_2)_{100-x}(Bi_2O_3)_x$ system

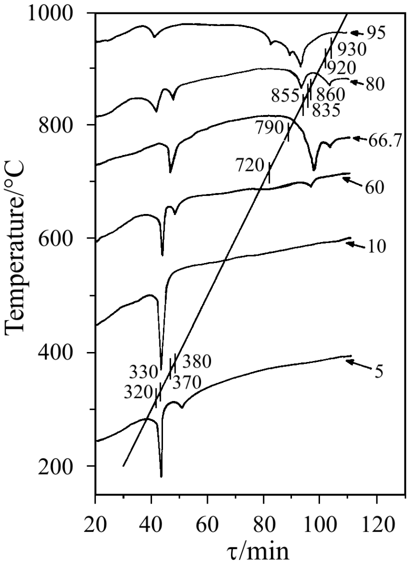

Fig. 2 DTA curves of the $(CdI_2)_{100-x}(Bi_2O_3)_x$ system

Some new lines appear in the diffraction pattern for the compositions (Fig. 1) containing between 20 and 95 mol% Bi_2O_3, which do not belong to the initial components CdI_2 and Bi_2O_3. They are related to the existence of a new (intermediate) phase A. When the contents of Bi_2O_3 in the alloys is increased from 20 to 60 mol% Bi2O3 the intensity (d_{040}=0.2375 nm and d_{410}=0.2338 nm) of the lines characteristic of the new phase A increases too, and the intensity of the lines characteristic of the compound CdI_2 is reduced (with x>60 these lines completely disappear). The sample received is one-phase at a component ratio CdI_2:Bi_2O_3=1:2, and some characteristic lines of the new phase A (Table 2) can be observed on the schematic diagram of the X-ray diffraction. What can also be observed in the concentration interval between 66.7 and 70 mol% Bi_2O_3 is a shift of the phase A lines towards reduction of the plane spacing, i.e. the existence of phase A-based solid solutions can be positively presumed. The presence of horizontal lines with T~380°C on the left of the composition for which

Table 2 Data from indexing of low-temperature phase α-CdI_2.2Bi_2O_3

No	d_{exp}/Å	100(I/I_{max})/%	$Q=1/d^2$	$h\,k\,l$	d_c/Å
1	9.703	27	0.0106	1 0 0	9.751
2	9.485	16	0.0111	0 1 0	9.478
3	9.076	4	0.0121	0 0 1	9.043
4	8.473	9	0.0139	$0\,\bar{1}\,1$	8.469
5	6.788	28	0.0217	$\bar{1}\,1\,0$, 1 1 0	6.797
6	5.528	3	0.0327	0 1 1	5.524
7	4.854	3	0.0424	2 0 0	4.876
8	3.398	18	0.0866	2 2 0	3.398
9	3.060	31	0.1068	$2\,3\,\bar{2}$	3.050
10	3.012	19	0.1102	0 0 3	3.014
11	2.803	7	0.1273	$\bar{1}\,2\,2$	2.795
12	2.507	4	0.1592	$3\,3\,\bar{3}$	2.508
13	2.375	100	0.1772	0 4 0	2.370
14	2.338	28	0.1830	4 1 0	2.361
15	2.329	30	0.1844	3 0 2	2.329
16	2.119	5	0.2227	2 4 0	2.131
17	2.089	5	0.2291	$1\,2\,\bar{5}$	2.073
18	1.997	4	0.2507	$5\,2\,\bar{2}$	1.997
19	1.936	4	0.2669	$5\,2\,\bar{1}$	1.936
20	1.819	7	0.3023	$\bar{3}\,4\,1$	1.819
21	1.712	11	0.3412	$\bar{1}\,5\,1$	1.712
22	1.671	6	0.3581	$3\,\bar{5}\,1$	1.670
23	1.528	4	0.4281	4 3 2	1.528
24	1.477	12	0.4581	$5\,\bar{1}\,3$	1.478
25	1.391	6	0.5171	5 1 3	1.394
26	1.332	6	0.5633	$5\,\bar{2}\,4$	1.332
27	1.328	5	0.5669	$5\,\bar{1}\,4$	1.328

x=66.7 mol% Bi_2O_3 and with T~320°C on the right x=75 mol% Bi_2O_3 is proving the existence of two polymorphic forms of the intermediate compound A (α-A and ß-A). The crossing of these horizontal lines for a second time indicates the existence of a range of homogeneity of the phase A. Upon X-rays analyses the lines of both the initial Bi_2O_3 and the transitional phase A can be observed between 75 and 90 mol% Bi_2O_3 whereas with increasing the contents of Bi_2O_3 in the samples, the intensity of the Bi_2O_3 lines increases too, and the intensity of CdI_2 decreases. The peculiarities observed in the diffraction pattern for the system CdI_2–Bi_2O_3 give us reasons to assume that the most likely composition of the new phase A is $CdI_2{\cdot}2Bi_2O_3$. The unit-cell parameters at low temperature modification of $CdI_2{\cdot}2Bi_2O_3$ (α-$CdI_2{\cdot}2Bi_2O_3$) are determined by the Ito method [18]: a=1.032 nm, b=1.046 nm and c=1.046 nm; α=115.02°, β=109.11° and γ=82.04°. The X-ray data of this phase is presented in Table 2. All diffraction patterns were taken into account when determining the unit cell parameters of α-$CdI_2{\cdot}2Bi_2O_3$, and on Fig. 1 only the strong patterns were marked.

The endothermal effect at 330°C (column 1 of Table 1) observed with the compositions containing up to 60 mol% Bi_2O_3 is most likely due to the appearance of a liquid phase and corresponds to the temperature of the eutectic equilibrium $L \xleftrightarrow{330℃} CdI_2+\beta\text{-}A$.

The other two endothermal effects are well represented as the first one does not depend on the composition (at T≈380°C, column 2 of Table 1) and this is more likely due to the reversible polymorphic transition of the hypothetical new phase A. The temperature of the second effect (column 10 of Table 1) is strongly dependent on the alloys composition and corresponds to the temperature of the liquidus line.

A series of non-variant equilibria have been registered in the high temperature field with compositions rich in Bi_2O_3 that are most probably connected with the polymorphism of Bi_2O_3 and the current heterogeneous interactions. As a result of the interactions two transitional phases are formed one of which (phase A) was already mentioned during the analysis of the X-ray diffraction results. Obtaining more than one intermediate phase with variable compositions, varying in wide concentration limits, some of which do not exist at a room temperature, seems to be typical of the binary systems having Bi_2O_3 as a component. In most of the cases intermediate phases are obtained by means of peritectic and peritectoidal, eutectic and eutectoidal, synthectic and other reactions and melt mainly incongruently or decompose over the solid phase [8, 19–24].

The effects at 860°C (column 9 of Table 1) are most probably connected to the syntactic interaction resulting in the formation of the intermediate phase A $CdI_2{\cdot}2Bi_2O_3$) $L_1+L_2 \xleftrightarrow{860℃} \beta\text{-}A$, which is evidenced by the reduction of these endoeffects area on the left and the right side of the point corresponding to composition x=66.7 mol% Bi_2O_3.

Thermoeffects outlining the binodal curve over this balance are very slight. At 845°C a peritectic reaction takes place as a result of which second intermediate phase B is generated with expected composition $CdI_2{\cdot}4Bi_2O_3$ ($\beta\text{-}A+L \xleftrightarrow{845℃} B$). At 835°C (column 7 of Table 1) a second peritectic reaction takes place under the $B+L \xleftrightarrow{835℃} \delta\text{-}Bi_2O_3$ (s. s.) diagram. As a rule solid solutions of the base δ-Bi_2O_3 are formed by a certain non-variant reaction: peritectic – as is the case, and also literature [19], eutectic [25], eutectoidal [20, 21, 26], etc. Other authors [19, 22–24, 28] also refer to a similar phase with such features in the system Bi_2O_3–TeO_2. As the borders of these intermediate phase B are localized with 4 points only, its contours are outlined with a dotted line. The phase B is stable in the temperature interval 375–845°C. At 375°C it decomposes in a eutectoidal reaction: $B\xleftrightarrow{375℃}\beta\text{-}A+\alpha\text{-}Bi_2O_3$. At 720°C it is reasonable that a second eutectoidal equilibrium of the type exists (degenerated eutectoide shown on Fig. 3 in the circle): $\delta\text{-}Bi_2O_3\xleftrightarrow{720℃}B+\alpha\text{-}Bi_2O_3$. It is worth noting that in the concentration interval between 65 and 75 mol% Bi_2O_3 (in the low temperature field of the system) the temperature of the polymorphic transition of the intermediate phase depends on the composition (columns 2 and 3 of Table 1), i.e. this phase has asymmetrical field of homogeneity facing the side rich in Bi_2O_3 that narrows to 0 mol% Bi_2O_3 when the temperature rises to T=860°C. This phase is to be written as $CdI_2(2+\Delta)Bi_2O_3$ $(0\leq \Delta \leq 1)$ at room temperature.

The complex physical-chemical interactions taking place in liquid and solid-state lead to the formation of intermediate phases $CdI_2{\cdot}2Bi_2O_3$ and $CdI_2{\cdot}4Bi_2O_3$, as well as to the non-linear progress of the dependency d(x) within the limits from 0 to 66.7 and from 75 to 100 mol% Bi_2O_3. The characteristic feature observed with x=66.7 (Fig. 2) confirms the hypothesis that an intermediate phase (phase A) is $CdI_2{\cdot}2Bi_2O_3$.

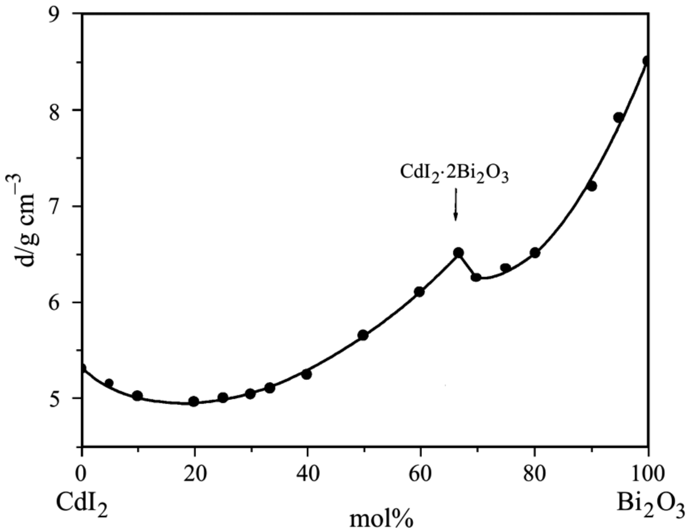

Fig. 3 Dependence $d(x)$ for samples of the $(CdI_2)_{100-x}(Bi_2O_3)_x$ system

On the base of the data of DTA, X-ray diffraction and the measurement of density a phase diagram of the system CdI_2–Bi_2O_3 is studied Fig. 3.

The phase diagram of the system CdI_2–Bi_2O_3 has a complex type and it is characterized with the following features:

1. Six non-variant equilibria exist: one of them is eutectic at 330°C, one-synthetic at 860°C, two-peritectic respectively at 845 and 835°C and two-eutectoidal, respectively, at 720 and 375°C.

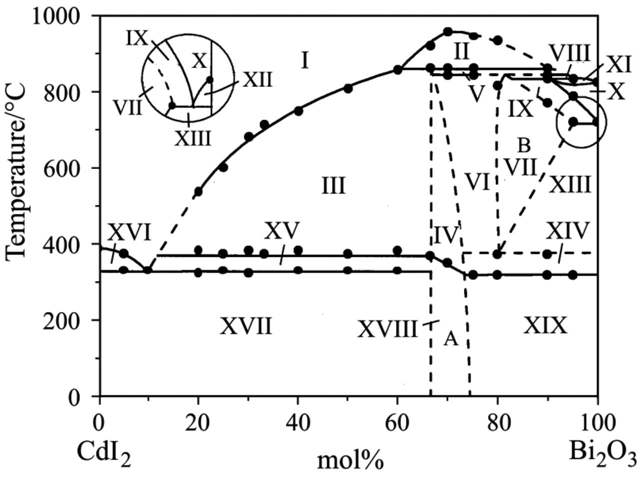

Fig. 4 Phase diagram of the CdI_2–Bi_2O_3 system. I – Liquid (melt-L); II – L_1+L_2; III – L+β-$CdI_2\cdot 2Bi_2O_3$; IV – β-$CdI_2\cdot 2Bi_2O_3$ (phase β-A); V – β-$CdI_2\cdot 2Bi_2O_3$+L; VI – β-$CdI_2\cdot 2Bi_2O_3$+$CdI_2\cdot 4Bi_2O_3$; VII – $CdI_2\cdot 4Bi_2O_3$ (phase B); VIII – $CdI_2\cdot 4Bi_2O_3$+L; IX – $CdI_2\cdot 4Bi_2O_3$+δ-Bi_2O_3; X– δ-Bi_2O_3; XI – L+δ-Bi_2O_3; XII– δ-Bi_2O_3+α-Bi_2O_3; XIII – $CdI_2\cdot 4Bi_2O_3$+α-Bi_2O_3; XIV – CdI_2+L; XV – L+α-$CdI_2\cdot 2Bi_2O_3$; XVI – β-$CdI_2\cdot 2Bi_2O_3$+α-Bi_2O_3; XVII – CdI_2+α-$CdI_2\cdot 2Bi_2O_3$; XVIII – α-$CdI_2\cdot 2Bi_2O_3$ (phase α-A); XIX – α-$CdI_2\cdot 2Bi_2O_3$+α-Bi_2O_3

2. Two new phases with changeable composition are formed in the system. The first one is with composition $CdI_2(2+\Delta)Bi_2O_3$, where $0\leq\Delta\leq1$. It exists in two polymorphic forms $\alpha \xleftrightarrow{320-380^\circ C} \beta$ and melts incongruently at 860±5°C. The other is in the range rich of Bi_2O_3. It melts incongruently at 845±5°C and exists from 375 to 845°C.

Conclusions

By the means of three independent methods the diagram of the system CdI_2–Bi_2O_3 is constructed (Fig. 4). As a result of complex physico-chemical processes in solid and liquid-state, two intermediate phases with compositions $CdI_2\cdot 2Bi_2O_3$ (phase A) and $CdI_2\cdot 4Bi_2O_3$ (phase B) are formed. They together with the initial compounds CdI_2 and Bi_2O_3, polymorphism of Bi_2O_3 and phase A form 19 phase fields, five of which are mono-phasic (I, IV, VII, X and XVIII) and the rest of them – two-phasic.

* * *

The authors acknowledge thankfully the financial support for this work from the Ministry of Education and Science (Fond ‘Scientific investigations’ – contract TN-1102).

References

1 A. S. Oworkin, D. J. Sasmor and E. R.V. an Artsdalen, J. Amer. Chem. Soc., 77 (1955) 1304.
2 R. F. Rolsen, Iodnie metallai i iodidai metallov, Metallurgia, Moskow (1968) (in Russian).
3 M. Tsubaki and K. Koto, Mat. Res. Bull., 19 (1984) 1613.
4 Z. G. Ivanova, V. S. Vassilev, S. V. Boycheva and N. Kirov, J. Non-Cryst. Solids, 232–234 (1998) 274.
5 V. S. Vassilev, Z. G. Ivanova, E. S. Dospeiska and S. V. Boycheva, J. Phys. Chem. Solids, 63 (2002) 815.
6 Yu. G. Vlasov, M. S. Miloshova, R. Avila Moreno, E. A. Bychkov and P. P. Antonov, Radiokhimia, 30 (1988) 95 (in Russian).
7 V. V. Kucha, A. V. Homich, V. A. Kravchenko and P. I. Perov, Izv. AN SSSR Neorg. Mater., 20 (1984) 314 (in Russian).
8 P. Schmidt, O. Bosholm and H. Oppermann, Z. Naturforsch., 52b (1997) 1461.
9 E. V. Siniakov, V. F. Katkov and Yu. G. Osetskii, Izv. AN SSSR Neorg. Mater., 16 (1980) 136 (in Russian).
10 A. Wojakowska, E. Krzyzak and A. Wojakowski, J. Therm. Anal. Cal., 65 (2001) 491.
11 M. Hichri, C. Favotto, H. Zamali, Y. Feutelais, B. Legendre, A. Sebaoun and M. Jemal, J. Therm. Anal. Cal., 69 (2002) 509.
12 E. Filipek, J. Therm. Anal. Cal., 56 (1999) 159.
13 T. Hashimoto, M. Yoshinaga, Y. Ueda, K. Komazaki, K. Acaoka and S. Wang, J. Therm. Anal. Cal., 69 (2002) 909.
14 E. Aragon and A. Sebaoun, J. Therm. Anal. Cal., 52 (1998) 523.
15 Z. Boncheva-Mladenova and V. S. Vassilev, Himia i Fizikohimia na Poluprovodnikovite Materiali, Narodna Prosveta, Sofia 1991, p. 180 (in Bulgarian).
16 American Society of Testing Materials, Philadelphia, 1969, ASTM 3-0470.
17 American Society of Testing Materials, Philadelphia, 1969, ASTM 27-53.
18 T. Ito, X-ray studies on polymorphism, Maruzen Co. Ltd., Tokyo 1950, p. 187.
19 L. A. Demina, V. A. Dolgih, V. A. Popovkin and A. V. Novoselova, Dokl. AN SSSR, 224 (1979) 94 (in Russian).
20 A. V. Shevchuk, V. M. Skorikov, Iu. F. Kargin and V. V. Konstantinov, J. Neorg. Chim., 30 (1985) 1519 (in Russian).
21 A. V. Shtenev, V. M. Skorikov and Yu. F. Kargin J. Neorg. Chim., 33 (1988) 721 (in Russian).
22 H. Oppermann, H. Göbel, H. Schadow, V. Vassilev and I. Markova-Deneva, Z. Anorg. Allg. Chem., 622 (1996) 2115.
23 H. Oppermann, H. Göbel, H. Schadow, P. Schmid, C. Hennig, V. Vassilev and I. Markova-Deneva, Z. Naturforsch, 54b (1999) 239.
24 H. Oppermann, H. Göbel, P. Schmid H. Schadow, V. Vassilev and I. Markova-Deneva, Z. Naturforsch., 54b (1999) 261.
25 F. V. Kalinchenko, M. P. Boraenkova and A. V. Novoselova, J. Neorg, Chim., 28 (1983) 2351 (in Russian).
26 B. Z. Nurgaliev, T. F. Vasekina, A. E. Baron, V. A. Popovkin and A. V. Novoselova, J. Neorg, Chim., 28 (1983) 735 (in Russian).
27 E. Bonshtedt-Kupletskaya, Opredelenie plotnosti mineralov, Nauka, Moscow 1963 (in Russian)
28 P. Schmid and H. Oppermann, Z. Anorg. Allg. Chem., 623 (1997) 174.