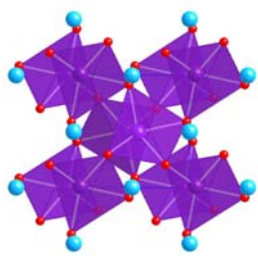


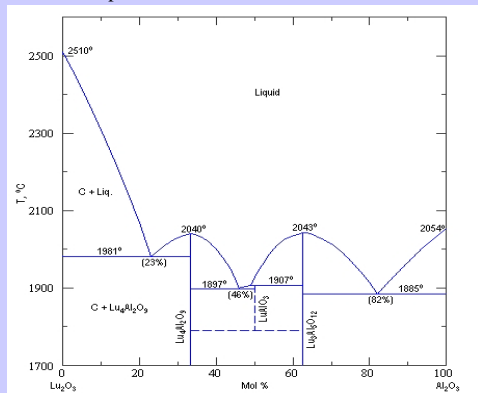
Phase Equilibria and Crystal Chemistry in the Lu₂O₃-Al₂O₃ System



YAIO₃

Introduction

Single crystal cerium-doped LuAlO₃ has the potential of being used in numerous applications including nuclear medicine, security monitoring, geophysical exploration, and non-destructive testing where efficient and fast scintillators are required. The calculated phase diagram for the Lu₂O₃-Al₂O₃ system [1] shows the compounds Lu₃Al₅O₁₂ with the garnet structure (LuAG) [2], LuAlO₃ with the perovskite structure (LuAP) [3], and Lu₄Al₂O₉ that crystallizes in the monoclinic crystal system (LuAM) [4]. The calculated phase diagram shows LuAlO₃ as an incongruently melting compound indicating that growing large crystals from the melt (vertical Bridgman or Czochralski methods) would be impossible. To experimentally determine the phase equilibria in the Lu₂O₃-Al₂O₃ system various compositions have been investigated using solid-state synthesis as well as the citrate-nitrate method. X-ray powder diffraction data revealed three phases present for most of the samples synthesized at lower temperatures using solid state techniques indicating that equilibrium had not been achieved. However, using the citrate-nitrate method nearly single phase Lu₃Al₅O₁₂ and Lu₄Al₂O₉ have been synthesized by firing at or below 1000 °C. The synthesis of nearly single phase Lu₄Al₂O₉ results in improved x-ray powder diffraction data for the phase.



PDFC Fig. 10396 system Lu₂O₃-Al₂O₃

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Solid-State Synthesis

Compositions of 20, 40, 60, and 80 mol% Al₂O₃ as well as 33.3, 50, and 62.5 mol% Al₂O₃ for the line compounds are mixed from pure oxide powders. After initially being pressed into a pellet and fired at 800° C the samples undergo cycles of grinding in an agate mortar and pestle, pressing into a pellet and then firing at higher temperatures up to a maximum of 1500° C



Citrate-Nitrate Method

Pure lutetium oxide powder and aluminum-nitrate monohydrate were weighed out based on the Lu-Al cation ratio for each line compound. The lutetium oxide was dissolved in concentrated nitric acid at ~60° C. The aluminum-nitrate was dissolved in deionized water, added to the solution, and stirred for three hours. Citric acid monohydrate dissolved in deionized water was added to the solution and again stirred for three hours. The solution was then placed on a hot plate at ~150° C to let the solvent evaporate, leaving a flaky precursor. The precursor for each compound was ground, pressed, and fired at 600° C. This process was repeated with the firing temperature raised to 1000° C.



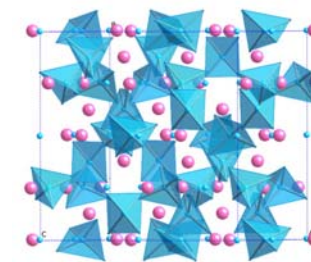
X-ray Powder Diffraction

The samples were ground with an agate mortar pestle and the powders were dispersed on single crystal Si zero background plates. For phase identification the powder diffraction data were collected on a Scintag PAD V diffractometer using Cu K_α radiation. Data were collected between 10 and 70 two-theta at a rate of 1° 2θ/min.

For Rietveld refinements the sample was contained in a deep well sample holder and data were collected on a PANalytical MPD X'Pert PRO diffractometer with an X'Celerator Real-Time Multiple Strip detector. Data were collected between 10 and 70 two-theta and the total data collection time was 10 minutes. The data were analyzed by the Rietveld method using the EXGUI graphical interface [5] for the General Structure Analysis System (GSAS) [6].

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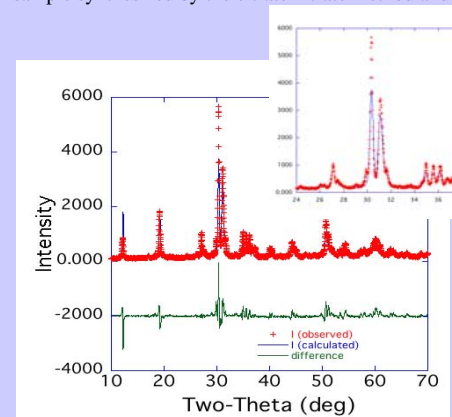


Lu₃Al₅O₁₂

Results

Temp (°C)	mol % Al ₂ O ₃						
	20	33.3 (4:2)	40	50 (1:1)	60	62.5 (3:5)	80
1000		LuAM (CN)					
1300	Lu ₂ O ₃ + LuAG +LuAP	Lu ₂ O ₃ + LuAG +LuAP	Lu ₂ O ₃ + LuAG +LuAP		?		?
1500	Lu ₂ O ₃ + LuAG			LuAG + Al ₂ O ₃	LuAG + Al ₂ O ₃		LuAG + Al ₂ O ₃

These results in the Table above indicate that samples synthesized using solid state techniques and fired at 1300 °C with less than 50 mol% Al₂O₃ have not reached equilibrium. For samples with greater than 50 mol% Al₂O₃ the x-ray powder diffraction data cannot be accounted for indicating the possibility of a new phase. LuAG is present for all samples fired at 1500 °C implying that LuAM is not present below this temperature. However, using the citrate nitrate method nearly single phase LuAM has been synthesized by firing at 800 °C. Firing at 1000 °C results in a sharper x-ray powder diffraction pattern. Shown below is the Rietveld refinement of the Lu₄Al₂O₉ sample synthesized by the citrate nitrate method and fired at 1000 °C.



Future work includes the synthesis of a large batch of single phase Lu₄Al₂O₉ for a neutron diffraction study. This data will be used for presenting improved powder diffraction data (the current PDF card for Lu₄Al₂O₉ is incomplete). Synthesis of the LuAlO₃ phase will also be undertaken using the citrate nitrate method.

References

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