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PHASE DIAGRAMS OF MgF_2–(Y, Ln)F_3 SYSTEMS

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By means of thermal and X-ray analyses with oxygen control, 14 phase diagrams of the systems MgF_2–(Y, Ln)F_3 have been obtained, where Ln are all lanthanides except Pm and Eu. All the systems are eutectic. Solid solutions up to 12 mole% MgF_2, which decompose by the eutectoid scheme, were detected based on high-temperature modifications of trifluorides of Y, Er, Tm, Yb and Lu, with a structure of the α-YF_3 type.

As fluoride materials find wide application in various fields of science and technology, the study of phase diagrams of the systems formed by magnesium fluoride and trifluorides of rare-earth elements is of great interest. For these systems hardly any data are available in the literature.

Fusibility diagrams of the systems MgF_2 with LaF_3 and YF_3, obtained by thermal analysis methods, are reported in [1, 2]. Both systems are of a eutectic type; no solid solutions based on the components were found. In the systems MgF_2-YF_3 thermal effects were observed below the eutectic temperature. These effects may be interpreted as the formation of a compound in the solid state at 10 mole% YF_3. Fusibility diagrams for the eutectic-type system MgF_2–ScF_3 were obtained in [3]. The width of the domain of solid solutions based on MgF_2, according to [3], does not exceed 5 mole% ScF_3. No other information on the systems MgF_2–(Y, Ln)F_3 is available.

The purpose of the present work is to study the phase diagrams of the MgF_2–(Y, Ln)F_3 systems.

Experimental

Starting materials were magnesium fluoride and trifluorides of rare-earth elements containing not less than 99.9% of the basic component. The preparation method and the purity of the magnesium fluoride are described in [4]. As the presence of even minute quantities of oxides and oxyfluorides in fluorides is known to affect the phase transitions greatly [5], the starting substances were pre-melted in a fluorinating atmosphere formed by teflon pyrolysis products. The oxygen contents of the specimens were determined by the method of vacuum-melting [6], and for (Y, Ln)F_3 were found to be 0.005–0.05 wt. %. For MgF_2 with an oxygen

content as low as 0.008 wt. %, a hazy white ingot is formed, due evidently to the precipitation of oxide as a second phase. Transparent single crystals used in the experiments contained 0.004 wt. % oxygen.

The X-ray powder diffraction data of MgF_2 were very near to the data published in [7, 8] and we indexed it in the tetragonal system with the unit cell parameters $a = 4.620 \pm 0.003$ Å and $c = 3.050 \pm 0.003$ Å.

Thermal analysis was carried out in a static atmosphere of highly-pure helium in a graphite-resistor furnace with molybdenum screens, using thin-walled molybdenum crucibles. The mass of the specimen was 1 to 5 g. Temperature was measured with a W5% Re/W20% Re thermocouple inserted from below. A molybdenum tip was used as the reference sample. Since high overcooling rather than overheating is characteristic of phase transformations in fluorides of rare earth elements [5] and magnesium [9], in order to construct the fusibility diagrams, heating curves were mainly used (with rates of 4–20°/min). The thermocouples were calibrated via the melting points of CaF_2 (1418° [5]), YF_3 (1152° [5]) and LiF (845° [10, 11]). This calibration was slightly different (± 3°) from the one we had used previously [12]. Two types of calibration plots were constructed, using both the beginning points and the extremal points of the thermal effects in the thermal curves. Reproducibility of the results in one series of experiments was ±2°, and in a different series ±5°. The average oxygen content of the specimens after thermal analysis was 0.009 wt. %.

To study subsolidus phase equilibria, the specimens were annealed under a fluorinating atmosphere in sealed Ni containers at 900° for 168 hours and quenched in running water. X-ray powder analysis was made with an AFV-202E diffractometer (Toshiba, Japan).

The weight losses of the specimens due to evaporation during thermal analysis amounted on the average to 1 wt. %. The compositons of the eutectics were checked by constructing the Tamman triangle. The determination accuracy is ±3 mole %.

The MgF_2-EuF_3 system was not studied and the MgF_2-SmF_3 system only partially, because during thermal analysis samarium and europium are partially reduced. Since no interaction of the components was recorded in the subsolidus parts of the $MgF_2-(Y, Ln)F_3$ systems, the following procedure was used to study the MgF_2-SmF_3 system. The pressed powder mixtures of components were heated in TA equipment. For construction of this phase diagram, only the thermal effects in the curve of the first heating were taken into account.

Results and discussion

The phase diagrams of the systems studied are shown in Fig. 1, and the coordinates of the non-variant points are presented in the Table. Temperatures of LnF_3 phase transformations are in good agreement (±5°) with the data reported in [13]. According to our results, the melting point of MgF_2 is 1260°, which almost agrees with literature values [8–1014]. No traces of a solid phase transition in MgF_2, described in [3], were detected.

All the systems are eutectic, the eutectic coordinates changing regularly in a sequence. According to the thermal data of unannealed specimens, the width of the domain of solid solutions based on MgF_2 does not exceed 1 mole%. In $MgF_2-(Y, Ln)F_3$ (Ln = Er–Lu) systems solid solutions have been found, which decompose according to the eutectoid scheme, based on the high-temperature modifications of trifluorides which crystallize in α-YF_3(α – UO_3) structural type [5, 13]. These phase domains widen with increasing lanthanide atomic number. We did not succeed in quenching and studying these solid solutions using the X-ray method, but their phase regions are easily detected by thermal analysis (Fig. 1b–g).

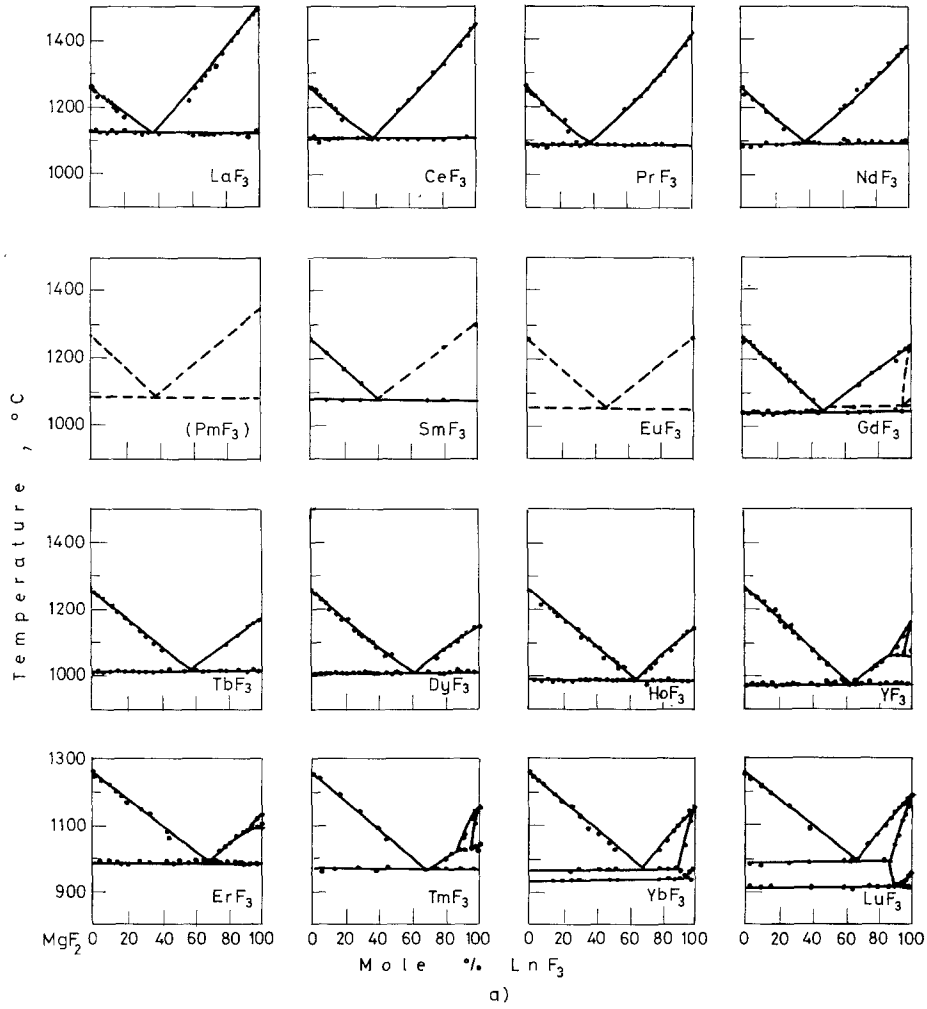
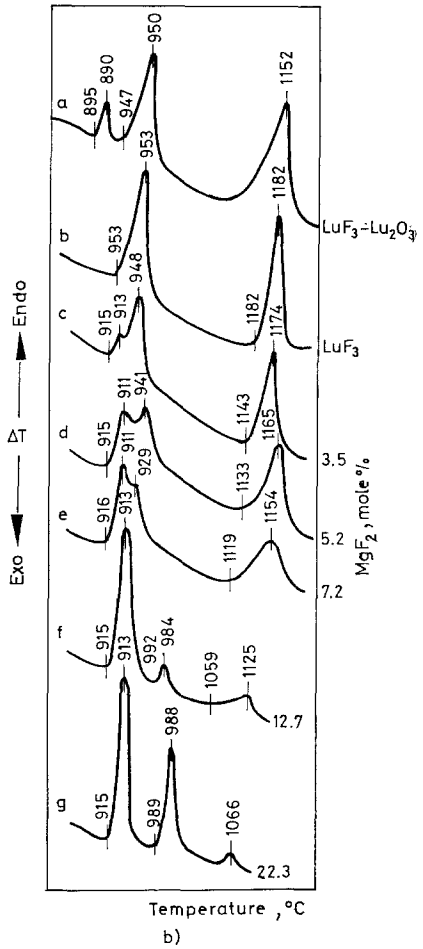


Fig. 1a). Phase diagrams for the $MgF_2-(Y, Ln)F_3$ systems

Eutectoid decompositions of solid solutions based on high-temperature modifications of yttrium group LnF_3 supercool by tens of degrees, as opposed to the eutectics.

In the MgF_2-GdF_3 system, addition of only 3 mole% MgF_2 to GdF_3 results in the disappearance of the GdF_3 polymorphic transition effect in the thermal curves and leads to the formation of a eutectic. Apparently, in this system, on the basis of α-GdF_3 (LaF_3 structural type), a solid solution of small width is formed, and decomposes according to the eutectoid scheme at a temperature close to the eutectic temperature (Fig. 1).

According to the thermal data for both annealed and unannealed specimens, the solubility of MgF_2 in rare-earth trifluorides having β-YF_3 type structure (see [5]) is very low (not over 1–2 mole%).



b)

Fig. 1b). Thermal curves of LuF_3 with impurity of Lu_2O_3 (a) and several compositions in MgF_2-LuF_3 system (b-g)

Table 1

Coordinates of non-variant points in the system MgF_2–(Y, Ln)F_3 (C–mole % MgF_2, t–°C)

R	Eutectic		Solid solutions of the type α-YF_3		
	C	t	C max	t decompos.	C decompos.
La	63	1125	—	—	—
Ce	62	1110	—	—	—
Pr	62	1092	—	—	—
Nd	61	1093	—	—	—
Sm	61	1076	—	—	—
Gd	48	1032	—	—	—
Tb	43	1015	—	—	—
Dy	38	1008	—	—	—
Ho	35	992	—	—	—
Er	33	984	3	1092	3
Tm	31	975	4	1033	4
Yb	32	967	9	940	8
Lu	33	992	12	915	10
Y	36	974	6	1060	6

X-ray analysis of specimens after thermal analysis and after annealing and quenching showed in all cases the presence of only two phases: MgF_2 and (Y, Ln)F_3. The fluorides of Ln = La–Nd were crystallized in the LaF_3 (tysonite) type structure; the fluorides of Ln = Gd–Lu and Y have the ortorhombic β-YF_3 type structure. The parameters of the unit cells in the phases, observed with an accuracy of ±0.007 Å, coincide with the parameters of the pure trifluorides [15], which also testifies to the absence of solid solutions of noticeable concentrations based on rutile (MgF_2), tysonite and β-YF_3 structural types.

In studying the MgF_2 – LuF_3 system, we also investigated the influence of oxygen impurity on the phase diagram characteristics. The small quantity of oxide in the LuF_3 is displayed in the presence of the additional thermal effect at 894° in the thermal curves (Fig. 2a). For the MgF_2–LuF_3 system with such a LuF_3 specimen the temperatures of the eutectic and liquidus were close to values obtained for oxygen-pure LuF_3, but at 10–30° below the eutectoid decomposition three additional thermal effects were observed.

Throughout the entire region of concentrations in the system MgF_2–YbF_3 a weak additional effect was registered ~ 20° below the eutectoid decomposition (not shown in Fig. 1), although in the thermal analysis of pure YbF_3 no additional effects were noted apart from fusion and polymorphic transition. X-ray analysis did not indicate the existence of any phases except MgF_2 and YbF_3.

The coordinates of non-variant points obtained for the systems MgF_2 with YF_3 and LaF_3 are in satisfactory agreement with the data in [1, 2]. In the system MgF_2–YF_3, in contrast to observations reported in [1], no thermal effects were

found in the solid state. These can also be assumed to be due to the contamination. X-ray analysis does not confirm the existence of any binary compound in this system.

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RÉSUMÉ — 14 diagrammes de phases des systèmes MgF_2 — (Y, Ln) F_3, où Ln représente tous les lanthanoïdes à l'exception de Pm et Eu ont été établis par études aux rayons X et analyse thermique, avec contrôle de l'oxygène. Tous ces systèmes présentent un eutectique. Des solutions solides jusqu'à 12 moles % de MgF_2 à décomposition eutectoïde ont été décelées à l'aide des transitions à haute température des trifluorures d'Y, Er, Tm, Yb et Lu du type α-YF_3.

ZUSAMMENFASSUNG — Durch Einsatz der Thermo- und Röntgenanalyse mit Sauerstoffkontrolle wurden 14 Phasendiagramme der Systeme MgF_2—(Y, Ln)F_3 erhalten, wobei Ln sämtliche Lanthanoide mit Ausnahme von Pm und Eu sind. Alle Systeme zeigten sich eutektisch. Feste, sich nach dem eutektoiden Schema zersetzende Lösungen bis zu 12 Mol% MgF_2 wurden an Hand der Hochtemperatur-Änderungen der Trifluoride von Y, Er, Tm, Yb, Lu mit α-YF_3-Struktur nachgewiesen.

Резюме — Используя термический и рентгено-фазовий анализ с контролем за содержанием кислорода, были получены 14 фазовых диаграмм для систем MgF_2 — (Y, Ln)F_3, где Ln-все лантаноиды, исключая Pm и Eu. Все системы являются эвтектичес-кими. Твердые растворы с содержанием до 12 мол.% MgF_2, разлагающиеся по эвтектоидной схеме, были обнаружены на основе высокотемпературных модификаций трифторидов Y, Er, Tm, Yb, Lu, имеющих структуру типа α-YF_3.