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MELTS OF
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CRYSTALLOGRAPHY

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Abstract**Full Text**

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ON THE SOLUBILITY OF YTTRIUM ALUMINATES AND GALLATES CONTAINING NEODYMIUM IN MELTS OF $\text{PbF}_2 \cdot 1.17\text{PbO} \cdot 0.35\text{B}_2\text{O}_3$ *(Presented by Academician N. V. Belov, July 17, 1969)*

The use of thermal analysis for the study of systems containing components with high melting temperatures is associated with great experimental difficulties. However, by using melts of inorganic compounds capable of dissolving various refractory substances, it is possible to melt such mixtures at considerably lower temperatures. In this case the mechanism of the processes taking place proves to be similar to the mechanism of salt equilibria in saturated aqueous solutions^{1,2}.

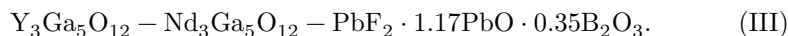
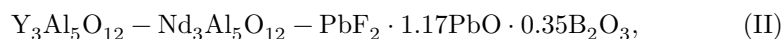
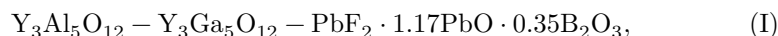
The analogy between the properties of solutions in melts of polar inorganic compounds and the properties of aqueous solutions of salts makes it possible to apply the solubility method to the investigation of refractory systems, since replacement of the solvent cannot introduce any fundamental changes into the calculation procedure. Accordingly, it becomes possible to determine graphically the compositions of the solid phases forming in the systems. Thus, the solubility method makes it possible to explain the mechanism of the processes of joint crystallization of a complex assemblage of refractory substances at temperatures lower than the melting temperatures of the initial components of the systems under study.

In the present work the solubility method was applied to determine the conditions for isomorphous substitution of aluminum by gallium and yttrium by neodymium during crystallization of yttrium-aluminum and yttrium-gallium garnets from a mixture of the corresponding oxides.

It is known that lead oxide and fluoride, lead oxide with an addition of boric anhydride, and also lead oxide and fluoride and boric anhydride are used very successfully as solvents for refractory oxides of rare-earth elements, aluminum, and gallium³⁻⁵. Thus, in all cases the solvents are complex mixtures of various inorganic compounds. Therefore, in order to obtain reproducible solubility data it is necessary to choose the composition of the solvent unambiguously. Such

compositions correspond to the points of invariant equilibria on the corresponding phase diagrams.

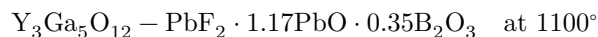
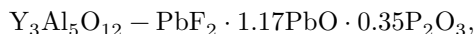
The solvent of composition $\text{PbF}_2 \cdot 1.17\text{PbO} \cdot 0.35\text{B}_2\text{O}_3$ (5) is the most convenient for work in the regime of isothermal evaporation; it was chosen by us for the study of the systems



As starting materials we used yttrium oxide, neodymium oxide, aluminum oxide, gallium oxide, reagent-grade lead fluoride, boric anhydride of analytical grade, and lead oxide of chemically pure grade.

The samples for the solubility study were prepared by grinding with alcohol the components of the corresponding compounds, taken in stoichiometric...

ratios. In addition, in studying solubility in the binary systems



preliminarily synthesized $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ with the garnet structure were used. The good reproducibility of the results obtained made it possible subsequently to dispense with the very laborious operations of synthesizing compounds with the garnet structure.

Solubility in systems (I), (II), and (III) was studied at 1100° by the isothermal method.

Homogenization of the mixtures was carried out in a high-temperature crystallization furnace; the temperature was then brought to 1100° and maintained constant to within $\pm 0.5^\circ$. After equilibrium had been established,

Fig. 1. *A*—Solubility isotherms in systems (I), (II), (III) at 1100°C . Dependence of the crystal-lattice parameter on concentration (*B*) and distribution curves (*V*) for $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (*a*), $\text{Nd}_3\text{Al}_5\text{O}_{12}$ (*b*), and $\text{Nd}_3\text{Ga}_5\text{O}_{12}$ (*c*).

samples of the solid and liquid phases were taken⁶. In the samples taken, neodymium, yttrium, aluminum, and gallium were determined quantitatively.

Figure 1. Solubility isotherms in systems (I), (II), (III) at 1100°C. Dependence of the crystal-lattice parameter on concentration (B) and distribution curves (V) for $Y_3Ga_5O_{12}$ (a), $Nd_3Al_5O_{12}$ (b), and $Nd_3Ga_5O_{12}$ (c)

Figure 1: Figure 1. Solubility isotherms in systems (I), (II), (III) at 1100°C. Dependence of the crystal-lattice parameter on concentration (B) and distribution curves (V) for $Y_3Ga_5O_{12}$ (a), $Nd_3Al_5O_{12}$ (b), and $Nd_3Ga_5O_{12}$ (c)

The compositions of the solid phases were determined graphically by the Schreinemakers residue method. Identification of the solid phases was also carried out by crystal-optical and X-ray methods.

It was established that the solid phases obtained were single crystals of $(Y, Nd)_3Al_5O_{12}$, $(Y, Nd)_3Ga_5O_{12}$, and $Y_3(Al, Ga)_5O_{12}$ with the garnet structure, containing no inclusions of solvent.

The solubility data for systems (I), (II), and (III) are presented in Fig. 1 and in Table 1. It follows from the figure that in all the systems studied, formation of solid solutions occurs.

Table 1

Solubility data (1100°)

Composition of the liquid phase, wt. %							Phase composition of the solid phase
System	System	System	System	System	System	System	Phase composition of the solid phase
$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$
1.17 PbO	1.17 PbO	1.17 PbO	1.17 PbO	1.17 PbO	1.17 PbO	1.17 PbO	$Y_3Al_5O_{12}$
0.35 B_2O_3	0.35 B_2O_3	0.35 B_2O_3	0.35 B_2O_3	0.35 B_2O_3	0.35 B_2O_3	0.35 B_2O_3	Solid solution
$Y_3Al_5O_{12}$	$Y_3Ga_5O_{12}$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$Y_3Ga_5O_{12}$	$Y_3Ga_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3AlGa_5O_{12}$
16.52	—	83.48	—	—	12.008 ± 0.001	12.046 ± 0.001	Same
12.01	3.99	84.00	24.94	13.00	12.096 ± 0.001	12.096 ± 0.001	Same
7.91	7.85	84.24	49.81	32.00	12.096 ± 0.001	12.096 ± 0.001	Same

Composition						
Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the solid phase (single crystal), wt. %	Phase composition of the solid phase
5.40	10.01	84.59	64.95	51.00	12.151 ± 0.001	Same
1.10	14.00	84.90	92.71	86.00	—	Same
—	15.00	85.00	100.00	100.00	12.279 ± 0.001	$Y_3Ga_5O_{12}$
System	System	System	System	System	System	System
$Y_3Al_5O_{12}$	$Nd_3Al_5O_{12}$	$Nd_3Al_5O_{12}$	$Nd_3Al_5O_{12}$	$Nd_3Al_5O_{12}$	$Nd_3Al_5O_{12}$	$Nd_3Al_5O_{12}$
$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$
16.52	—	83.48	—	—	12.005 ± 0.001	$Y_3Al_5O_{12}$
15.73	0.77	83.50	4.64	1.05	12.007 ± 0.001	Solid solution $(Y, Nd)_3Al_5O_{12}$
14.98	1.52	83.50	9.21	1.93	12.01 ± 0.001	Same
12.60	3.50	83.80	23.64	2.98	12.012 ± 0.001	Same
12.16	4.34	83.50	26.21	4.39	12.016 ± 0.001	Same
11.99	4.51	83.50	27.33	5.62	12.017 ± 0.001	Same
9.12	7.38	83.50	44.71	10.53	12.029 ± 0.001	Same
8.40	8.10	83.50	49.12	11.41	12.034 ± 0.001	Same
8.05	8.45	83.50	51.23	21.42	12.059 ± 0.001	Solid solution $(Y, Nd)_3Al_5O_{12}$ and $(Y, Nd)AlO_3$

Composition						
Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %	Composition of the liquid phase, wt. %
System	System	System	System	System	System	System
$Y_3Ga_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$	$Y_3Al_5O_{12}$
$1.17PbO$	$1.17PbO$	$1.17PbO$	$1.17PbO$	$1.17PbO$	$1.17PbO$	$1.17PbO$
$0.35B_2O_3$	$0.35B_2O_3$	$0.35B_2O_3$	$0.35B_2O_3$	$0.35B_2O_3$	$0.35B_2O_3$	$0.35B_2O_3$
$Y_3Ga_5O_{12}$	$Nd_3Ga_5O_{12}$	$PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$	$Nd_3Ga_5O_{12}$	$Nd_3Ga_5O_{12}$	$Nd_3Ga_5O_{12}$	$Nd_3Ga_5O_{12}$
15.00	—	85.00	—	—	12.279 ± 0.002	$Y_3Ga_5O_{12}$
12.88	1.37	85.75	9.61	2.97	12.304 ± 0.002	Solid solution $(Y, Nd)_3Ga_5O_{12}$
11.51	2.15	86.34	15.69	6.10	12.330 ± 0.002	Same
9.26	2.99	87.75	24.41	6.77	12.333 ± 0.002	Same
7.34	3.99	89.67	35.10	7.89	12.343 ± 0.002	Same
6.21	4.20	89.59	40.35	10.72	12.365 ± 0.002	Solid solution $(Y, Nd)_3Ga_5O_{12}$ and $(Y, Nd)GaO_3$

The solubility isotherm of system (I) is a crystallization branch of a continuous series of solid solutions of composition $Y_3(Al, Ga)_5O_{12}$ with the garnet structure.

The solubility isotherms in systems (II) and (III) correspond to crystallization of a limited series of solid solutions. In all cases the crystallization branches of pure $Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$ are infinitely small. The region of existence of the solid solutions $(Y, Nd)_3Al_5O_{12}$ and $(Y, Nd)_3Ga_5O_{12}$, which have the garnet structure, is small, and the saturated solutions corresponding to eutoni-

points, have the compositions: 8.05 wt.% $Y_3Al_5O_{12}$, 8.45 wt.% $Nd_3Al_5O_{12}$, and 83.50 wt.% $PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$; 6.21 wt.% $Y_3Ga_5O_{12}$, 4.20 wt.% $Nd_3Ga_5O_{12}$, and 89.59 wt.% $PbF_2 \cdot 1.17PbO \cdot 0.35B_2O_3$.

A further increase in the neodymium concentration leads in both systems to the transition of crystallization into a multiphase region. The limiting neodymium content in $(Y, Nd)_3Al_5O_{12}$ is 12.20 wt.%, and in $(Y, Nd)_3Ga_5O_{12}$ it is 4.75 wt.%.

Crystallo-optical observations, the course of the Schrainemakers rays, the linear dependence of lattice parameters on concentration, and also the character of the distribution curves of neodymium and gallium (Fig. 1) indicate the existence, in the systems studied, of solid solutions in the indicated concentration ranges.

The results obtained confirmed the previously drawn analogy with the properties of aqueous salt solutions, the validity of the phase-rule calculation of the variance of the systems studied, and showed that the constructed solubility diagrams are in complete agreement with the parameters determining the state of salt equilibrium systems (1, 2).

Thus, using the solubility isotherms in systems (I), (II), and (III), it is possible to obtain crystals of solid solutions of any preassigned composition.

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