

## FUSION TEMPERATURES OF RARE EARTH METAL TRIHALIDES

I. A. KAHWA

Chemistry Department, University of Dar es Salaam, P. O. Box 35061, Dar es Salaam, Tanzania

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The fusion temperatures ( $T_f$ ) of rare earth metal trihalides  $\text{LnX}_3$  ( $\text{Ln} = \text{La} - \text{Lu}$ ,  $\text{Y}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) typically decrease to a minimum, before taking on an upward trend as the ionic radius of  $\text{Ln}^{3+}$  decreases. This trend is associated with the variations in the energetic stability of the coordination polyhedron around  $\text{Ln}^{3+}$ . A good correlation is obtained between the variations in the energetic stability of the crystal structure of  $\text{LnX}_3$  and  $T_f$ .

The fusion temperatures ( $T_f$ ) of a large number of rare earth metal trichlorides ( $\text{LnCl}_3$ ), tribromides ( $\text{LnBr}_3$ ) and triiodides ( $\text{LnI}_3$ ) are now known with satisfactory accuracy [1–3]. A prominent feature of the trend shown by the variations of  $T_f$  with increasing atomic number of the rare earth metal atom  $\text{Ln}$  ( $\text{Ln} = \text{La} - \text{Lu}$ ) is the occurrence of a minimum value of  $T_f$  for each of the three trihalide series (at  $\text{Ln} = \text{Tb}$  for  $\text{LnCl}_3$ ,  $\text{Ln} = \text{Sm}$  for  $\text{LnBr}_3$  and  $\text{Ln} = \text{Pr}$  for  $\text{LnI}_3$ ) (Table 1).

Table 1

Cation radii ( $r_i$ ) of  $\text{Ln}^{3+}$  and fusion temperatures ( $T_f$ ) of the  $\text{LnX}_3$  compounds.  $T_f$  values are from ref. 3 unless otherwise indicated

Ln	$r_i, \text{\AA}$	Fusion temperatures ( $T_f$ ), °C		
		$\text{LnCl}_3$	$\text{LnBr}_3$	$\text{LnI}_3$
La	1.061	852 <sup>a</sup>	789	772
Ce	1.034	831 <sup>a</sup>	—	752
Pr	1.031	778 <sup>a</sup>	691	737
Nd	0.995	754 <sup>a</sup>	684	775
Sm	0.964	668 <sup>a</sup>	640	850
Eu	0.950	624 <sup>b</sup>	702	877
Gd	0.938	628 <sup>a</sup>	—	926
Tb	0.923	588	827	946
Dy	0.908	718	881	955
Ho	0.894	718	914	986
Y	0.892	721	904	1004
Er	0.881	774	950	1020
Tm	0.869	824	952	1015
Yb	0.858	865	956	—
Lu	0.848	905	1025	1050

a: ref. 1    b: ref. 2

We have found that the variations in  $T_f$  are critically influenced by the radius of the  $\text{Ln}^{3+}$  cation. To explain this phenomenon, a close relationship between  $T_f$  and the energetic stability of the solid states of  $\text{LnX}_3$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) has been assumed. In accordance with this view,  $\text{LnX}_3$  compounds which are energetically relatively unstable fuse at low temperatures, and those which are energetically relatively more stable fuse at high temperatures.

### Experimental

The fusion temperatures (Table 1) used for this study are those reported in references [1–3]. The ionic radii ( $r_i$ ) of  $\text{Ln}^{3+}$  used to compare the fusion temperatures are averages obtained from several structures by Shannon and Prewitt [4] and refer to  $\text{Ln}^{3+}$  in hexacoordination.

The sources of the structural data used are appropriately indicated in the text.

### Results and discussion

A plot of  $T_f$  vs.  $r_i$  is given in Fig. 1. The three curves show systematic variations in  $T_f$  as  $r_i$  varies; minima are observed at  $\text{Ln} = \text{Tb}$  for  $\text{LnCl}_3$ ,  $\text{Ln} = \text{Sm}$  for  $\text{LnBr}_3$  and  $\text{Ln} = \text{Pr}$  for  $\text{LnI}_3$ .

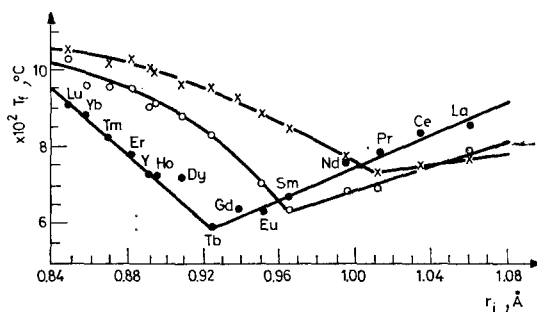


Fig. 1. Fusion temperatures ( $T_f$ ) of rare earth metal trichlorides (filled circles), tribromides (open circles) and triiodides (crosses) vs.  $r_i$

To explain these results, it is important to consider the relative stabilities of the  $\text{LnX}_3$  structures. Considerable polarization of the  $\text{X}^-$  anions by the highly charged  $\text{Ln}^{3+}$  cations is indicated by the relatively short  $\text{X}-\text{X}$  internuclear distances found in the known room-temperature structures of  $\text{LnX}_3$  (Table 2) [5–7]. In the case of  $\text{LnCl}_3$ , the average  $\text{Cl}-\text{Cl}$  distances lie in the range 3.31–3.49 Å, as compared to the theoretical value of 3.62 Å based on the ionic radius 1.81 Å for  $\text{Cl}^-$ . Short  $\text{X}-\text{X}$  distances are also found in the room-temperature structures of  $\text{UX}_3$  (Table 2) [8–10]. The  $\text{F}-\text{F}$  distances in  $\text{LnF}_3$  and  $\text{CeF}_3$  [15] are 2.728 and 2.710 Å, respectively, in good agreement with the theoretical value of 2.72 Å and the generally better

Table 2

Observed averages of X-X ( $\bar{d}_{X-X}$ ) and Ln-X ( $\bar{d}_{Ln-X}$ ) distances, effective ionic radii of Ln<sup>3+</sup> or U<sup>3+</sup> ( $r^+$ ) and X<sup>-</sup> ( $r^-$ ) and the radius ratio  $r^+/r^-$ . Probable errors in the last one or two digits appear in brackets

LnX <sub>3</sub> /UX <sub>3</sub>	$\bar{d}_{X-X}$ , Å	$r^-$ , Å	$\bar{d}_{Ln-X}$ , Å	$r^+$	$r^+/r^-$	Ref.
LnCl <sub>3</sub> ; Ln = La	3.412 (3)	1.706	2.951 (2)	1.245	0.730	6
Nd	3.356 (3)	1.678	2.898 (2)	1.220	0.727	6
Eu	3.321 (3)	1.661	2.863 (2)	1.203	0.724	6
Gd	3.312 (3)	1.656	2.854 (2)	1.198	0.723	6
Tb	3.458 (28)	1.729	2.808 (20)	1.079	0.624	5
Y	3.578 (30)	1.789	2.650 (30)	0.861	0.481	7
UX <sub>3</sub> ; X = Cl	3.394 (3)	1.697	2.957 (3)	1.260	0.742	9
Br	3.582 (3)	1.791	3.090 (2)	1.299	0.725	8
I	4.043 (12)	2.022	3.277 (10)	1.255	0.621	10

ability of the F<sup>-</sup> anion to resist polarization. The critical influence of polarization on the crystal structure of LnX<sub>3</sub> is put in perspective if the effective ionic radius of X<sup>-</sup> ( $r^-$ ), defined as one half the average of the observed X-X internuclear distances, and the effective ionic radius of Ln<sup>3+</sup>, defined as the difference between the average of the observed Ln-X distances and  $r^-$ , are used to obtain the radius ratio  $r^+/r^-$ . The empirical radius ratios so obtained (Table 2) are generally in good agreement with Pauling's geometrical rules for the stability of coordination polyhedra [12]. Within the limits of experimental error (except for TbCl<sub>3</sub> and UI<sub>3</sub>), these radius ratios are close to the value 0.732 required by Pauling for nona- and octa-coordination, and indicate that the high coordination number structure forms become increasingly unstable as the size of Ln<sup>3+</sup> decreases. Therefore, the alarming comments in several publications that octa and nona-coordinations in LnX<sub>3</sub> and UX<sub>3</sub> are obtained at significant variance with Pauling's radius ratio restrictions [8, 13, 14] are not justified, and appear to arise from the use of ionic radii which are not satisfactorily representative of the actual ionic environment.

The trend in Fig. 1, however, can not be explained in terms of covalence in the Ln-X bonds. The most satisfactory interpretation is obtained on assuming a close relationship between the variations in the energetic stability of the crystal structures and the variations in  $T_f$ . Differential thermal analysis (DTA) or a combination of DTA and X-ray crystallography [1, 2, 15] have revealed the absence of morphological transitions between room and fusion temperatures in some LnCl<sub>3</sub> compounds. A detailed study of NpBr<sub>3</sub> (UCl<sub>3</sub> structure) [13] confirmed the stability of the room-temperature structure between liquid nitrogen and its sublimation ( $\approx 800^\circ$ ) temperatures. It may thus be assumed that the trend shown by the relative energetic stabilities of the room-temperature structures of LnX<sub>3</sub> (Table 2) is reproduced without modifications of energetic significance at high temperatures. With this consideration, the good agreement between the points at which the minima in  $T_f$  occur

(Fig. 1) and the points at which the room-temperature structures are known to switch from one form to another is understood. The summary of  $\text{LnX}_3$  and  $\text{MX}_3$  ( $M =$  member of the actinium series) structures [13] indicates that the switch from nona- or octa-coordination to hexa-coordination occurs at  $\text{Ln} = \text{Tb}$  for  $\text{LnCl}_3$ ,  $\text{Ln} = \text{Eu}$  for  $\text{LnBr}_3$  and  $\text{Ln} = \text{Nd}$  for  $\text{LnI}_3$ . The occurrence of  $\text{LnX}_3$  with  $\text{Ln}^{3+}$  in nona-coordination and octa-coordination on the same side of the  $V$  curves (Fig. 1) indicates that the  $\text{UCl}_3$  and  $\text{PuBr}_3$  structures in  $\text{LnX}_3$  compounds have only small energetic differences. This is in good agreement with the observation that changes occurring in the room-temperature structures of  $\text{LnX}_3$  as the radius of  $\text{Ln}^{3+}$  decreases, do so with relatively small changes in molecular volume ( $Mv$ ) if the change is from the  $\text{UCl}_3$  to the  $\text{PuBr}_3$  structure, while relatively large  $Mv$  changes occur if the transition is from the  $\text{PuBr}_3$  to the  $\text{AlCl}_3$  or  $\text{FeCl}_3$  structures [6, 7, 11, 13, 16, 17].

It may thus be concluded that as the size of  $\text{Ln}^{3+}$  decreases the high coordination number (8, 9) modifications of  $\text{LnX}_3$  become increasingly unstable, and the energy required to randomize the crystal units (an essential feature of melting) decreases. When these modifications become too energetically unstable to exist, a lower coordination number (6) is adopted around  $\text{Ln}^{3+}$ , and a greater packing efficiency (and hence a greater energetic stability) is achieved as the size of  $\text{Ln}^{3+}$  decreases further. Accordingly, the  $T_f$  values decrease to a minimum and then take on an upward trend as the size of  $\text{Ln}^{3+}$  decreases. These results confirm the observations of Ubbelohde [18] that clear ideas about the melting process should be sought from the crystal structure.

### Conclusion

Although the association of high-temperature physical phenomena with physical properties at room temperature generally requires caution, in view of the above observations variations in the energetic stability of the coordination polyhedron around  $\text{Ln}^{3+}$  is the most satisfactory explanation of the results in Fig. 1. Strictly, the  $T_f$  values should be correlated with the radii corresponding to the coordination numbers applicable in the crystal structures, but this does not seem to be important for the comparisons made.

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ZUSAMMENFASSUNG — Die Schmelztemperaturen ( $T_f$ ) der Trihalide der Seltenen Erdmetalle  $\text{LnX}_3$  ( $\text{Ln} = \text{La} - \text{Lu}$ ,  $\text{Y}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) gehen mit abnehmendem Ionenradius von  $\text{Ln}^{3+}$  auf typische Weise durch ein Minimum. Dieser Trend wird mit den Unterschieden in der energetischen Stabilität der um das  $\text{Ln}^{3+}$ -Ion angeordneten Koordinationspolyeder in Verbindung gebracht. Es wurde eine gute Korrelation zwischen der energetischen Stabilität der Kristallstruktur und  $T_f$  erhalten.

Резюме — Температуры плавления трехгалогидных соединений редкоземельных элементов  $\text{LnX}_3$  ( $\text{Ln} = \text{La} - \text{Lu}$ ,  $\text{Y}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) сначала уменьшаются до минимума перед тенденцией к увеличению с уменьшением ионного радиуса редкоземельных элементов. Такая тенденция связана с изменением энергетической устойчивости координационного полиэдра вокруг  $\text{Ln}^{3+}$ . Получена хорошая корреляция между изменением энергетической устойчивости кристаллических структур  $\text{LnX}_3$  и их температурами плавления.