



# The $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$ system: Relationships for equilibrium-phase and supercooled states

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## Abstract

The phase diagram of the  $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$  system has been defined showing all three compounds existing in the system, i.e. with molar ratios 2:1, 1:1 and 3:5, which exhibit strongly differing stabilities. The range of stability of the perovskite phase has been estimated to lie approximately in between 1750 and 1930 °C. The range of solid solutions of the garnet phase and the lower border of stability of the monoclinic phase are also shown in the diagram.

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## 1. Introduction

Since many decades, the rare-earth aluminum garnets and perovskites are of high interest to solid-state laser research and technology [1]. More recently, they gained also importance, as scintillator host materials in many application fields, in particular in nuclear medical imaging [2]. For the latter application, high density and atomic number become important to provide for high stopping power and high detection efficiency for gamma-rays. In this respect, compounds existing in the  $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$  system are most attractive, since they include large amounts of heavy lutetium and are transparent in the UV range of emission of rare-earth luminescent ions, such as  $\text{Ce}^{3+}$  or  $\text{Yb}^{3+}$ . One of them, lutetium aluminum perovskite doped with trivalent cerium ( $\text{LuAlO}_3\text{--Ce}^{3+}$ , LuAP) possessing high density (8.34 g/cm<sup>3</sup>), high photoelectric fraction (32.1% for 511 keV), fast decay (18 ns) and relatively high

light yield (11,400 ph/MeV) is one of the prime scintillator materials for next generation positron emission tomography (PET). The crystal clear collaboration (CCC) [3] has developed small animal PET scanners called Clear PET, which employ  $\text{LuAlO}_3$  and similar crystals.  $\text{LuAlO}_3$  is an unstable compound and exhibits complexities in solidification behavior; understanding of processes resulting from thermal instability requires knowledge of phase relationships and is crucial for development of reliable production technologies of quality single crystals.

Phase relations in  $\text{Ln}_2\text{O}_3\text{--Al}_2\text{O}_3$  systems have been studied for all members of the lanthanide (Ln) family [4]. Four types of compounds exist in these systems, i.e. with molar ratio of oxides equal to 2:1, 1:1, 3:5 and 1:11. Stability and physical properties of these compounds depend on the electron shell structure, intrinsic basicity, cation size, and coordination number of the rare earth, as well as the coordination number of Al. Thus, 1:1 compounds ( $\text{LnAlO}_3$ ) based on large rare earths are stable compounds, while stability drastically decreases upon moving to smaller rare earths [4]. The possibility of

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formation of the end-member,  $\text{LuAlO}_3$ , under normal pressures was being even denied until the work [5], in which growth of  $\text{LuAlO}_3$  single crystals by Czochralski method was reported. In order to reveal the conditions of formation of the perovskite phase, phase equilibria in the  $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$  system were studied in Ref. [6] and the phase diagram was defined in the temperature range 1000–2300 °C. Subsolidus relations in the system were studied in air by traditional methods of heating and quenching. The solidus and liquidus lines were determined in argon atmosphere using the Galakhov micro-furnace [7]. Note that Lu and Al have stable oxidation states (III) in a wide range of the oxidizing–reducing potential [8], so that the changes in phase states in condensed systems will not depend on the change in the mentioned limits of the partial pressure of oxygen in the co-existing gaseous phase;  $\text{Lu}_2\text{O}_3$  does not exhibit polymorphism and exists only in a cubic form stable up to the melting point [9].

It was shown [6] that  $\text{Lu}_4\text{Al}_2\text{O}_9$  (monoclinic structure) and  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  (garnet-type structure) could be sintered by means of solid-state reactions technique upon heating of stoichiometric mixtures of lutetium oxide and alumina, while it was not possible to manage with preparation of the perovskite phase by applying the same technique. The  $\text{LuAlO}_3$  compound was obtained by crystallization of undercooled melts [5,6]. Studies of thermal stability of  $\text{LuAlO}_3$  single crystals grown by Czochralski techniques have shown that  $\text{LuAlO}_3$  decomposes separating  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  and  $\text{Lu}_2\text{O}_3$  phases, when heated above 1000 °C; the phases observed upon heating to the melting point were  $\text{Lu}_4\text{Al}_2\text{O}_9$  and  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  [6,10]. Stability range of the perovskite phase was thus not established and a conclusion was made suggesting a metastable character of its formation upon solidification of the melt. The perovskite phase was not for this reason shown on the equilibrium phase diagram of the  $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$  system; a metastable version was given for the portion of the diagram with the thermal maximum of the perovskite phase [6]. Two eutectic points (between 2:1 and 3:5, and between 3:5 and alumina) and one reactionary point, in which the 2:1 phase decomposes into  $\text{Lu}_2\text{O}_3$  and liquid, were shown in the diagram.

Further studies [11–14] employing the vertical Bridgman process in argon/hydrogen atmosphere have shown that high quality  $\text{LuAlO}_3$  single crystals can be obtained under conditions near to equilibrium. It was observed that in unseeded melts the perovskite phase could be nucleated only if a sufficiently high degree of supercooling was present at the solidification point (see Refs. [11,14] for more details); when formed, the perovskite phase is stable above the spontaneous solidification point and melts at ~1900 °C [12]. It has been also shown that the ability of melts to undergo supercooling is governed by the overheating temperature and the time of heating in the molten state [13,14]. Basing on the solidification behavior of  $\text{LuAlO}_3$ , schemes were developed providing for growth of high quality crystalline material, the details of which were described in Ref. [14].

The accumulated results indicate quite complex phase relationships in the  $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$  system, which can be described by various versions of phase diagrams. The objective of this study is to define the phase diagram of the  $\text{Lu}_2\text{O}_3\text{--Al}_2\text{O}_3$  system, and more especially, the part concerning the perovskite phase.

## 2. Experimental procedure

Stoichiometric mixtures of  $\text{Lu}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  were prepared from high (99.99%) purity component oxides taken in 1:1 ratio and heat treated under argon/hydrogen atmosphere in a resistively heated vertical Bridgman furnace described in Ref. [14]. Heat treatments were performed at temperatures above 1650 °C and applying high rates of heating and cooling that seemed critical to the results. The treatments were performed under the following conditions: argon/hydrogen atmosphere, raising rate ~3000 °C/min, heating time 5 min followed by rapid cooling. To provide for rapid heating, the samples were introduced into the hot zone, which was preliminarily heated to the selected temperature. After the heating, the samples were rapidly pulled down to the cold zone. The raising rate was estimated by measuring the time space required for melting of samples (followed visually) in runs, in which the selected temperature was slightly exceeding the melting point. Another set of 1 $\text{Lu}_2\text{O}_3$ :1 $\text{Al}_2\text{O}_3$  mixtures were heat treated in the Galakhov resistively heated tungsten micro-furnace [7] under the following conditions: argon or helium atmosphere, raising rate ~3000 °C/min, heating time 3 min, and rapid sample cooling.

The phases present in the heat treated samples were identified by X-ray powder diffraction technique (DRF-2.0).

## 3. Results and discussion

1 $\text{Lu}_2\text{O}_3$ :1 $\text{Al}_2\text{O}_3$  mixtures heat-treated both in the Bridgman furnace and Galakhov micro-furnace have shown similar phase compositions. At treatment temperatures below 1750 °C the perovskite phase is not observed: the phases present are either 3:5 and  $\text{Lu}_2\text{O}_3$  (at treatments temperatures at 1650 °C and lower temperatures), or 2:1 and 3:5<sub>ss</sub> (at treatment temperatures in the range from 1650 to ~1750 °C). The perovskite phase has been detected in 1 $\text{Lu}_2\text{O}_3$ :1 $\text{Al}_2\text{O}_3$  charges subjected to heat treatments at 1880–1900 °C.

Stability of the perovskite phase at temperatures above 1700 °C was observed in annealing experiments [15], in which the single crystals were raised from room temperature to ~1700 °C at a rate ~2000 °C/min to escape phase decomposition that would otherwise proceed at lower temperatures during slow rate heating of samples. Single crystals of  $\text{LuAlO}_3$  decomposed into 3:5 and 2:1 when heated in the Galakhov micro-furnace at a temperature near to 1930 °C [10]. On the other hand, studies of solidification of melts in Ref. [11] have shown that the

perovskite phase can be nucleated only when sufficiently high supercooling is present at the solidification point. Thus, it can be concluded that the  $\text{LuAlO}_3$  perovskite has a narrow stability range, approximately located at 1750–1930 °C, outside which it decomposes separating the two neighboring phases:  $\text{Lu}_4\text{Al}_2\text{O}_9$  and  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ .

The phase diagram of the  $\text{Lu}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  system in argon–hydrogen atmosphere is presented in Fig. 1 showing all three chemical compounds ( $\text{Lu}_4\text{Al}_2\text{O}_9$ ,  $\text{LuAlO}_3$  and  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ ) existing in the system and which exhibit different stabilities. In contrast to the earlier phase diagram [6], the present diagram shows the range of stable existence of the perovskite phase, confirmed by experimental results obtained in this work on formation of  $\text{LuAlO}_3$  by solid-state reactions of lutetium and aluminum oxides. Since this range is very small, the exact boundaries have been defined only approximately and therefore are shown by a dotted line. Due to narrow existence range, high temperatures involved and slow rate of formation, it is difficult to obtain homogeneous perovskite samples by solid-state reactions. In some cases, when the treatment duration is insufficient or the applied temperature does not match the stability range of the perovskite phase, the latter cannot be formed and a two-phase equilibrium is being established between 2:1 and 3:5. The range of existence of the 1:1 phase could not be revealed under slow rate heating and cooling, therefore this phase can be considered as stable only under certain conditions. The kinetic factor in heat treatments of 1 $\text{Lu}_2\text{O}_3$ :1 $\text{Al}_2\text{O}_3$  mixtures is probably the most important in explaining the different results obtained in Ref. [6] and in the present study (experiments [6] were performed under rates 200–400 °C/h of heating and cooling). Single crystals of the perovskite phase can be optimally obtained at cooling the melts from temperatures above the liquidus line

and running crystallization at a temperature matching the range of its stable existence.

The monoclinic (2:1) phase shown on the earlier phase diagram [6] as stable over the whole temperature range has, according to Ref. [11], a lower border of stability (Fig. 1), but is more stable than the perovskite phase. This is confirmed also by observation that formation of the monoclinic phase  $\text{Lu}_4\text{Al}_2\text{O}_9$  takes place at 1650 °C and higher temperatures [6], but the samples treated below the melting point are commonly multiphase and contain in addition 3:5 and  $\text{Lu}_2\text{O}_3$  phases. This phase transforms at high temperature annealing into 3:5 and  $\text{Lu}_2\text{O}_3$  [11].  $\text{Lu}_4\text{Al}_2\text{O}_9$  melts incongruently at 2000 °C, above which liquid and  $\text{Lu}_2\text{O}_3$  are in equilibrium [6]. Single phase  $\text{Lu}_4\text{Al}_2\text{O}_9$  solidifies in the absence or low (~0–30 °C) degree of melt supercooling [11], therefore it can be optimally obtained near to the peritectic melting at around 2000 °C (Fig. 1).

The garnet phase,  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ , is the most stable in the system; it is stable over the whole range from room temperature up to the temperature of congruent melting at 2060 °C (Fig. 1). This compound can be easily obtained in single-phase polycrystalline form by solid-state reactions or in the form of single crystals by melt techniques. At high melt supercoolings (200–240 °C) and absence of a seed, formation of  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  at cooling down the 3:5 melts from temperatures above the liquidus line is impossible [11] (similar behavior is known for  $\text{Y}_3\text{Al}_5\text{O}_{12}$  [16,17] and  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  [18] melts and has been attributed to difficulties of nucleation in supercooled melts of the garnet phase with 160 atoms in the unit cell, as compared to other phases [16]). It has been also shown [19] that the equimolar 3:5 compound has a concentration homogeneity range (about 4 mass%  $\text{Lu}_2\text{O}_3$ ). As compared to the earlier phase diagram [6], the range of garnet solid solutions is also shown in the figure. In order to obtain high quality  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  single crystals, the starting melts must contain a slight excess of  $\text{Lu}_2\text{O}_3$  to compensate the octahedral site occupancy by lutetium ions.

The phase diagram is defined in argon/hydrogen atmosphere however, since there are no variations in oxidation states due to valence transitions, there should be only small (if any) effect of partial pressure of oxygen upon the form of the phase diagram.

#### 4. Conclusions

Part of the phase diagram of the  $\text{Lu}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  system concerning the perovskite phase is defined (Fig. 1) basing on experimental results obtained in the present work and in earlier studies [6,10–14]. The range of stability of the perovskite phase is quite small, approximately 1750–1930 °C, that is the major factor placing difficulties in crystal growth of this compound from the melt. The garnet phase,  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ , is stable over the whole range from room temperature up to the temperature of congruent melting at 2060 °C and has a solid solution homogeneity

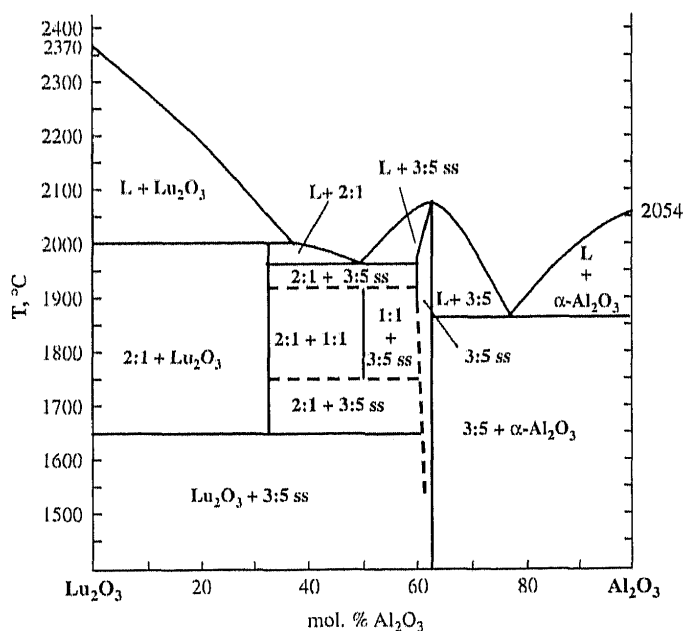


Fig. 1. The phase diagram of the  $\text{Lu}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  system.

range of about 4 mass%, which is also shown on the present diagram. The monoclinic phase,  $\text{Lu}_4\text{Al}_2\text{O}_9$ , is stable in a limited temperature range, approximately 1650–2000 °C.

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