Phase Equilibria in BaF_2–(Y, Ln)F_3 Systems*

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Data are presented on phase equilibria at $877 \pm 10°C$ in the systems BaF_2–(Y, Ln)F_3, where Ln = Sm–Lu. All the systems show cubic solid solutions based on BaF_2 and variable composition phases

$$Ba_{4\mp x}Ln_{3\pm x}F_{17\pm x}$$

of structure derived from the CaF_2 type (rhombohedral distortion). Syngony and unit cell dimensions have been determined on monocrystals; crystallographic parameters of ten trigonal phases have been adduced. The existence of solid solutions of BaF_2 in high-temperature α-LnF$_3$(LaF$_3$ type) at the given isothermal section indicates stabilization of the LaF$_3$ structure type by heterovalent isomorphous replacement. In the systems BaF_2–(Y, Ln)F_3 with Ln = Dy–Yb, monoclinic compounds BaR_2F_8 are formed. X-ray parameters, derived from single crystal and polycrystalline specimens, of six monoclinic BaR_2F_8 compounds are presented. In the BaF_2–LuF$_3$ system we have isolated and studied for the first time a compound of the approximate composition $BaLu_2F_8$ which crystallizes in rhombic syngony and has a marked range of homogeneity.

Introduction

Interest in investigating BaF_2–(Y, Ln)F_3 systems has been generated by use of phases of variable composition and of double salts that are formed in these systems as active laser elements (1, 2) for converting ir quanta into visible light (3–6).

Data published (7–11) on phase compositions and state diagrams for BaF_2–(Y, Ln)F_3, where Ln = La, Gd, Yb, are rather contradictory and do not display any regularity in change of diagram type on going from "light" to "heavy" lanthanides. Except for the simple eutectic system BaF_2–LaF$_3$ (8), the treatment by the authors of thermal analysis results contradicts the phase rule in all cases. Individual reports on the phase composition of the BaF_2–(Y, Ln)F_3 systems are presented in (12–16, 3, 5).

Recently, there has appeared a report (3) on the formation of a new phase in BaF_2–(Y, Ln)F_3 systems which the authors describe as $BaRF_5$ (R = Y, Lu); Refs. (6, 9) confirm this.

Except for proof that $BaRF_5$ belongs to trigonal syngony, other X-ray parameters of this phase were not given in (3). According to the data in (5, 10), the composition of the new phase is $3BaF_2 \cdot 2RF_3$ (R = Y, Yb). Results of X-ray studies on $BaGdF_5$ (9) amd $3BaF_2 \cdot 2YbF_3$ (10) have been published.

The purpose of the present study is to give systematic information on phase composition in the systems BaF_2–(Y, Ln)F_3, structure of the phases formed, and some of their properties. This information is partially contained in publications (16–19); here we present the phase parameters for all the systems BaF_2–(Y, Ln)F_3, where Ln = Sm–Lu.

Samples were prepared by heating the corresponding fluorides (oxygen content $0.02 - 0.07$ wt%) at $877 \pm 10°C$ in sealed nickel containers in a fluorinating atmosphere. [Actually a series of isothermal sections from 800 to 1100°C has been investigated, of which the 877°C isotherm offers the most complete, though not exhaustive, representation of the phase composition in the BaF_2–(Y, Ln)F_3 systems.] The oxygen content in the samples after thermal treatment was no higher than 0.15% by weight. The annealing

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time was 200 hr; quenching was in running water.

Phase composition was determined by X-ray (diffractometer AFV-201, Japan, Cu$K\alpha$ radiation), petrographic (transparent cross-section), and immersion methods. The spacing of compositions was 1–3 mole%.

Investigation of monocrystals was carried out by Laue (W radiation), oscillation (Cu$K\alpha$), and photographing reciprocal lattice (Mo$K\alpha$) methods. Single crystal lattice parameters, representative of the various structural types, were determined on the single crystal diffractometer from pinacoid reflections of high orders ($130° < 2\theta < 164°$). For the series of isostructural compounds, unit cell parameters were calculated from measurements on the powders taken on a "Hillger" diffractometer (England) with step by step scanning through $0.02°$ in 2θ Cu (BaF$_2$, $a = 6.2001$ Å, served as internal standard).

Results of phase composition determination in the systems BaF$_2$–(Y,Ln)F$_3$ (Ln = Sm–Lu) at

FIG. 1. Phase compositions in the systems BaF$_2$–(Y, Ln)F$_3$ at $877 \pm 10°$C isotherm.

$877 \pm 10°$C are presented in Fig. 1. The phase composition of all the systems (except BaF$_2$–LuF$_3$) is of the same type and is represented by cubic disordered solid solutions based on BaF$_2$ (phase I), ordered phase II (rhombohedral distortion of the CaF$_2$ type), hexagonal phases with tysonite structure LaF$_3$ (phase III), and monoclinic compounds BaR$_2$F$_8$ (phase IV). In the system BaF$_2$–LuF$_3$, compounds were formed that crystallize with rhombic syngony (phase V).

1. Cubic Disordered Solid Solutions (Phase I) of Fluorite Type Structure

Phase I is formed in all the systems. The limiting content of (Y,Ln)F$_3$ at the isotherm given corresponds to 23–26 $\pm$ 2 mole%. Table I gives the unit-cell parameters for the saturated cubic solid solutions of fluorite structure at $877°$C. X-ray data, obtained on annealed specimens of BaF$_2$–(Y,Ln)F$_3$, where Ln = Sm, Gd, Ho, Lu, have been presented earlier (12–14). As follows from (13), raising the temperature significantly broadens the field where phase I forms and in a number of cases the range overlaps the field in which phase II exists at $877°$C. The incongruent character of the melting of type II phases was confirmed not long ago (7, 10) in systems with YF$_3$ and YbF$_3$.

2. Phases with Structure Derived from the CaF$_2$ Type (Phase II)

In all the systems (Fig. 1), phase II is characterized by rhombohedral distorted cells of the fluorite type with clearly defined superstructure reflections. The study of single crystals of composition 0.575 BaF$_2$·0.425 TmF$_3$ confirmed their belonging to trigonal syngony with hexagonal primitive cell parameters $a = 29.3 \pm 0.1$ Å and $c = 40.8 \pm 0.1$ Å. The idealized relations of the parameters of the hexagonal primitive cells of phase II to the initial fluorite subcells are $a_{hex} \cong a_{cubic} \cdot 7/\sqrt{2}$; $c_{hex} = a_{cubic} \cdot 4\sqrt{3}$ (19).

In all the systems in the isothermal section given, phases II are separated from the cubic solid solutions by a clearly defined biphase field. Phases II possess marked fields of homogeneity not mentioned in previous studies (3–5). This may partly explain the contradictory opinions on the composition of phases II which appear in the literature.

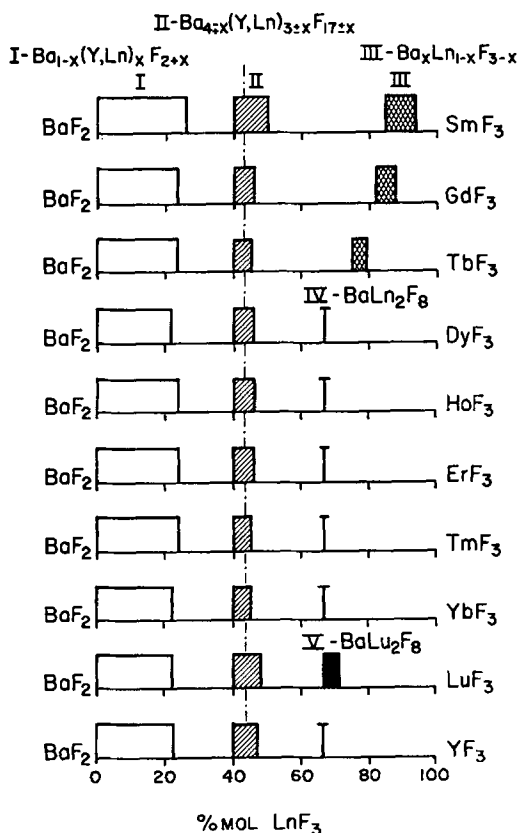The problem of the nature of phase II and its

TABLE I

UNIT-CELL PARAMETERS OF PHASES I AND II

Phase I Fluorite structure type		Phase II Rhombohedral distorted fluorite type				
	Cubic unit cell parameters		Hexagonal unit cell parameters		Rhombohedral unit cell parameters	
Ba$_{1-x}$(Y,Ln)$_x$F$_{2+x}$	a ± 0.005 Å	Ba$_{4 \mp x}$(Y,Ln)$_{3 \pm x}$F$_{17 \pm x}$	a ± 0.02 Å	c ± 0.03 Å	a ± 0.02 Å	α $\pm 3'$
Ba$_{0.74}$Sm$_{0.26}$F$_{2.26}$	6.056	Ba$_{3.85}$Sm$_{3.15}$F$_{17.15}$	29.62	41.29	21.95	84°52′
Ba$_{0.76}$Gd$_{0.24}$F$_{2.24}$	6.045	Ba$_{3.99}$Gd$_{3.01}$F$_{17.01}$	29.53	41.16	21.87	84°56′
Ba$_{0.76}$Tb$_{0.24}$F$_{2.24}$	6.043	Ba$_{3.92}$Tb$_{3.08}$F$_{17.08}$	29.45	41.00	21.81	84°56′
Ba$_{0.77}$Dy$_{0.23}$F$_{2.23}$	6.033	Ba$_{3.99}$Dy$_{3.01}$F$_{17.01}$	29.37	40.92	21.75	84°56′
Ba$_{0.77}$Ho$_{0.23}$F$_{2.23}$	6.030	Ba$_{3.99}$Ho$_{3.01}$F$_{17.01}$	29.30	40.84	21.70	84°56′
Ba$_{0.76}$Er$_{0.24}$F$_{2.24}$	6.027	Ba$_{4.025}$Er$_{2.975}$F$_{16.975}$	29.29	40.76	21.68	84°58′
Ba$_{0.76}$Tm$_{0.24}$F$_{2.24}$	6.011	Ba$_{4.025}$Tm$_{2.975}$F$_{16.975}$	29.19	40.66	21.62	84°56′
Ba$_{0.77}$Yb$_{0.23}$F$_{2.23}$	6.000	Ba$_{3.85}$Yb$_{3.15}$F$_{17.15}$	29.11	40.58	21.57	84°52′
Ba$_{0.76}$Lu$_{0.24}$F$_{2.24}$	5.988	Ba$_{3.99}$Lu$_{3.01}$F$_{17.01}$	29.07	40.48	21.53	84°56′
Ba$_{0.76}$Y$_{0.24}$F$_{2.24}$	6.040	Ba$_{3.85}$Y$_{3.15}$F$_{17.15}$	29.26	40.72	21.66	84°58′

interrelationship with the cubic solid solutions at high temperatures needs further investigation, which will be carried out. Phases II may be parts of a series of fluorite solid solutions of "light" LnF$_3$ (beginning with SmF$_3$) in BaF$_2$, stabilized according to temperature because of gradual reorganization of structure brought about by increased concentration of LnF$_3$. In the case of the "heavy" LnF$_3$, phases II may become independent chemical compounds with incongruent melting character. From the multiplicity of parameters for the true cells and the cubic subcells of phase II, we are inclined to the belief that in the latter case the most probable composition of the compounds is Ba$_{4 \mp x}$(Y, Ln)$_{3 \pm x}$F$_{17 \pm x}$. Table I gives the results of the determination of the parameters of the true hexagonal and corresponding rhombohedral unit cells of phase II for compositions close to the ideal.

TABLE II

CRYSTALLOGRAPHIC PARAMETERS OF THE COMPOUNDS Ba(Y,Ln)$_2$F$_8$

Compound BaR$_2$F$_8$	Unit cell parameters Å			Monoclinic angle β $\pm 3'$	Molar volume Å^3	X-ray density ρ, g/cm^3
	a ± 0.003	b ± 0.004	c ± 0.002			
BaDy$_2$F$_8$	7.023	10.567	4.289	99°47′	156.82	6.50
BaHo$_2$F$_8$	6.991	10.538	4.275	99°45′	155.20	6.62
BaEr$_2$F$_8$	6.969	10.493	4.262	99°45′	153.59	6.74
BaTm$_2$F$_8$	6.931	10.455	4.240	99°40′	151.44	6.87
BaYb$_2$F$_8$	6.919	10.440	4.238	99°42′	150.87	6.99
BaY$_2$F$_8$	6.972	10.505	4.260	99°45′	155.86	4.97

3. Solid Solutions with Structures of the Type LaF₃ (Phase III)

The most important features of the tysonite phases at the 877°C isotherm are their stability at lower temperatures than would correspond to any tysonite modification of α-LnF$_3$ and the displacement of the saturation limit toward the LnF$_3$ ordinate on going from systems with TbF$_3$ to systems with SmF$_3$, in contrast to near constancy of this limit at 1000°C (17). Since in preparation of the samples, the approach to equilibrium in all cases occurs without superheating, detection of tysonite phases at lower temperatures than for polymorphic transitions of tysonite α-LnF$_3$ to rhombic β-LnF$_3$ (20) indicates stabilization of the structure type LaF$_3$ by isomorphous replacements of Ln^{3+} for Ba^{2+}, which are accompanied by formation of anion vacancies. Earlier this phenomenon was studied by us in the systems CaF$_2$–(Y, Ln)F$_3$ (21). In reference (22) the authors claim that their obtained phases Sr$_y$Tl$_{1-y}$F$_{3-y}$ are the first example of stabilization of structure type LaF$_3$ by anion vacancies. However, the first to show the possibility of such was Ref. (23), which presented the examples of stabilization known at that time.

4. Compounds of the Type BaR₂F₈ (Phase IV)

Phases IV have been studied previously (16–18); they are double compounds of stoichiometric composition BaLn$_2$F$_8$, crystallizing in monoclinic syngony, belonging to space group $C2/m$–C$^3_{2h}$. The basic crystallographic parameters of Ba(Y, Ln)$_2$F$_8$ are presented in Table II. The results of indexing diffractograms of BaTm$_2$F$_8$ are given in Table III; assignment of (hkl) was based on intensity measurements of exposures made earlier on single crystals (18).

Comparison of the phase composition of the BaF$_2$–LnF$_3$ systems at 1000°C (17) with the 877°C isotherm discloses essential differences. At 877°C, the monoclinic compounds BaLn$_2$F$_8$ are formed significantly earlier in the series of LnF$_3$—in the given case, beginning with DyF$_3$, whereas at 1000°C, they appear only with systems beginning with ErF$_3$ (14, 17). In the BaF$_2$–LuF$_3$ system, a new compound is formed which differs sharply in X-ray powder diagram from monoclinic BaLn$_2$F$_8$ (phase V, Fig. 1). Hence, in the series of rare earth element trifluorides, structure type monoclinic BaTm$_2$F$_8$ (18) goes through all stages of stability from

TABLE III

RESULTS OF INDEXING X-RAY POWDER PHOTOGRAPHS BaTm₂F₈

I/I_0	$d_{expt'}$ Å	$d_{calc'}$ Å	h k l
25	4.180	4.180	0 0 1
25	3.628	3.626	1̄ 1 1
100	3.415	3.416	2 0 0
30	3.268	3.265	0 2 1
20	3.170	3.169	1 1 1
55	3.105	3.104	1 3 0
3	2.898	2.894	2 0 1̄
3	2.860	2.860	2 2 0
1	2.588	2.589	1 3 1̄
9	2.533	2.532	2 2 1̄
5	2.407	2.406	1 3 1
25	2.219	2.216	0 4 1
		2.219	2 2 1
3	2.078	2.076	2 4 0
1	2.059	2.059	1 1 2̄
2	2.000	1.999	1 5 0
5	1.944	1.940	2 4 1̄
		1.941	0 2 2
10	1.935	1.933	2 0 2̄
35	1.907	1.907	3 3 0
5	1.844	1.843	3 1 1
12	1.839	1.839	1 5 1̄
1	1.816	1.813	2 2 2̄
8	1.800	1.798	1 3 2̄
3	1.789	1.788	2 4 1
5	1.771	1.770	1 5 1
5	1.743	1.743	0 6 0
12	1.708	1.708	4 0 0
12	1.677	1.675	1 3 2
3	1.664	1.663	2 0 2
2	1.651	1.649	3 3 1
1	1.624	1.624	4 2 0
1	1.609	1.608	0 6 1
3	1.603	1.602	4 2 1̄
4	1.553	1.552	2 6 0
		1.554	2 4 2̄
7	1.529	1.540	3 5 0
4	1.503	1.502	3 5 1̄
1	1.493	1.493	2 6 1̄
3	1.448	1.447	4 0 2̄
3	1.438	1.438	1 5 2̄
1	1.416	1.412	3 1 2
1	1.401	1.400	1 1 3̄
3	1.395	1.395	4 2 2̄
		1.395	3 5 1̄

formation only at sufficiently low temperatures in the case of BaF$_2$–DyF$_3$ (probably with incongruent melting character) through stable, congruently melting compounds, e.g., BaYb$_2$F$_8$ (10) and BaY$_2$F$_8$ (7), to the system BaF$_2$–LuF$_3$,
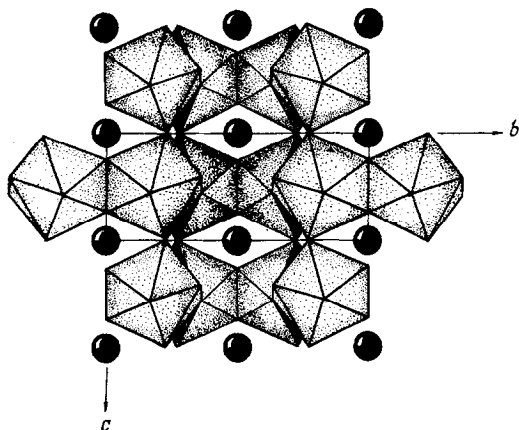
FIG. 2. Projection of the structure of BaTm₂F: along [110] (black circles are barium atoms).

where at 877°C there is formed a compound of another structure type. From a structural investigation of $BaTm_2F_8$ (18), it follows that the stability of this type of compound is basically determined by the dimensions of the rare earth polyhedra, i.e., in the final analysis by the ionic radii of Ln^{3+}, which form a rigid three-dimensional framework, in the interstices of which (channels along the c axis) are distributed the atoms of barium (Fig. 2). The coordination number of barium is 12 and the change of barium for a cation of smaller size (strontium and especially calcium) leads to a sharp decrease in the stability of this structure type. Proportional to the increase in radius of the rare earth ion, the polyhedra become too large for barium, and, in systems with trifluorides of the rare earth elements of the cerium subgroup, monoclinic compounds are not formed. Monoclinic compounds of structure type $BaTm_2F_8$ are formed not only in the systems BaF_2–$(Y,Ln)F_3$; Ref. (24) obtained the isotype phase $BaTl_2F_8$ in the system BaF_2–TlF_3.

5. Phase V

In the BaF_2–LuF_3 system, we have for the first time separated and studied a new phase characterized by a marked range of homogeneity from 66.6 to 72 mole % LuF_3. X-ray investigation of single crystals of the composition $BaF_2 \cdot 2LuF_3$ indicated that this phase belongs to rhombic syngony with unit cell parameters: $a = 6.95 \pm 0.03$ Å; $b = 8.11 \pm 0.04$ Å; $c = 22.05 \pm 0.10$ Å.

In analogy with other systems of BaF_2–LnF_3 (Ln = Dy–Yb), one can suggest that the rational composition $BaF_2 \cdot 2LuF_3$ corresponds to a

chemical compound which differs crystallographically from the monoclinic $BaLn_2F_8$ (Ln = Dy–Yb) which were studied earlier.

The authors of Ref. (3), describing the phases BaR_2F_8 with R = Y, Lu, make no difference between the structures of these compounds, assigning both to monoclinic synogony. They err in suggesting that the compounds BaR_2F_8 were first obtained in (3). The first information on BaR_2F_8 appeared in (14).

Conclusions

1. Phase equilibria in the systems BaF_2–$(Y, Ln)F_3$, where Ln = Sm–Lu, have been investigated at $877 \pm 10°C$.

2. The phase composition of all the systems in the concentration range from 0 to 50 mole % $(Y,Ln)F_3$ is uniform and is represented by disordered cubic solid solutions based on BaF_2. In the region 39–49 mole % $(Y,Ln)F_3$ there is formed in all the systems a phase of variable composition, derived from the CaF_2 type (rhombohedral distortion with superstructure). For the first time we have presented X-ray parameters for nine phases of this type; unit-cell dimensions and syngony were precisely defined on monocrystals.

3. In the systems BaF_2–LnF_3 (Ln = Sm–Tb), we have found phases with structure of the LaF_3 type, appearing as solid solutions of BaF_2 in high-temperature tysonite modifications of α-LnF_3. The formation of these phases below temperatures of the field of stability of pure tysonite α-LnF_3 indicates stabilization of the latter by heterovalent isomorphous replacement of Ln^{3+} for Ba^{2+}.

4. It has been shown that monoclinic compounds $Ba(Y, Ln)_2F_8$ are formed in systems with Ln = Dy–Yb. For the first time, we have presented crystallographic parameters of all the monoclinic phases determined on monocrystals and polycrystalline samples.

5. In the system BaF_2–LuF_3, there is formed a compound of the approximate composition $BaLu_2F_8$, which crystallizes in rhombic syngony.

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