



# On the melting behaviour of calcium monoxide under different atmospheres: A laser heating study

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## Abstract

The melting behaviour of calcium monoxide has been revisited by quasi-containerless laser heating under controlled atmosphere. The current results suggest that the large discrepancy in the literature data for the melting temperature of CaO is probably linked to the influence of the environmental oxidising/reducing conditions. The CaO solidification point measured in this work is  $(3222 \pm 25)$  K in an oxidising environment, in agreement with previous research performed under similar conditions. In a reducing atmosphere, the liquid/solid transition occurs at a slightly, but systematically lower, less accurately reproducible temperature,  $(3192 \pm 40)$  K. These phase transition temperatures are not depending on the external pressure, up to 0.3 MPa. In the latter case, radiance and optical spectroscopy measurements revealed a more abundant formation of colour centres, i.e. a higher concentration of oxygen defects in the material, which can affect the thermodynamic stability of the solid at very high temperatures. A similar behaviour may be expected to occur in multi-component material systems including CaO.

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## 1. Introduction

The main goal of the present work is the reassessment of the melting point of CaO and its dependence on the environmental conditions. Known for centuries as a geological material and a disinfectant, CaO (also called calcia or burnt-lime) is a common alkaline-earth oxide with fcc NaCl crystal structure.<sup>1</sup> CaO is produced by dissociation of CaCO<sub>3</sub> upon heating, according to the well known equilibrium<sup>1</sup>:



Equilibrium (1) is easily reversible at room temperature, which makes CaO relatively unstable in contact with the CO<sub>2</sub> of the air. Reaction (1) occurs whenever lime-based minerals are brought to high temperature. Knowledge about the

high-temperature behaviour of calcia is therefore paramount for the study of number of these minerals under extreme conditions, especially in relation to their mechanical stability, optical properties and equation of state.<sup>2,3</sup>

On the other hand, very numerous applications justify the great technological interest of CaO, that make its chemical industry production second only to that of H<sub>2</sub>SO<sub>4</sub>.<sup>1</sup> Broadly employed in the chemical and construction industries, it can also be used as a source of heat when put in contact with water: an exothermal reaction occurs with a production of calcium hydroxide. Furthermore, recent studies on Inert Matrix Nuclear Fuel (IMF)<sup>4,5</sup> suggest calcia also as a stabilising element for this innovative anti-proliferation nuclear fuel.

An especially interesting property is that it can withstand temperatures above 1800 K without dissociating or melting that is, it can be considered as a refractory material.

### 1.1. The controversial melting point of CaO

The melting/freezing point of CaO is certainly higher than all the International Temperature Scale 1990 (ITS90) established

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Table 1  
CaO melting temperatures reported in the literature.

$T_m$ (K)	Reference	Experimental approach
2863	Noguchi et al. (1966) <sup>8</sup>	Solar furnace (uncertain)
2890	Panek (1979) <sup>9</sup>	Electrical furnace
2833	Shevchenko (1979) <sup>10</sup>	Electrical furnace
3223	Foex (1966) <sup>11</sup>	Solar furnace
2886	Hlaváč (1982) <sup>12</sup>	Electrical furnace
3178	Yamada (1985) <sup>7</sup>	Solar furnace
3200	NIST JANAF	REVIEW
3222	This work	Laser heating

references.<sup>6</sup> It had even been studied as a new higher temperature standard reference,<sup>7</sup> save for the obvious large discrepancy in the available experimental data. The existing values for the melting temperature of CaO vary between 2833 K and 3223 K<sup>7–12</sup> (Table 1). Lower melting temperatures were generally obtained with traditional crucible heating techniques. With the sole exception of the solar furnace heating experiments performed by Noguchi et al.<sup>8</sup>, where the clear thermal arrest observed above 3100 K was arbitrarily attributed to a liquid/gas transition rather than a solid/liquid one, experimental methods in which the contact between burnt lime samples and their containment was limited systematically yielded higher values. This observation led Foex<sup>11</sup> and Yamada<sup>7</sup> to the conclusion that the reported “lower” melting/solidification temperatures did not correspond to pure CaO, but rather to compositions that largely reacted with their containment. Consequently, the high melting/freezing point measured by these latter Authors has been retained in the JANAF Tables,<sup>13</sup> which report for CaO (3200 ± 50) K. If the 1986 study by Yamada et al.<sup>7</sup> is the latest experimental work available, further discussion on the calcia melting behaviour can be found in more recent literature about phase diagram studies of the Ca–O system<sup>14</sup> or thermodynamic optimisation (CALPHAD) of systems including CaO as an end member.<sup>15–24</sup> In particular, Pelton et al.<sup>15,16</sup> criticised the high melting point of burnt lime reported in the JANAF tables, noticing the good agreement between data reported at lower temperature, and the fact that a lower melting point would be thermodynamically more consistent with phase equilibria assessed for multi-component systems including CaO. In this interpretation, the higher-temperature phase transition reported by Foex<sup>11</sup> and Yamada<sup>7</sup> was attributed to CaO boiling rather than melting. More authors<sup>14,17–19</sup> recently accepted the viewpoint of Pelton et al., whereas others<sup>20–24</sup> used in their phase diagram assessment the JANAF data. The reasons of the existing discrepancies and controversy can be understood in the light of the complex high temperature behaviour of calcia, from both an optical and chemical viewpoints.

### 1.2. Optical properties

CaO exhibits a particular optical behaviour when it is heated beyond a temperature ranging between 2000 K and 2200 K. It then emits a dazzling bright white light called limelight or Drummond light, known since the beginning of the 19th Century,<sup>26–27</sup> and already largely used in high-power light sources, film projection and illuminating devices without any physical explanation

of the involved phenomena. The most recent assessment of this subject is due to Kubarev,<sup>27</sup> who experimentally observed a rather abrupt evolution of calcium oxide from an optically hardly absorbing body to an almost ideal black body in a temperature range from 2000 K to 2300 K (see Appendix I). Materials with this behaviour can be called “semitransparent”, although the term is probably somewhat misleading. The optical phenomenon is in fact more precisely related to a “low-absorptivity”–“high absorptivity” transition. The material can be either highly transparent or highly reflective, depending of the photon energy, in its “low absorptivity” state. When the critical temperature identified by Kubarev<sup>27</sup> was reached, the emissivity  $\varepsilon_\lambda$  (equal to the absorptivity within the validity of Kirchhoff’s law)<sup>25</sup> of calcium oxide increased by a factor of about 10, which implied a complete change of the whole optical behaviour of this material. Considering  $\varepsilon_\lambda \approx 1$  at high temperature, Kubarev obtained a reasonable value of 0.1 at low temperature, which was in agreement with emissivity values found for other “white” oxides.

The only possible technique to measure phase transitions at  $T > 2500$  K is optical pyrometry, based on the detection of the sample thermal radiance. Optical pyrometers measure the “radiance temperature”  $T_\lambda$ , which can only be converted into real temperature  $T$  if the sample’s emissivity  $\varepsilon_\lambda$  is known, as indicated by Eq. (2)<sup>25</sup>:

$$\frac{1}{T} = \frac{1}{T_\lambda} + \frac{\lambda}{c_2} \cdot \ln \varepsilon_\lambda \quad (2)$$

where a value of 14,388  $\mu\text{m K}$  is used<sup>25</sup> for the fundamental constant  $c_2$  (cf. Appendix I). It can therefore be understood how a sudden change in emissivity makes it particularly difficult to measure stable thermograms on a calcia specimen heated beyond the melting point, unless the sample itself is either contained in another black-body shaped material (with, however, a high contamination risk), or shaped itself as a black body cavity (which however induces a large uncertainty due shape loss upon melting). The first approach was adopted in research based on crucible furnace heating,<sup>9,10</sup> the latter by Yamada et al.<sup>7</sup>, Noguchi et al.<sup>8</sup> and Foex<sup>11</sup> who employed a solar furnace heating technique. In the current work, the sample surface is directly measured in parallel to the sample emissivity, which allows an in situ determination of the sample real temperature.

Further details about radiance emission of a hot sample are given in Appendix I.

### 1.3. Chemical properties

The most fundamental high-temperature chemical property of calcia for the present study is the solubility of oxygen in liquid Ca. Calcium is well known to exist only as a pure metal or a divalent cation. Nonetheless, Bevan and Richardson<sup>28</sup> estimated that above the Ca + CaO eutectic temperature (1107 K ± 1.5 K), liquid calcium can dissolve oxygen up to an oxygen atomic fraction  $x(\text{O}) = 0.13$ – $0.15$  at 1523 K, whereas the solubility experimentally observed by Zaitsev and Mogutnov<sup>18</sup> at temperatures closer to Ca boiling (approximately 1800 K) are of the order of  $x(\text{O}) = 0.10$ . No experimental information is available beyond such temperature range up to the melting point of CaO.

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