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Interaction Between PbF_2 and EuS in Saline Melt NaCl-KCl

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Ability to interaction between PbF_2 and EuS in NaCl-KCl saline melt is established by methods of luminescent spectroscopy and the X-ray diffraction analysis. Mutual quenching of intensive blue luminescence of Eu^{2+} and, partially, of yellow luminescence of PbF_2 in the solidified solutions-melts on the basis of NaCl-KCl is observed, that confirms exchange reaction with formation of PbS particles. Formation of abnormal phases "NaCl" and "KCl" with the changed parameters of lattices, and also of PbFCl phase is revealed, and also possibility of occurring phases of PbS, β - PbF_2 and NaF in separate specimens is not excluded.

Keywords: Saline melt, Dissolution, Lead sulfide, Fluorides, Interaction.

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I. Theoretical part

Zero-dimensional nanoparcticles ("quantum dots") of metal chalcogenides (CdS, PbS, etc.) find wide application as materials for light-emitting diodes, solar batteries, bio-labels and in other areas, techniques etc. [1, 2]. Basically, they are obtained in aqueous solutions and non-aqueous water systems with participation of stabilizers of the various nature. Studying of possibility of synthesis of quantum dots of metals chalcogenides, in particular PbS, in saline melts with their subsequent stabilisation at crystallisation it is our interest.

The mechanism of PbS quantum dots (QDs) formation in saline melts by dissolution of individual compound, probably, we realise with great difficulty. By the preliminary thermodynamic estimates spent according to the concept [3-6] developed by us, its solubility in molten NaCl-KCl at 700°C (973 K) is rather low - an order of 10^{-3} % mol. That doesn't allow to reach necessary values of supersaturation for massive nucleation only due to a temperature gradient (so, solubilities) at crystallisation of melt. This problem can be solved by realisation of chemical interaction (for example, exchange reaction) between compounds with much higher values of solubility or almost entirely dissolved in saline melts. In particular, those PbF_2 and EuS which solubility in NaCl-KCl melt at 700°C, according to calculations, comprises 12.1 and 0.45 mol.%, accordingly [4, 5].

According to the offered concept, the dissolution mechanism consists in course of exchange reactions between dissolved substance and most acidic component of saline melt, in this case, NaCl:

$$PbF_2 + 2NaCl \leftrightarrow PbCl_2 + 2NaF, \tag{1}$$

$$EuS + 2NaCl \leftrightarrow EuCl_2 + Na_2S, \tag{2}$$

whereby are formed compounds having ions common with the melt. Secondary processes of complexion, for example, are possible as well:

$$2KCl + EuCl_2 \leftrightarrow K_2[EuCl_4], \tag{3}$$

and

$$PbCl_2 + PbF_2 \leftrightarrow 2[PbF]Cl, \tag{4}$$

Last of compound remains in an invariable kind in the course of crystallisation of the melt [4, 7].

A preliminary thermodynamic estimation of possibility of course of exchange reaction under the scheme:

$$PbF_2 + EuS \leftrightarrow PbS + EuF_2 \tag{5}$$

by means of the approximate equation

$$\Delta G^0_T \approx \Delta H^0_{298} - T\Delta S^0_{298}, \tag{6}$$

under condition of T = 973 K results in value Δ = -170 kJ/mol, i.e. reaction is quite possible. Thus, it is possible to hope for its successful course not only in a solid-state, but also in saline melt.

II. Experimental part

For reception of saturated solution-melt of EuS it is carried out by annealing (~2 hours)in the vertical furnace of surplus of dissolved substance with molten salt at 700°C in ceramic (Al_2O_3) crucible in the inert gas (helium) for prevention of oxidation and hydrolysis of the sample. In case of PbF_2 the quantity of dissolved substance is taken by such that it completely, without the rest has passed in solution (in this case its content comprised 7.6 wt. %, or 3.0 mol. %). Thus, one of reagents, PbF_2 is taken with considerable extent (~ in 6.67 times) in comparison with another one, i.e. EuS.

Initial reagents are received in a various ways. Europium(II) sulphide is synthesised from elemental europium and sulphur of high cleanliness in the two-zone evacuated reactor made of quartz glass in specially picked up mode of heating [5]. Lead fluoride has been received in JV "New materials and technologies" (Odessa) by fluorination of $PbCO_3$ with NH_4F and the subsequent meltdown in the graphite reactor placed in the induction furnace of heating. Salts (NaCl, KCl) of high cleanliness before use were melted in the inert medium at 700°C, and then alloyed in the reactor from quartz glass in a stoichiometric parity (1:1). In solidified saline melt in case of solution of EuS in NaCl-KCl the ground part (non - dissolved part EuS of black colour), and the top part of a purely white, with a bluish shade solution-melt are accurately divided. In case of solidified solution-melt of PbF_2 in NaCl-KCl the ground part is not identified, all samples have white colouring (without a blue shade). For interaction studying between solutions PbF_2 and EuS in NaCl-KCl saline melt samples of individual solutions of substances were mixed in equal proportions on weight and melted together in the inert medium at the same temperature.

The received systems are analyzed by methods of the X-ray diffraction analysis (XRD) and of luminescent spectroscopy.

The X-ray diffraction measurements were carried out at a laboratory Bragg-Brentano diffractometer (X΄Pert Pro Alpha1 MPD, Panalytical) equipped with Cu X-ray tube, a monochromator and position-sensitive linear detector. The measurements were done at the temperature of 24(2)ºC. For determination of lattice parameters of the component phases, the Le Bail method was chosen [8].

Luminescence spectra were recorded on automated diffraction spectrometer SDL-1 with photo – multiplier FEU-79 in the interval of 400-700 nm. A luminescence was exited by mercury lamp DRS-250, with extraction of UV - radiation by optical filter UFS-2.

At grinding of solidified solution-melt of EuS rather appreciable smell of hydrogen sulphide that is indirect acknowledgement of presence of Na_2S was felt, so, confirming course of reaction (2) at dissolution of europium sulphide in saline melt. It was not observed at all in a case of sample of PbF_2 in system NaCl-KCl. It is necessary to notice that rather weak (hardly notable) smell was felt at grinding of mixes of PbF_2 and EuS in saline system. The last testifies to sharp reduction of Na_2S content after their interaction.

The sample of solidified solution-melt of PbF_2 in system NaCl-KCl exhibits an appreciable luminescence (yellow colour), and the spectrum of a luminescence

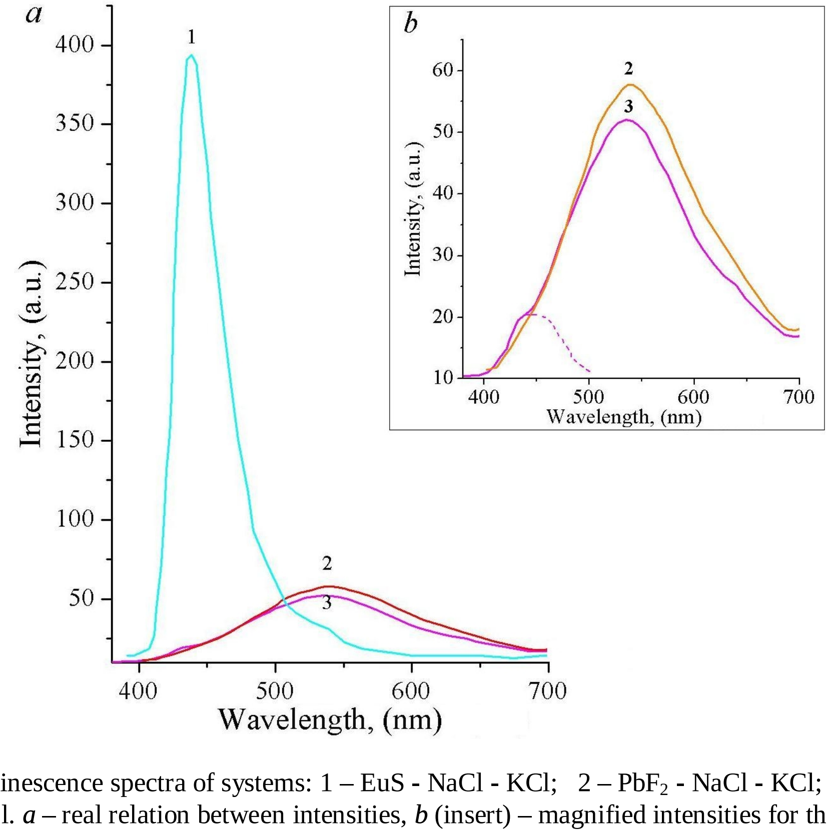

Fig. 1. The luminescence spectra of systems: 1 – EuS - NaCl - KCl; 2 – PbF_2 - NaCl - KCl; 3 – EuS - PbF_2 - NaCl – KCl. *a* – real relation between intensities, *b* (insert) – magnified intensities for the curves 2, 3.

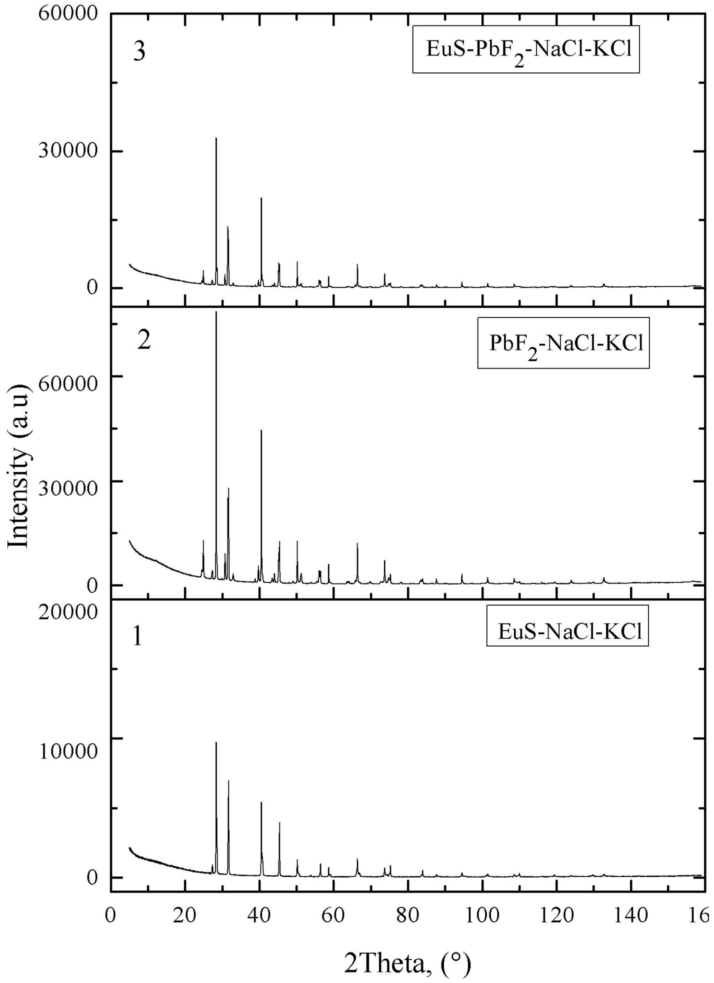

Fig. 2. X-ray diffraction spectra of systems: 1 – EuS - NaCl - KCl; 2 – PbF_2 - NaCl - KCl; 3 – EuS - PbF_2 - NaCl – KCl.

looks like rather wide unstructured band with a maximum at 540 nm.

The essence of electronic transitions in PbFCl (the basic product of interaction), responsible for a luminescence, up to the end is not found out.

Solidified saline solution of EuS in system NaCl-KCl exhibits a high-intensity luminescence of blue colour with a maximum at 435-440 nm (fig.1*b*), at that time initial EuS at all does not reveal luminescent properties (as, however PbF_2). It is shown that it is caused by 5*d* - 4*f* electronic transitions in Eu^{2+} ions [9].

Character of a luminescence and spectrum of a luminescence of saline melt, containing products of interaction PbF_2 and EuS, changes itself in comparison with those for a solution of pure PbF_2 a little, namely: intensity of a yellow luminescence considerably decreases, and in a luminescence an additional lilac tone reveals.

At the same time almost completely disappears an intensive blue luminescence, peculiar for solidified melt of EuS in NaCl-KCl. Character of the luminescence spectrum, is similar to that for solidified melt of PbF_2 in NaCl-KCl. However, intensity of bands slightly becomes lower (fig.1,*a*, a curve 2); feature of a spectrum is the shoulder in the field of 440 nm, probably, due to presence of the rests of Eu(II) compounds exhibiting a luminescence described above.

All specified features, probably, reflect interaction between components of both saline melts which can be presented by the scheme:

$$PbFCl + NaF + Na_2S + K_2[EuCl_4] \rightarrow$$

$$PbS\downarrow + EuF_2\downarrow + 3NaCl + 2KCl, \qquad (7)$$

As a result of reaction content of PbFCl should decrease, and as a sequence, intensity of its luminescence should fall. Thus practically final fracture of complex Eu(II) chloride with transformation in EuF_2 should result quenching of an intensive blue luminescence of Eu^{2+} ions (EuF_2 as well as EuS does not exhibit luminescence [8]).

Interaction course in saline solutions-melts proves to be true due to XRD analysis data. At consideration of diffractogram (fig. 2) of the solidified melts attracts attention presence of Europium sulphide and lead fluoride in the melts were not found. In enough presence of phases of NaCl and KCl with much altered, in comparison with the standard, parameters of a crystal lattices (tab.1). Really, "abnormal" phases of NaCl and KCl (are designated as "NaCl" and "KCl", accordingly), essentially different in parameters of lattices from standard values, are, as a matter of fact, the rests of the solid solutions which chemical composition can be written down in the form of $Na_{1-x}K_xCl$ and $K_{1-x}Na_xCl$.

For the clear reasons parameters of the first of them are higher, and the second - lower in comparison with standard values (tab.1).

Table 1

Crystallographic parameters of the initial materials and products of their interaction (XRD analysis data)

System	Phase composition	Syngony, space group	Parameters of the cell, Å		Chemical formula	Value of x
			Experimental	Standard (PDF No)		
PbF_2-NaCl-KCl	NaCl	*cub.*Fm3m	a=5.6431	(05-0628) a=5.6402	$Na_{1-x}K_xCl$	0.005
	"NaCl"	*cub.*Fm3m	a=5.6694	(05-0628) a=5.6402	$Na_{1-x}K_xCl$	0.045
	KCl	*cub.* Fm3m	a=6.2912	(41-1476) a=6.2917	~KCl	—
	"KCl"	*cub.* Fm3m	a=6.2720	(41-1476) a=6.2917	$K_{1-x}Na_xCl$	0.030
	PbFCl	*tetragon.* P4/nmm	a=b=4.1092, c=7.2435	(26-0311) a=b=4.1104 c=7.2325	PbFCl	—
EuS-NaCl-KCl	NaCl	*cub.* Fm3m	a=5.6422	(05-0628) a=5.6402	$Na_{1-x}K_xCl$	0.003
	"NaCl"	*cub.* Fm3m	a=5.6587	(05-0628) a=5.6402	$Na_{1-x}K_xCl$	0.028
	KCl	*cub.* Fm3m	a=6.2909	(41-1476) a=6.2917	$K_{1-x}Na_xCl$	0.001
	"KCl"	*cub.* Fm3m	a=6.2523	(41-1476) a=6.2917	$K_{1-x}Na_xCl$	0.060
PbF_2-EuS-NaCl-KCl	NaCl	*cub.* Fm3m	a=5.6432	(05-0628) a=5.6402	$Na_{1-x}K_xCl$	0.005
	"NaCl"	*cub.* Fm3m	a=5.6695	(05-0628) a=5.6402	$Na_{1-x}K_xCl$	0.045
	KCl	*cub.* Fm3m	a=6.2917	(41-1476) a=6.2917	~KCl	—
	"KCl"	*cub.* Fm3m	a=6.2474	(41-1476) a=6.2917	$K_{1-x}Na_xCl$	0.068
	PbFCl	*tetragon.* P4/nmm	a=b = 4.1102, c = 7.2404	(26-0311) a=b=4.1104 c=7.2325	PbFCl	—
	PbS	*cub.* Fm3m	a=5,936 (?)	(05-0592) a=5.9362		

Using the well-known Vegard law:

$$a_i = a_1 (1–x) + a_2x, \qquad (8)$$

where x – molar part of an impurity, a_i, a_1, a_2 - parameters of a cubic structure of, accordingly, a solid solution and its components, it is possible to calculate a chemical composition of phases easily.

As appears from the data resulted in tab.1, values of x comprise of an order of 0.03-0.07, or 3-7 mol. %. Thus, in case of system EuS-NaCl-KCl value of x for "KCl" considerably (more than in 2 times) exceed those for "NaCl" that corresponds to a parity of extents of the limited solid solutions in the field of the disintegration beginning below low 500°C. It, probably, is connected with rather low solubility of EuS in molten system NaCl - KCl and, hence, weak influence of the dissolved substance on character of phase equilibriums in system. In system PbF_2-NaCl-KCl the return parity, i.e. value of x for a phase "NaCl" is higher, than for "KCl", is observed.

Obviously, well soluble in molten NaCl - KCl compound PbF_2, makes essential impact on equilibrium in salt system, in particular, on parity NaCl : KCl, considerably reducing content of NaCl due to reaction (1). It, undoubtedly, affects solubility of components in solid state as well. System PbF_2-EuS-NaCl-KCl in this plan is intermediate, namely: a parity of x is about the same as in case of system EuS-NaCl-KCl, but nevertheless is slightly lower. This fact is caused by some reduction of influence of PbF_2 on the composition of saline melt because of its dilution and interaction of components.

As to products of exchange reactions between dissolved substances with saline melt, predictably, on diffractogram of systems with participation of PbF_2 (fig. 2) reflexes of PbFCl are most accurately expressed as well. It is necessary to notice that parameters of a lattice of this phase considerably are a little higher in comparison with the standard values (tab. 1) that probably, is caused by some deviation of its composition from stoichiometry aside $PbCl_2$.

Unfortunately, in case of system EuS-NaCl-KCl it was not possible by means of XRD analysis to find out and moreover, to identify products of interaction of EuS with saline melt, probably, owing to their very insignificant contents.

The question of identification of phase of PbS in products of interaction of saline solutions-melts of PbF_2

and EuS is principal. On its presence specifies (truly, not so convincing) the weak peak on diffractogram of solidified melt of system at 2θ = 26.04° that practically coincides with the standard value. However, absence or insufficient intensity of other peaks on diffractogram, corresponding to the given phase, does not allow to treat unequivocally given result and the more so to calculate exact value of parameter of its lattice. As to other products, some of undisclosed diffraction peaks for systems comprised of PbF_2 and NaCl-KCl, should be presumably attributed to NaF and β - PbF_2 both of cubic syngony as well.

Conclusions

1. Interaction at dissolution of PbF_2, EuS with system NaCl-KCl, and also exchange reactions between the dissolved substances are investigated.

2. Solidified melt of solution of EuS in NaCl-KCl exhibits the intensive blue luminescence caused by 5*s* → 4*f* electronic transitions in Eu^{2+} ions. The nature of a yellow luminescence in solidifies melt of PbF_2 in NaCl-KCl is not established. Interaction between two systems results in quenching of a blue luminescence practically to zero.

3. In saline systems phases of NaCl, KCl, and also solid solutions on their basis which structure depends on the nature of dissolved substances, and also phase PbFCl are identified. Presence of separate reflexes on diffractograms of solidified melts specify in possibility of formation NaF, β - PbF_2 (in case of systems with PbF_2), and also PbS (as product of interaction between systems).

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[1] V. Gribachev, Komponenty i tehnologii 9, 127 (2009).
[2] Ch. Pul-ml, F. Oujens, Nanotehnologii (Tehnosfera, Moskva, 2009).
[3] S.O. Tarasenko, V.F. Zinchenko, A.O. Omel'chuk, S.V. Dev'jatkin, Spec. Vipusk Naukovogo visnika Chernivec'kogo universitetu (himichni nauki) 134 (2008).
[4] S.O. Tarasenko, V.F. Zinchenko, Є.V. Timuhin, Є.O. Zhiharєva, I.P. Kovalevs'ka, Ukraïns'kij himichnij zhurnal 74(2), 71 (2008).
[5] V.F. Zinchenko, S.A. Pavlinchuk, S.B. Meshkova, Z.M. Topilova. Rasplavy 6, 35 (2013).
[6] V.F. Zinchenko, E.V. Timuhin, S.A. Pavlinchuk, A.V. Nechiporenko, L.V. Sadkovskaja Jelektrohimija. 48(10), 1100 (2012).
[7] V.F. Zinchenko, E.V. Timuhin, S.A. Tarasenko, I.P. Kovalevskaja. Rasplavy 6, 86 (2007).
[8] J. Rodriguez-Carvajal, Newslett. IUCr Commission Powd. Diffr. 26, 12 (2001).
[9] P. Dorenbos. J. Luminescence 104, 239 (2003).

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Взаємодія між PbF_2 і EuS у сольовому розтопі NaCl-KCl

Здатність до взаємодії між PbF_2 і EuS у сольовому розтопі NaCl-KCl була встановлена методами люмінесцентної спектроскопії та рентгенівського фазового аналізу. Спостерігається взаємне гасіння синьої люмінесценції Eu^{2+} і, частково, жовтої люмінесценції PbF_2 у застиглих розчинах-розтопах на основі NaCl-KCl, що є відображенням обмінної реакції з утворенням часток PbS. Виявлено утворення аномальних фаз "NaCl" і "KCl" зі зміненими параметрами ґраток, а також можливість присутності фаз PbS, β – PbF_2 і NaF в окремих плавах.

Ключові слова: сольовий розтоп, розчинення, сульфіди, фториди, взаємодія.