THE THERMAL STABILITY OF
LiNaR$_2$F$_8$ (R = Ho-Lu, Y) COMPOUNDS

P.P. FEDOROV, L.V. MEDVEDEVA, O.S. BONDAREVA,
B.I. SOBOLEV

Institute of Crystallography, USSR Acad. Sci., Moscow, USSR

The series of monoclinic compounds with the general formula Li-NaR$_2$F$_8$ (R = Ho-Lu, Y) has been described in [1-3]. These compounds may be used as promising host materials for luminofors [4]. The crystal structure of LiNaR$_2$F$_8$ has been studied in [1,3] for R=Y, Yb. The structure may be described as a three-dimensional framework built of [RF$_8$] bicapped trigonal prisms connected by edges and corners. The Li and Na cations occupy their positions in channels.

According to [1], Y-compound decomposes at 695 ± 5 C°. No other data concerning thermal stability of these compounds are available. Since possible practical application of these materials is determined by their stability we studied the thermal stability of the whole series of LiNaR$_2$F$_8$ compounds.

EXPERIMENTAL

In this work, the LiNaR$_2$F$_8$ compounds were studied by differential thermal analysis (DTA) and powder X-ray diffraction techniques. For synthesis we used LiF optical grade single crystals, NaF ("highly pure" grade) and rare earth trifluorides ("chemically pure" grade) as starting materials. Sodium and rare-earth fluorides were remelted in advance in a fluorinating atmosphere of teflon thermal decomposition products.

The DTA was carried out in thin-wall graphite crucibles in static helium atmosphere by the method described elsewhere [5,6]. The specimens were annealed in sealed nickel containers in fluorinating atmosphere (products of thermal decomposition of teflon and BaF$_2$·HF). The containers were quenched in water, at a cooling rate of about 100 Ks^{-1}. X-ray diffraction analysis of the specimens was carried out on AVF-202E and HZG-4 diffractometers with Ni-filtered CuK$_a$ radiation.

RESULTS

We found that the synthesis of $LiNaR_2F_8$ compounds upon melting of the components taken in stoichiometric amounts always leads to the formation of a three-component mixture: X-ray powder diffraction patterns correspond to the superposition of the reflections of $LiRF_4$ compounds [7,8], fluorite-type phases (F) which are formed in $NaF-RF_3$ systems [9-14] and $LiNaR_2F_8$ compounds. It evidences incongruent-type melting of $LiNaR_2F_8$ compounds and (or) their decomposition upon cooling. The DTA thermal heating curves of $LiNaR_2F_8$ (R = Ho – Tm, Y) exhibit 4 thermal effects, figure 1. The effects at about 700° C evidently correspond to non-variant processes. The annealing of a previously melted specimen of $LiNaY_2F_8$ at 500 °C for 473 h leads to its complete decomposition. Its subsequent annealing at
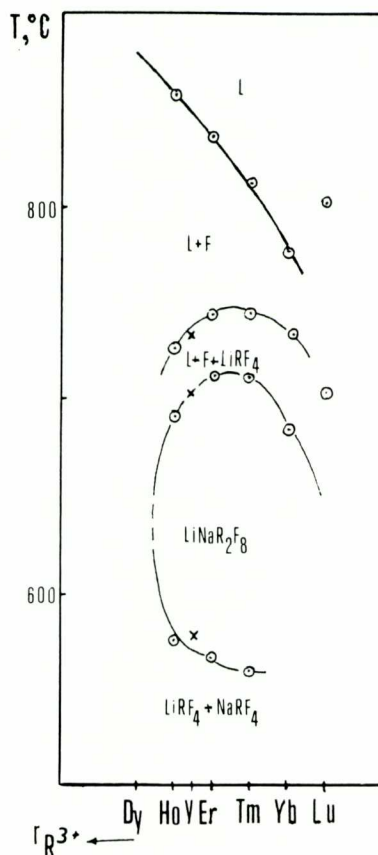

Fig. 1. Thermal stability of $LiNaR_2F_8$ compounds.

660 °C for 215 h and at 600° C for 50 h leads to secondary resynthesis of the compound. On the basis of these data the thermal effect at 580 °C can be interpreted as the formation of LiNaY$_2$F$_8$ in the solid state.

Figure 2 shows a suggested scheme of phase equilibria using our experimental data in the section LiYF$_4$-NaYF$_4$ of the system LiF-NaF-YF$_3$. The LiNaY$_2$F$_8$ compound is stable in a narrow temperature range: 580 ± 5 °C is
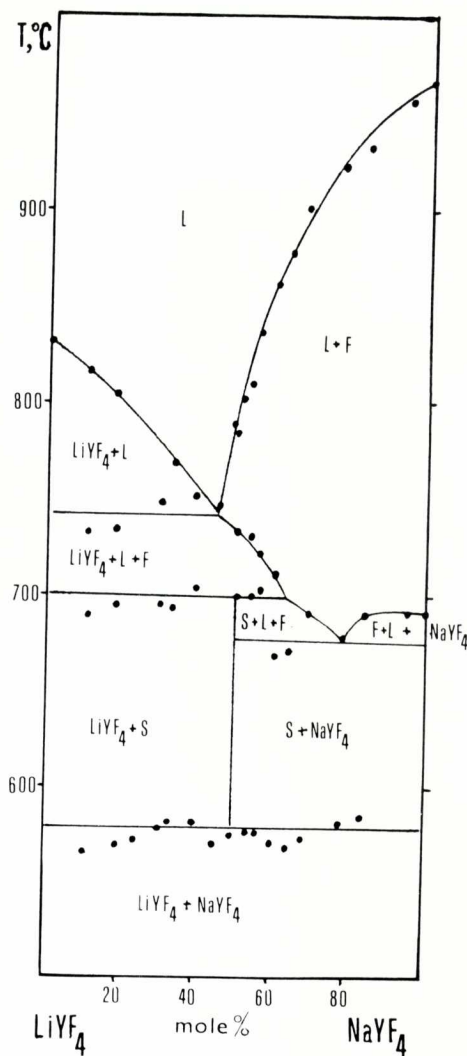

Fig. 2. Polythermal section LiYF$_4$ - NaYF$_4$ of the LiF-NaF-YF$_3$ ternary system. L : melt, S : LiNaY$_2$F$_8$, F : fluorite-type phase Na$_{0.5-x}$R$_{0.5+x}$F$_{2+2x}$.

the temperature of the formation of this compound upon heating, and at 700 $\pm$ 5 °C it melts incongruently. $NaYF_4$ is dimorphic: the low-tempera-ture β-$NaYF_4$ modification crystallizes in the $NaNdF_4$ structural type; the high-temperature modification is a disordered fluorite-type one, which can dissolve additional amount of YF_3 (phase F). The temperature of the trans-formation is 790 $\pm$ 5 °C [9,11].

Figure 3 shows a scheme of stable sections of a ternary LiF-NaF-YF_3 sys-tem at two temperatures: below the thermal stability of the 1:1:2 compound at 500 °C and at 660 °C, where the 1:1:2 compound is stable. The pseudo-trigonal compound NaY_2F_7 [15,16] has been obtained in the NaF-YF_3 sys-tem at 600 ° and 660 °C, but not $Na_5Y_9F_{32}$, as described in [9].

The thermal behaviour of others $LiNaR_2F_8$ is similar to the behaviour of the yttrium compound. The interpretation of thermal effects (figure 1) was
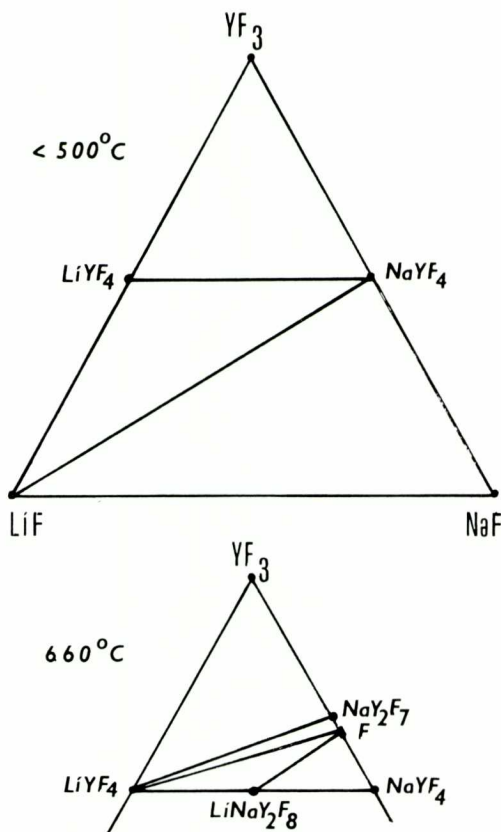

Fig. 3. Scheme of stable sections of the solid state of the LiF-NaF-YF_3 ternary system: a) at 500 °C;   b) at 660 °C.

made by analogy with the LiF-NaF-YF₃ system. The temperatures of thermal effects for $LiNaLu_2F_8$ do not correspond to the general tendency. Probably, the type of phase equilibria in the LiF-NaF-LuF₃ system differs from other RF₃ systems.

We have been unable to prepare 1:1:2 compounds for Dy and larger rare-earth cations. We also tried to prepare such type compounds for smaller Sc^{3+} and In^{3+} cations and we have obtained $Li_3Na_3R_2F_{12}$ garnets (R = In, Sc) [17], mixed with other phases.

The region of $LiNaR_2F_8$ stability, determined by us (figure 1) is in good agreement with the recommendation [2] for the temperature of the synthesis of these compounds, as well as the temperature of $LiNaY_2F_8$ decomposition agrees with the data given in [1]. X-ray characteristics of the compounds are practically identical with the data presented in [1-3]. The formation of $LiNaR_2F_8$ upon cooling of the melt inside the DTA equipment starts at 50-100°C below the equilibrium temperature.

DISCUSSION

Thus, the field of stability of $LiNaR_2F_8$ has an ellipse-like shape in the system of coordinates "temperature-ionic radius of trivalent cations". The narrow interval of ionic radii of R^{3+} cations, where $LiNaR_2F_8$ structure is stable, can be connected with the crystal-chemical toleration of 8-coordinated polyhedra of [RF₈] for a limited number of rare earth elements.

The $LiNaR_2F_8$ compounds are not stable under normal conditions, so the application of any materials on such a basis is problematic.

Our results can be interpreted in terms of morphotropy, i.e., change of stability of the given structure type of the group of compounds with the given stoichiometry with changes in the qualitative chemical composition. The phenomenon of polymorphism (phase transitons in the coordinates "temperature-pressure") and morphotropy (phase transitions in the coordinates "temperature-ionic radii") have very much in common, see figure 4. As the compressibilities of anions are greater than those of cations, an increase in pressure yields similar crystallochemical effects as an increase in the cationic radius.

For polymorphysm, there is the Clausius-Clapeyron thermodynamical relation, which connects the slope of the curve of phase equilibria in the coordinates "temperature-pressure" with changes of the molecular volume V and entropy S upon phase transformation. This equation is correct for equilibrium of n+1 phases in n-component systems [18]. As for morphotropy, no strict quantitative relations are known up to now. It is probable that dT/dr = ± ∞ at T = °K [19].

PHASE TRANSFORMATIONS

POLYMORPHISM
(T;P)
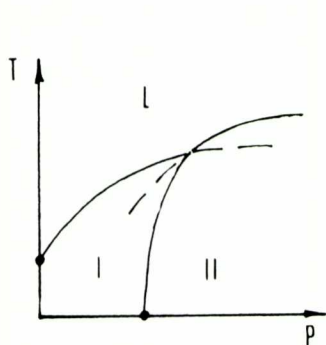
MORPHOTROPY
(T;$r_{cat.}$)

P ↑ ~ $r_{cat.}$ ↑

T

l

I

II

P

T

l

I

II

r_{cat}
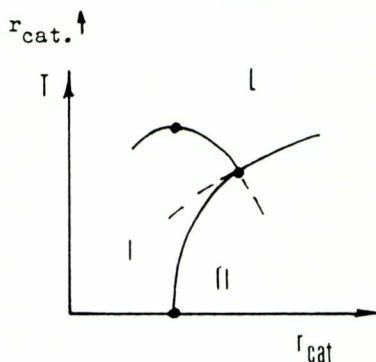
THERMODYNAMICS

Clausius-Clapeyron
relation

$dT/dP = \Delta V/\Delta S$

(V - volume, S - entropy;
n components, n+1 phases)

$dT/dP = 0$, $\Delta V = 0$

$dT/dP = \pm\infty$, $\Delta S = 0$ (T = 0)

?

$dT/dr = \pm\infty$ at T = 0

GENERAL CASE

Tammann, 1903

T

$\Delta V{=}0$

$\Delta S{=}0$

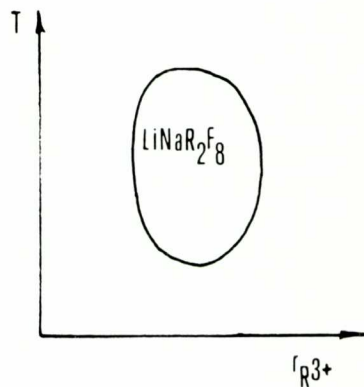$\Delta S{=}0$
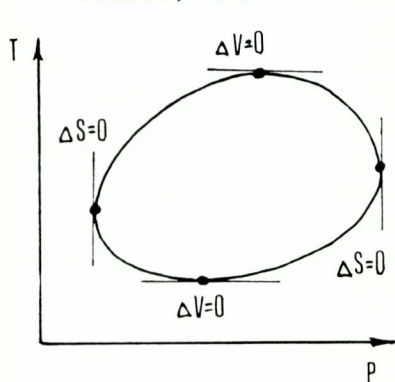
$\Delta V{=}0$

P

T

$LiNaR_2F_8$

r_{R3+}

Fig. 4. Relations between the phenomena of polymorphism and morphotropy.

On the basis of formal thermodynamic theory Tanmann predicted at the turn of the century the general case of polymorphic transition: closed ellipse-like curve [20,21]. Such a case has not been realized experimentally. The series of $LiNaR_2F_8$ compounds gives a similar example, but a morphotropic one.

ABSTRACT

The processes of formation and decomposition of $LiNaR_2F_8$ (R = Ho-Lu, Y) compounds have been studied using thermal and X-ray phase analysis techniques. The thermal stability of this structural type passes through the maximum in the family of rare earth elements, namely, erbium and thulium. All the compounds melt with decomposition and dissipate in solid state at temperatures below 500 °C. The stability region of these compounds in the coordinates "temperature – R^{3+} ionic radius" has an elliptical shape. Polymorphic and morphotropic structural changes are analyzed as similar phenomena, considered in different coordinates.

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