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Mechanism and Kinetics of Formation of $La_2SrFe_2O_7$ and $Nb_2SrFe_2O_7$

E. A. Tugova[a], V. F. Popova[a], I. A. Zvereva[b], and V. V. Gusarov[a]

[a] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, nab. Admirala Makarova 2, St. Petersburg, 199034 Russia*
e-mail: katugova@inbox.ru
[b] *St. Petersburg State University, St. Petersburg, Russia*

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Abstract — Phase formation processes in the systems Ln_2O_3–SrO–Fe_2O_3 (Ln = La, Nd) in air in the temperature range 1200–1500°C were studied. The synthesis of the complex ferrites $La_2SrFe_2O_7$ and $Nb_2SrFe_2O_7$ involves the formation of the intermediate compounds $LnFeO_3$ and $LnSrFeO_4$ and occurs by the same mechanism as the synthesis of the corresponding aluminates, but much faster.
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Perovskite-like layered compounds attract researchers' attention due to their unique electrophysical, catalytic, and optical properties [1–3]. Oxides $Ln_2SrM_2O_7$ (Ln is a rare-earth element, M = Al, Fe) are of the $Sr_3Ti_2O_7$ structural type and belong to Ruddlesden–Popper phases [4, 5].

The mechanism and kinetics of solid-phase reactions of the $Ln_2SrAl_2O_7$ (Ln = La–Ho) formation were studied in [6–8]. It was found that these compounds are formed via certain intermediates. The intermediate phases for Ln = La–Sm are $LnAlO_3$ and $LnSrAlO_4$ [6, 7], and for Ln = Gd–Ho, the intermediate compound is $SrAl_2O_4$ [8–10].

Polycrystalline samples of $Ln_2SrFe_2O_7$ (Ln = La, Nd, Sm, Gd) were prepared by the solid-phase synthesis in an oxygen atmosphere [11], whereas single crystals of $Eu_2SrFe_2O_7$ were prepared from a solution in a PbO melt [12]. However, data on the mechanism and kinetics of formation of $Ln_2SrFe_2O_7$ are lacking.

Phase equilibria in the system $LaFeO_3$–$LaSrFeO_4$ were studied in [13], and one compound $La_2SrFe_2O_7$ stable in the subsolidus region and melting incongruently was found. In this study we examined the mechanism and kinetics of solid-phase reactions of the formation of $Ln_2SrFe_2O_7$ (Ln = La, Nd) in air.

A charge with the stoichiometric composition corresponding to the compound $La_2SrFe_2O_7$ was subjected to thermal analysis in the course of heating to 1400°C (Fig. 1); two strong endothermic effects at 344–422 and 489–578°C, accompanied by weight loss of 4.59 and 1.58%, respectively, were revealed. These effects correspond to the stepwise dehydration of $La(OH)_3$ with the formation of lanthanum oxyhydroxide and oxide, respectively, which is proved by the sample weight loss and by the data on the decomposition temperature of lanthanum hydroxide [14]. The presence of lanthanum hydroxide in the starting mixture is caused by the specific procedure of sample preparation, involving powdering and mixing of components in distilled water, and by the reactivity of lanthanum oxide toward water. Starting from 730°C, two more endothermic effects accompanied by a weight loss are clearly seen in the thermogram (Fig. 1). They are complete at 1100°C. These effects result from the decomposition of strontium carbonate conjugated with the formation of $LaSrFeO_4$, as follows the X-ray diffraction patterns.

As the temperature is increased to 1200–1300°C, a sharp increase in the rate of formation of $LnSrFeO_4$ and $LnFeO_3$ (Ln = La, Nd) is observed, the starting oxides completely disappear from the mixtures, and $Ln_2SrFe_2O_7$ starts to form (see table).

The X-ray diffraction pattern of the sample of the stoichiometric composition $Nb_2SrFe_2O_7$ heat-treated at 1200°C (Fig. 2) shows that, along with a small amount of the final reaction product, it contains the compounds $NdFeO_3$ (perovskite structural type) and $NdSrFeO_4$ (K_2NiF_4 structural type). It is known that at temperatures exceeding 1380°C iron(III) oxide dissociates to form Fe_3O_4 [15]. The thermal analysis (DTA, TG) of the mixture of the stoichiometric composition $La_2SrFe_2O_7$ (Fig. 1) in air revealed no effects attributable to changes in the iron(III) oxidation

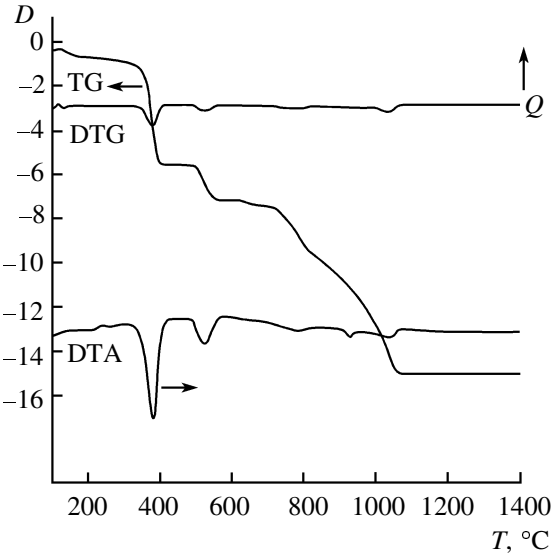

Fig. 1. Results of differential thermal analysis of the starting mixture of the composition $La_2SrFe_2O_7$. (*D*) Weight loss, mg (initial sample weight 99.6 mg) and (*Q*) thermal effect (the arrow denotes the direction of exothermic effects).

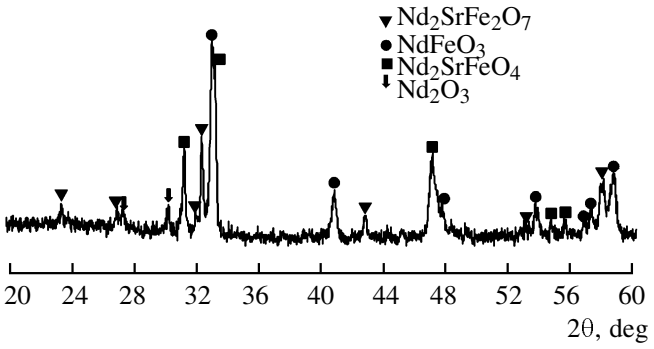

Fig. 2. X-ray pattern of the reaction mixture corresponding in the stoichiometric composition to $Nb_2SrFe_2O_7$ after calcination for 3 h at 1200°C.

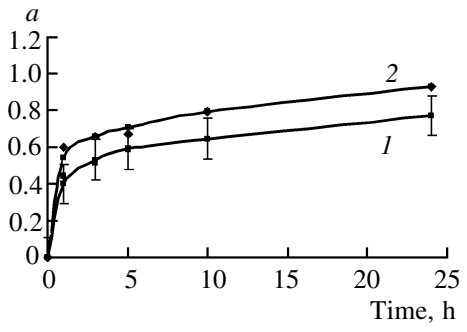

Fig. 3. Kinetics of the $La_2SrFe_2O_7$ formation: (*1*) 1300 and (*2*) 1400°C. (*a*) Degree of conversion to $La_2SrFe_2O_7$.

state. The results of the thermal analysis and also the data of X-ray phase analysis of the samples obtained by heat treatment in the annealing–quenching mode (see table) show that the intermediate compounds $LnFeO_3$ and $LnSrFeO_4$ are formed fairly rapidly at temperatures of up to 1200°C. This fact suggests that the intermediate compounds are formed at temperatures lower than the temperature of the Fe_2O_3 conversion to Fe_3O_4 and that the iron(III) state is stabilized in $LnFeO_3$ and $LnSrFeO_4$.

When the mixtures are sintered in the range 1400–1500°C, the rate of the $Ln_2SrFe_2O_7$ formation increases owing to the reaction of $LnSrFeO_4$ with $LnFeO_3$ (see table). The solid-phase reaction at 1500°C, performed for 3 h, is complete, yielding the final synthesis product, $La_2SrFe_2O_7$ or $Nb_2SrFe_2O_7$.

The degree of conversion to the final product $La_2SrFe_2O_7$ was determined for temperatures of 1300 and 1400°C in relation to the reaction time in the range 1–24 h. This is illustrated by kinetic curves in Fig. 3.

A comparative analysis of the kinetics of $La_2Sr\cdot Fe_2O_7$ and $La_2SrAl_2O_7$ formation shows that the degree of the aluminate conversion in 24 h at 1300°C does not exceed 0.2, and for the ferrite it is 0.8 [6]. This fact indicates that the rate of the ferrite formation considerably exceeds the rate of the aluminate formation and requires lower temperatures.

Our results show that the compounds $Ln_2SrFe_2O_7$ (Ln = La, Nd) are formed by a solid-phase reaction of the simple oxides, occurring by the same mechanism (through the same series of intermediate compounds) as the formation of compounds $Ln_2SrAl_2O_7$, but at a considerably higher rate.

Phase composition of products formed by sintering of metal oxide mixtures corresponding to the stoichiometry of the compounds $Ln_2SrFe_2O_7$ (Ln = La, Nd)

Heat treatment mode		Phase composition of samples after heat treatment
temperature, °C	duration, h	
1200	3–5	$LnFeO_3$, $LnSrFeO_4$ (starting components, traces), $Ln_2SrFe_2O_7$ (traces)
1300	3–24	$Ln_2SrFe_2O_7$ (traces), $LnFeO_3$, $LnSrFeO_4$
1400	1–24	$Ln_2SrFe_2O_7$, $LnFeO_3$ + $LnSrFeO_4$ (traces)
1500	3	$Ln_2SrFe_2O_7$

EXPERIMENTAL

The thermal experiments (TG, DTG, and DTA curves were recorded) were performed on a Paulik–Paulik–Erdey Q-1500C (MOM, Hungary) device at a heating rate of 10 deg min^{-1}. The phase analysis of the sintered products was performed by X-ray diffraction with a DRON-3 diffractometer (CuK_α radiation, Ni filter).

The following chemicals were used for preparing the starting mixtures: La_2O_3, Nd_2O_3 (SST grade, 99.99% content of the main component), $SrCO_3$ [ultrapure 7-2 grade, TU (Technical Specification) 6-09-01-659-91], and Fe_2O_3 (analytically pure grade, dried for 2 h at 300°C). The reactant mixtures corresponding to the $Ln_2SrFe_2O_7$ stoichometry were thoroughly triturated with distilled water in a corundum mortar, dried, and pressed as cylinders 15 mm in diameter and 3–4 mm thick under a pressure of 500 MPa. The crucible with samples was placed in a cold furnace, heated to a required temperature, kept at this temperature for a required time, and cooled with the furnace. The samples were sintered in air in a furnace with platinum heaters. The temperature in the reaction zone and the heating time were controlled with an RIF-101 precision (±1°) programmed temperature regulator.

The quantitative compositions of the reaction mixtures were determined by quantitative X-ray phase analysis in the range of 2θ angles 35°–45°. The choice of this range was governed by the fact that it covers the characteristic reflections of the mixture components: for $LaFeO_3$, 2θ = 39.44°; for $LaSrFeO_4$, 2θ = 43.51°; and for $La_2SrFe_2O_7$, 2θ = 44.13°. The calibration was carried out using the mixtures of equivalent amounts of the components: $LaFeO_3$–$La_2SrFe_2O_7$ (1 : 1) and $LaSrFeO_4$–$La_2SrFe_2O_7$ (1 : 1). The ratio of their intensities for equimolar amounts is as follows: $I(39.44) : I(43.51) : I(44.23) = 0.565 : 0.761 : 1$.

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