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Thermochemical and Structural Aspects of the Stability of Lamellar Structures

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Abstract — Thermochemical and crystal chemical analysis of the tolerance of the complex aluminates $LnCa(Sr)AlO_4$ to the decomposition into $LnAlO_3$ and Ca(Sr)O were performed.

Existence conditions and stabilization modes of complex inorganic compounds are fundamental problems of inorganic and structural chemistry. At present considerable theoretical and practical study is being given to electrical, magnetic, optical, catalytic, and mechanical properties of lamellar structures. However, in practical application of such structures one inevitably faces the problem of their stability and possible changes in their properties. Thus, unstable lamellar structures can, under certain conditions, decompose into structurally related phases.

Combined research into structural and thermodynamic properties of polyelement oxides may gain insight into the stability of structurally complex compounds. However, sufficiently correct thermodynamic properties of compounds in the condensed state are presently impossible to obtain by rigorous theoretical calculations. Therefore, there is an evident gap between abundant structural and insufficient thermochemical data for complex oxides. This gap can be overcome in two ways: by accelerated development of sophisticated experimental techniques and by development of new approaches to thermochemical description of the complex oxides whose crystal chemical parameters are already available. In this connection a polyhedral description which allows one to trace even slight variations in thermochemical properties on the formation of complex oxides from simple holds promise. Over the past years new methods for arbitrarily estimating thermodynamic properties of complex oxides, accounting for changes in cation coordination and tolerance factors and defining conditions for existence of complex structures have been proposed [1, 2].

In the present work we performed a thermochemical and crystal-chemical analysis of the stability of a series of aluminates that crystallize in the K_2NiF_4 structural type (see fugure; space group *I4/mmm*) and relate to the Ruddlesden–Popper phases $A_n^{+3}A^{+2}B_nO_{3n+1}$ (A^{+3} is a rare-earth metal cation, A^{+2} is an alkaline-earth metal cation, and B is Al or 3*d* metal) [3]. These phases are formed by the block principle from intergrowing perovskite (P) and rock salt (RS) fragments with ...$(P)_n(RS)(P)_n(RS)$... layer alternating. In these compounds, A atoms are 9- or 9- and 12- coordinate and B atoms are incorporated in BO_6 octahedra that form layers perpendicular to the structure axis. As shown in [4–6], these oxides feature a heterovalent stoichiometric isomorphism of A^{+3} and A^{+2} cations that occupy common structural sites, as well as a strong anisotropy of interatomic cation–anion interactions.

Structural aspects of the stability of the phases in hand have been considered in detail in [4, 5]. Let us summarize briefly the principal conclusions of these works, concerning the K_2NiF_4 structural type.

A widely used geometric criterion of the stability of perovskite-like complex oxides is the tolerance factor (*t*) [7] that allows for the degree of compatibility of the P and RS layers [Eq. (1)].

$$t_{P-RS} = \frac{R_A + R_O}{\sqrt{2}(R_{Al} + R_O)}. \quad (1)$$

Here R_i is ionic radius, $R_A = (R_A^{+3} + R_A^{+2})/2$ or, more rigorously, Eq. (2).

$$t_{P-RS} = \frac{d_{A-O}}{\sqrt{2}\, d_{Al-O}}. \quad (2)$$

Here d_{A-O} and d_{Al-O} are the mean interatomic distances in AO_9 and AlO_6 polyhedra, respectively. It is experimentally established that the oxide structure is stable if Eq. (3) is fulfilled.

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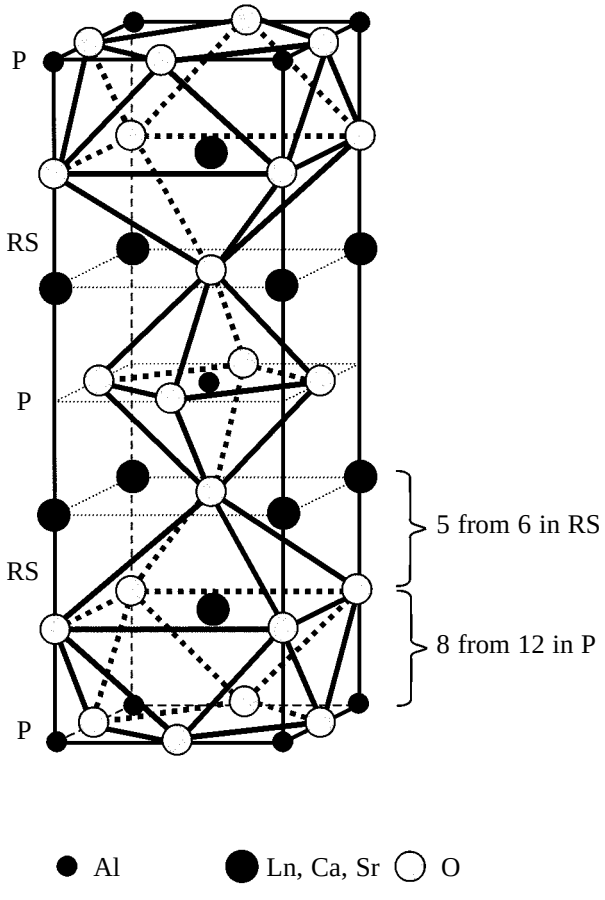
Table 1. Tolerance factors (t) and formation enthalpies of compounds from oxides ($\Delta_f H^{ox}$, kJ mol^{-1})

Parameter	Oxide				
	$YCaAlO_4$	$LaCaAlO_4$	$LaSrAlO_4$	$NdCaAlO_4$	$GdCaAlO_4$
t	0.941	0.949	0.965	0.946	0.946
$\Delta_f H^{ox}(7)$		–66	–102		
$\Delta_f H^{ox}(8)$		–62	–100		
$\Delta_f H^{ox}(9)$	–98	–107	–125	–103	–103
$\Delta_f H^{ox}$(exp)			–97.7		

$$0.85 \le t \le 1.0. \quad (3)$$

Table 1 lists the t factors for five compounds, calculated with experimental interatomic distances [6]. The oxides in hand meet condition (3), but the $LaCaAlO_4$ aluminate is distinguished by its thermal instability [8, 9] and undergoes decomposition above 900°C [scheme (4)] into $LaAlO_3$ (perovskite structure) and CaO (rock salt structure).

$$LaCaAlO_4 > LaAlO_3 + CaO. \quad (4)$$



AlO_6 and $(Ln,Ca)O_9$ coordination polyhedra in the unit cell of $LnCa(Sr)AlO_4$ lamellar complex oxides.

Comparison of the tolerance factors of lamellar oxides and related oxides with the perovskite structure shows that condition (3) is necessary but insufficient. Of importance is the difference in the tolerance factors Δt: If it is considerable, more stable is the perovskite complex, which is the case with $LaCaAlO_4$. This fact reflects the difficulty in adaptation of certain ions (here calcium) to oxygen tetrahedra on passing from one crystal structure to another.

The thermochemical aspect of the assessment of the tolerance of $LnCa(Sr)AlO_4$ to decomposition involves calculation by Eq. (6) of the enthalpy of reaction (5).

$$LnCa(Sr)AlO_4 = LnAlO_3 + Ca(Sr)O, \quad (5)$$

$$\Delta_r H = \Delta_f H(LnAlO_3) + \Delta_f H[Ca(Sr)O] - \Delta_f H[LnCa(Sr)AlO_4]. \quad (6)$$

The reaction is thermodynamically probable, if $\Delta_r H < 0$, whereas $LnCa(Sr)AlO_4$ is stable at $\Delta_r H > 0$.

Because of the lack of entropy data for many of the compounds we failed to calculate the Gibbs energies of the reactions. However, solid-phase reactions most commonly have low entropies below 1000–1200°C, and enthalpy estimates will suffice.

The crystal-chemical evidence for lamellar oxides is indicative of a considerable structural and bond anisotropy associated with the strain produced by junction of two not fully commensurate layers. The intergrowth of two parent structures (perovskite and rock salt) in forming a lamellar structure is most commonly facilitated by the distortion of BO_6 octahedra and AO_9 polyhedra by simultaneous lengthening and shortening of axial (along the c axis) B–O and A–O bonds, respectively. Therewith, B atoms remain 6-coordinate, as in perovskite, whereas the environment of A atoms changes substantially. Their 9-coordinate state can be considered as partly formed from 12-coordinate, like Ln atoms in oxides with the perovskite structure, and 6-coordinate, like alkaline-

Table 2. Enthalpies of changes in cation coordination numbers (δH) [12]

Cation	Change in coordination number	δH, kJ mo^{-1}	Cation	Change in coordination number	δH, kJ mo^{-1}
Ca^{+2}	$6 \to 9$	–50	Nd^{+3}	$6O + 2\square \to 8$	4
	$6 \to 12$	–56		$6O + 2\square \to 12$	–19
Sr^{+2}	$6 \to 9$	–90	Gd^{+3}	$6O + 2\square \to 8$	33
	$6 \to 12$	–110		$6O + 2\square \to 12$	–16
La^{+3}	$7 \to 9$	–31	Y^{+3}	$6O + 2\square \to 8$	71
	$7 \to 12$	–33			

metal atoms in oxides with the rock salt structure (see figure) [8].

The thermochemical aspect of the assessment of the tolerance of $LnCa(Sr)AlO_4$ to decomposition involves consideration of the enthalpy of a reaction involving change in the coordination numbers of the cations.

$$\underset{9\ 9}{LnCa(Sr)AlO_4} = \underset{12\ 6}{LnAlO_3} + \underset{6}{Ca(Sr)O}.$$

The coordination numbers of the cations in their oxygen environments are shown under the formulas.

The formation enthalpies $\Delta_f H_{298}(LnAlO_3)$ (Ln = Y, La, Nd, Gd) were calculated by the formation enthalpies of aluminates from simple oxides ΔH^{ox} and $\Delta_f H_{298}$, systematized in the handbook [10] which offers at present the best system of consistent thermal constants. The $\Delta_f H^{ox}(LaSrAlO_4)$ value of –97.7 kJ mol^{-1} was reported in [11]. For $YCaAlO_4$, $LaCaAlO_4$, $NdCaAlO_4$, and $GdCaAlO_4$, no experimental $\Delta_f H^{ox}$ values are available, but they can be estimated by arbitrary equations like (7) and (8) based on thermochemical data [12].

$$\Delta_f H^{ox}[LnCa(Sr)AlO_4] = 6.6 + 0.9\Sigma\delta H, \text{ kJ mol}^{-1}, \quad (7)$$

$$\Delta_f H^{ox}[LnCa(Sr)AlO_4] = 23.57 + 0.98\Sigma\delta H - 113.2(1 - t), \text{ kJ mol}^{-1}. \quad (8)$$

Here $\Sigma\delta H$ is the sum of the enthalpies of changes in cation coordination numbers on the formation of the compound from simple oxides and t is the tolerance factor.

The δH values for the change in the coordination number of Y, Nd, and Gd in going from Ln_2O_3 with the Tl_2O_3-type structure to the $LnCa(Sr)AlO_4$ ($6O + 2\square > 9$ transition, $\square$ is vacancy) are unknown, which make Eqs. (7) and (8) impractical. In this case, one make use of the more approximate, "purely structural" Eq. (9).

Table 3. Formation enthalpies of oxides ($\Delta_f H_{298}$, kJ mol^{-1})

Oxide	$-\Delta_f H_{298}$	Oxide	$-\Delta_f H_{298}$	Oxide	$-\Delta_f H_{298}$
CaO	635.1	La_2O_3	1795	$LaAlO_3$	1795.2
SrO	590.5	Nd_2O_3	1808.4	$NdAlO_3$	1789.4
Al_2O_3	1675.8	Gd_2O_3	1820.4	$GdAlO_3$	1785.8
Y_2O_3	1905	$YAlO_3$	1798.8		

$$\Delta_f H^{ox}[LnCa(Sr)AlO_4] = 3[-55.4 + 388(1 - t)], \text{ kJ mol}^{-1}. \quad (9)$$

Table 1 lists the formation enthalpies of $LnCa(Sr)\cdot AlO_4$, calculated by Eqs. (7)–(9). In the calculations we used the δH(M) values listed in Table 2 [1, 2] and the $\Delta_f H_{298}$ values for simple oxides and $LnAlO_3$, listed in Table 3 [10]. The $\Delta_f H_{298}$ values were calculated with $\Delta_f H^{ox}(YCaAlO_4)$ –98, $\Delta_f H^{ox}(LaCaAlO_4)$ –62, $\Delta_f H^{ox}(NdCaAlO_4)$ –103, $\Delta_f H^{ox}(GdCaAlO_4)$ –103, and $\Delta_f H^{ox}(LaSrAlO_4)$ –97.7 kJ mol^{-1}. The choice of the $\Delta_f H^{ox}$ value for $LaCaAlO_4$ is motivated by the fact that the two-parameter equation (8) best fits the limited set of thermochemical data for compounds of the K_2NiF_4 type [1]; this is evidenced by a comparison of the $\Delta_f H^{ox}$ values for $LaSrAlO_4$, calculated by Eqs. (7)–(9) and obtained experimentally.

Table 4 lists the calculated enthalpies $\Delta_r H$ of the decomposition of $LnCa(Sr)AlO_4$ into $LnAlO_3$ and CaO or SrO. The $\Delta_f H^{ox}$ value for $LaCaAlO_4$ can be calculated by an alternative and a more traditional way, based on the assumption that the $\Delta_f H^{ox}(CaMO_x) - \Delta_f H^{ox}(SrMO_x)$ difference (M is an element that forms a more "acidic" oxide) is roughly constant. Analysis of thermochemical data for 10 pairs of related Ca and Sr compounds ($CaAl_2O_4/SrAl_2O_4$, $CaTiO_3/SrTiO_3$, $CaWO_4/SrWO_4$, etc.) leads to $\Delta_f H^{ox}(CaMO_x) = \Delta_f H^{ox}(SrMO_x 24)) + (50 \pm 10)$ kJ mol^{-1}, implying that Ca compounds are formed from oxides by less exothermic reactions than Sr compounds. This result is generally not inconsistent with the dif-

Table 4. Decomposition enthalpies of $LnCa(Sr)AlO_4$ into $LnAlO_3$ and Ca(Sr)O ($\Delta_r H$, kJ mol^{-1})

Decomposition reaction	$\Delta_r H$
$YCaAlO_4 = YAlO_3 + CaO$	90
$LaCaAlO_4 = LaAlO_3 + CaO$	20
	–12[a]
$LaSrAlO_4 = LaAlO_3 + SrO$	38
$NdCaAlO_4 = NdAlO_3 + CaO$	56
$GdCaAlO_4 = GdAlO_3 + CaO$	65

[a] Alternative estimate.

ference of the accepted values [$\Delta H^{ox}(LaCaAlO_4 - LaSrAlO_4)$ = –62–(–98) = 36 kJ mol^{-1}) and close to the mean difference 50 ± 10 kJ mol^{-1}. This variant of calculations gives $\Delta_r H$ –12 kJ mol^{-1} < 0 for the decomposition of $LaCaAlO_4$. Probably, Eq. (9) provides overestimated (in absolute value) $\Delta_f H^{ox}$ for $YCaAlO_4$, $NdCaAlO_4$, and $GdCaAlO_4$, as seen from a comparison of the results for $LaSrAlO_4$ and $LaCaAlO_4$, obtained by different equations. Nevertheless, even if the $\Delta_f H^{ox}$ values are increased by 40%, the decomposition enthalpies of $YCaAlO_4$, $NdCaAlO_4$, and $GdCaAlO_4$ still remain essentially positive.

It should be noted that at $\Delta_r H \sim |40$ kJ| one can predict with confidence reaction at fairly low temperatures [13], whereas the enthalpy of most polymorphous transitions is ~10 kJ mol^{-1} [10]. Our estimates for $\Delta_r H$ suggest that $LaCaAlO_4$ is the only of the oxides in hand, that may decompose at high temperatures, while the other complex oxides $LnCa(Sr)AlO_4$ are thermochemically stable, as evidenced by the experimental data and structural aspects of stability.

Thus, the "enthalpy" calculation of the direction of the decomposition reaction of compounds of the K_2NiF_4-type structure is fairly consistent with crystal-chemical data and the experimentally observed thermal instability of the $LaCaAlO_4$ oxide in the series of isostructural compounds $LnCa(Sr)AlO_4$.

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