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Spectroscopic investigation of the thermal decomposition of europium oxalate [1]

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Abstract

The mechanism associated with the thermal decomposition of europium oxalate remains enigmatic, despite the fact that considerable attention has been given to it. Various Eu(II) and Eu(III) intermediates have been invoked to explain experimental observations of the decomposition. We have used Raman and luminescence spectroscopies in conjunction with differential thermal analysis to pursue further the thermal decomposition of europium oxalate. Our results are consistent with the sequential formation of two trivalent, oxycarbonate intermediates; evidence for a divalent europium intermediate was not obtained.

INTRODUCTION

The mechanisms and chemical intermediates associated with the thermal decompositions of the trivalent lanthanide oxalates, $Ln_2Ox_3 \cdot nH_2O$ (where Ox is $C_2O_4^{2-}$) have been studied in the past by a variety of thermal and spectroscopic techniques. The extensive interest in these decomposition processes derives largely from the importance of the insoluble oxalates in the separation of the lanthanides from other metals by precipitation and for preparing the oxides of the lanthanides. Although most practical applications involve decomposition in air, there is also a fundamental interest in the dependence of the decomposition processes upon the atmosphere, and investigations have been carried out using inert, reducing and oxidizing atmospheres [1].

Most of the results reported in the literature for the decompositions of the hydrated trivalent lanthanide oxalates are consistent with stepwise dehydration followed by the thermal decomposition of the anhydrous oxalate to the sesquioxide via a dioxycarbonate intermediate, $Ln_2O_2CO_3$ [2]. For europium sesquioxalate decahydrate, there is general agreement that dehydration occurs in three steps below ≈200°C: $Eu_2Ox_3\ 10H_2O \rightarrow$

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$Eu_2Ox_3 \cdot 6H_2O \rightarrow Eu_2Ox_3 \cdot 4H_2O \rightarrow Eu_2Ox_3$ [3]. However, the mechanism associated with the subsequent thermal decomposition of anhydrous Eu_2Ox_3 remains enigmatic, presumably reflecting the particular accessibility of the divalent state of europium.

Based upon differential thermal analysis (DTA), infrared absorption (IR) and thermogravimetric (TG) measurements, Glasner and coworkers [4, 5] concluded that Eu_2Ox_3 decomposed via a divalent intermediate (EuOx) in atmospheres of O_2, N_2 and CO_2; the decomposition finally proceeded to the fully oxidized (trivalent) sesquioxide only in O_2. Gallagher et al. [6] used Mössbauer, emission and IR spectroscopies, and various thermal analysis techniques to characterize this decomposition. They found no evidence for a divalent europium intermediate and instead postulated the formation of a novel carbonyl carbonate intermediate, $Eu_2O_2(OCOCO_2)$, to account for the inferred europium trivalence and the TG-derived stoichiometry. More recent investigations of europium sesquioxalate decomposition have suggested other Eu(III) intermediates such as $Eu_2O(CO_3)_2$ [7], the same intermediates as for trivalent lanthanide oxalates [8], and divalent europium intermediates [9].

It is evident that the process of the thermal decomposition of europium sesquioxalate is somewhat elusive to empirical determinations, and apparent that the mechanism is indefinite and is dependent upon the nature of the atmosphere and other experimental parameters, e.g., heating rate, etc. Recognizing this potential variability, we have undertaken to further characterize the intermediates formed using luminescence and Raman spectra. As indicated by Gallagher et al. [6] and others [10], the luminescence (emission) spectra of europium compounds provide a definitive indication of the metal valence (2 or 3) and, for certain materials, can also offer information on the local site symmetry and bonding of the metal ions. Complementary information on the nature of the ligands bonded to the metal ion is provided by the "fingerprint" vibrational spectroscopies, IR and Raman. Several IR studies of Eu_2Ox_3 decomposition have been described [6–9] and we report here the corresponding Raman spectra. In addition, DTA experiments were carried out to aid in the interpretation of the spectroscopic results.

EXPERIMENTAL

Two $Eu_2Ox_3 \cdot nH_2O$ commercial samples (99.99% rare earth content (REC) purity) and one prepared by precipitation using standard techniques [2] were studied. The decomposition of all three specimens gave essentially the same results. Due to the particularly evanescent nature of four of the ten lattice waters in the fully hydrated europium oxalate decahydrate, decomposition to the hexahydrate occurs close to room temperature and the degree of initial hydration (n in $Eu_2Ox_3 \cdot nH_2O$) of the starting sesquioxalates may have varied between 6 and 10. The six more strongly bound, coordinating waters are retained to somewhat higher temperatures [3]. As it was the decomposition of the anhydrous oxalate that was of particular interest, this uncertainty in the degree of hydration was deemed acceptable. The gadolinium and terbium sesquioxalate hydrates studied here were also commercial products (99.99% REC purity).

Thermograms were obtained with a Perkin-Elmer DTA 1700 high-temperature differential thermal analyzer using a heating rate of 10°C min^{-1}. Because of the uncertainty in the initial oxalate compositions, i.e., the degrees of hydration, and in the energy calibration of the thermal analyzer, the samples were not weighed but the 60 mm^3 Al_2O_3 DTA cups were approximately half-filled. The thermal analyzer was located inside an argon-atmosphere glove box and purified argon was passed over the samples during decomposition. The placement of the thermal analyzer inside a high-purity inert atmosphere glove box precluded DTA studies of the decompositions in oxidizing or reducing atmospheres. A detailed description of this DTA facility and the experimental procedures has been provided elsewhere [11].

For spectroscopic studies, the samples (<1 mg) were contained in quartz capillaries. Open capillaries were used for air-decomposition studies. To eliminate the possible effect of the oxidizing (air) atmosphere upon the decomposition of $Eu_2Ox_3 \cdot nH_2O$, a capillary was also connected to a volume, i.e., a wide neck, of ≈ 10 cm^3 that was sealed-off under a vacuum of <1 Pa.

To obtain emission spectra, the samples were near-reasonantly excited to the $^5D_2$ electronic state of Eu^{3+} using the 465.8 nm line of a 6 W Argon-ion laser. Non-resonant excitation (using the 457, 488 or 514 nm Ar-ion lines) was used to obtain Raman spectra. The photon flux impinging on the sample was minimized (≤ 100 mW) to avoid localized heating and possible decomposition. Such laser heating effects were of particular concern for samples in vacuum.

The emitted (luminescence) or scattered (Raman) light was collected at 90° from the incident laser excitation and passed through a 1-meter double monochromator with a resolution of 0.5 cm^{-1} at 514 nm. The emitted/scattered light was detected by a photon counting system that employed a multichannel analyzer which was interfaced to a computer for spectral analysis. Fluorescence lifetimes were measured using a mechanical beam chopper to provide a pulsed excitation source and a gated photon counter to determine the time-dependence of the emission signal.

The samples were placed adjacent to a monitoring thermocouple inside a furnace which could be heated to a maximum temperature of ≈ 900°C while acquiring spectra. After obtaining initial room temperature spectra, the sample temperature was increased incrementally and spectra were acquired after thermal stabilization for ≈ 15 min. Spectra were obtained at increasing temperatures until either decomposition was apparently complete or the spectroscopic features became unresolved due, for example, to increasing spectral background at high temperatures.

RESULTS AND DISCUSSION

Differential thermal analysis

Figure 1 shows DTA thermograms for the decomposition of $Eu_2Ox_3 \cdot nH_2O$ and $Gd_2Ox_3 \cdot nH_2O$ in an argon atmosphere. These results were found to be reproducible; a thermogram similar to that for $Gd_2Ox_3 \cdot nH_2O$ was also obtained for $Tb_2Ox_3 \cdot nH_2O$. The two or three closely-spaced endotherms evident for each oxalate sample below ≈300°C were attributed to dehydration. The DTA results at higher temperatures suggest that decomposition of the resulting anhydrous gadolinium and

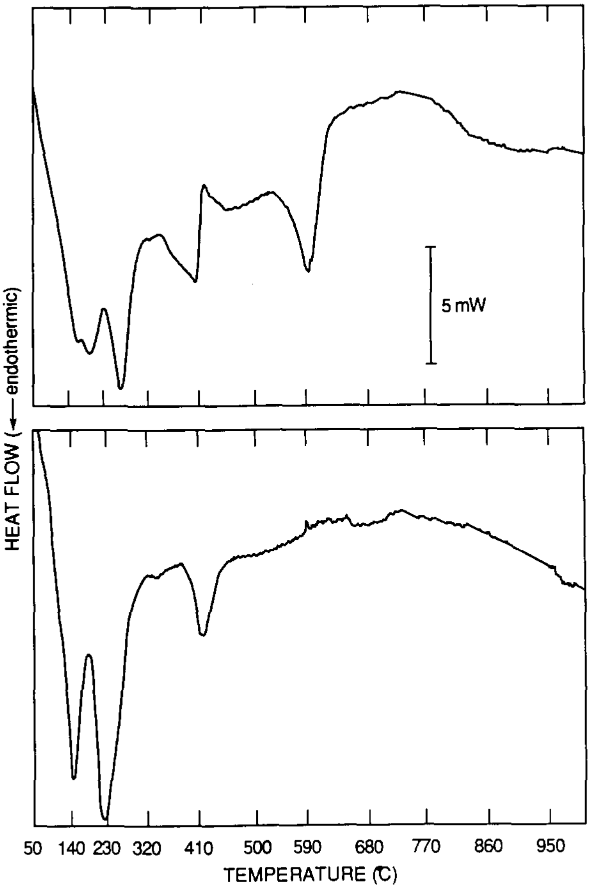

Fig. 1. DTA thermograms for $Eu_2Ox_3 \cdot nH_2O$ (top) and $Gd_2Ox_3 \cdot nH_2O$ (bottom), acquired while heating at 10°C min^{-1} in Ar.

terbium sesquioxalates occurred over a relatively narrow temperature range around 400°C.

The DTA results for Eu_2Ox_3 (Fig. 1) were indicative of a more complex decomposition process. This is in contrast to the results for gadolinium and terbium but is in accord with various previous studies on europium. The decomposition of the europium salt occurred in at least two separate steps, commencing at a lower temperature (≈350°C) but not completed until ≈620°C. In the thermograms for Eu_2Ox_3 decomposition, there is a reproducible, albeit inconclusive, indication of a small exothermic feature at ≈420°C (see Fig. 1). Although large exothermic features are commonly evident during decompositions of oxalates and other compounds in air, and are generally associated with some oxidation process (of the solid or gaseous decomposition products), such features under inert atmosphere conditions are more unusual. In summary, the inert-atmosphere DTA results for the europium salt suggested a relatively complex decomposition process which may involve more than one intermediate phase.

Raman spectroscopy

Figure 2 shows Raman spectra obtained for a $Eu_2Ox_3 \cdot nH_2O$ sample undergoing thermal decomposition in air. The vibrational assignments for

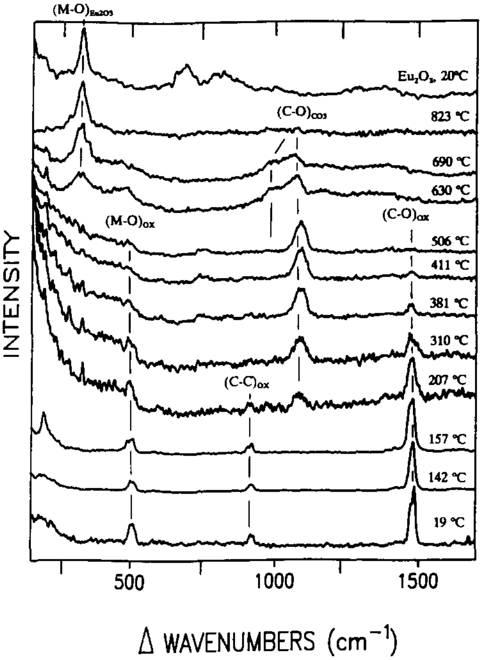

Fig. 2. Raman spectra for $Eu_2Ox_3 \cdot nH_2O$ decomposing in air. A room-temperature spectrum independently obtained for Eu_2O_3 (cubic C-type [11]) is included for comparison. The peaks have been assigned to the indicated moieties.

the oxalate moieties are indicated in Fig. 2: $(M–O)_{ox}$ represents the europium–oxygen stretch; $(C–C)_{ox}$ the carbon–carbon stretch; and $(C–O)_{ox}$ the carbon–oxygen stretch. These assignments are in accord with those recently provided by Morris and Hobart [12]. In addition, the less distinct features below ≈300 cm^{-1} are attributed to the deformation modes of the europium–oxalate chelate ring [12].

The peak which appears at ≈1100 cm^{-1} above 200°C was assigned to the carbonate (or carbonate-like) carbon–oxygen stretch. Raman spectra were obtained here for a commercial sample of $Eu_2(CO_3)_3$ and confirmed that the dominant carbonate feature occurs in this spectral region. As is evident by comparison with the Eu_2O_3 spectrum included in Fig. 2 (top), the strong peak at ≈300 cm^{-1} in the high-temperature spectra is indicative of the sesquioxide product. The absence of the sesquioxide Eu^{3+} $^5D_1 \rightarrow {}^7F_0$ fluorescence at ≈700 cm^{-1} in these high-temperature decomposition spectra is consistent with some other Eu_2O_3 spectra obtained in our laboratory where it was found that this feature was not invariably evident.

The appearance of the peak at ≈1100 cm^{-1} beginning above 200°C, and concurrent with the diminution of the oxalate peaks, suggests a carbonate (or carbonate-like) decomposition intermediate, which is consistent with previous studies using, for example, IR spectroscopy. A second peak or shoulder to this peak at a slightly lower energy (≈1000 cm^{-1}) appears above ≈600°C. Coinciding with the appearance of this shoulder peak is the initial indication of the peak assigned to the oxide (M–O) stretch at ≈300 cm^{-1}. These changes in the spectra above ≈600°C are indicative of a second intermediate.

Although the thermogram in Fig. 1 (top) was obtained under argon rather than air atmosphere, it is noted that there appears to be a correlation between the DTA peaks and the stages of decomposition suggested by the Raman spectra. Often the essential difference between decompositions carried out under oxidizing and inert atmospheres is due to the oxidation of gaseous decomposition products. Thus, Eu_2Ox_3 may decompose to the same final product (Eu_2O_3) via essentially the same intermediates under both air and inert atmospheres, with the only substantial difference between the processes being the degree of oxidation of the CO(g) generated.

The sequence of Raman spectra shown in Fig. 2 is essentially consistent with the interpretation of Gallagher et al. [6], who proposed a more complex trivalent intermediate which formed prior to the dioxymonocarbonate intermediate. These authors postulated a "carbonyl carbonate", $Eu_2O_2(OCOCO_2)$, as this intermediate, suggesting that its vibrational spectroscopic features could be similar to those of the carbonate. Thus, although the feature evident here at ≈1100 cm^{-1} is indicative of a carbonate, it might not be inconsistent with such a "carbonyl carbonate" species. However, Hartman and Hisatsune [13], who originally proposed

$(OCOCO_2)^{2-}$ as a "transition complex" in the case of alkali metal oxalate decompositions, recognized that such a postulated radical ion intermediate would undoubtedly be short-lived. It seems unlikely that such a transient intermediate would be discernable on the time scale of the thermal analytical and spectroscopic experiments reported here.

Perhaps a more plausible explanation for the sequence of Raman spectra shown in Fig. 2 is the decomposition scheme proposed by Shyamala et al. [7]; $Eu_2Ox_3 \rightarrow Eu_2O(CO_3)_2 \rightarrow Eu_2O_2CO_3 \rightarrow Eu_2O_3$. According to this scenario, the intermediate Raman peak at $\approx 1100\,cm^{-1}$ would be due to the monoxy-dicarbonate and the peak at $\approx 1000\,cm^{-1}$, which appears at higher temperatures, to the dioxy-monocarbonate. The increasing oxide-like character of the successive intermediates, as suggested by the initial appearance of the peak at $\approx 300\,cm^{-1}$ concurrent with the formation of the second intermediate, would also be consistent with such an explanation.

Luminescence spectroscopy

Luminescence spectra obtained for the decomposition of $Eu_2Ox_3 \cdot nH_2O$ in air are shown in Fig. 3. The emission peaks have been assigned to the

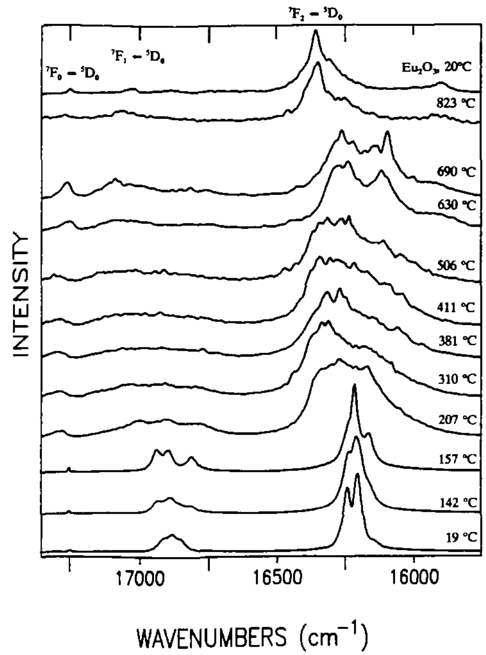

Fig. 3. Luminescence spectra for $Eu_2Ox_3 \cdot nH_2O$ decomposing in air. A room-temperature spectrum independently obtained for Eu_2O_3 (cubic C-type [11]) is included for comparison. The peaks have been assigned to the indicated Eu^{3+} electronic transitions.

$^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) electronic transitions of the Eu^{3+} ion. Although the detailed structures of the luminescence peak manifolds reflect the local site symmetry about the Eu^{3+} ion, and can be used to derive structural information [10], the spectral resolution obtained here (especially at higher temperatures) was adequate only for the qualitative identification of the stages of the decomposition process, and the determination of the europium valence at each stage.

Whereas the low-temperature (<200°C) Raman spectra were virtually identical, the corresponding luminescence spectra showed substantial differences over this temperature range. The oxalate vibrations monitored by the Raman spectra are essentially independent of the degree of hydration. In contrast, the luminescence properties are sensitive to the change in symmetry about the Eu^{3+} ion upon dehydration, and the marked changes in the splittings of the electronic transitions below 200°C were taken to reflect progressive dehydration.

Above 200°C the changes evident in the luminescence spectra correlate well with the corresponding Raman spectra. The first decomposition intermediate is manifested, above ≈200°C, by the disappearance of the $^5D_0 \rightarrow {}^7F_1$ manifold and the concurrent shift and broadening of the $^5D_0 \rightarrow {}^7F_0$ manifold. The second intermediate is indicated above ≈600°C by the appearance of a second (lower energy) peak in the $^5D_0 \rightarrow {}^7F_2$ manifold. The 823°C decomposition spectrum corresponds to that of europium sesquioxide.

The luminescence spectra for the decomposition of $Eu_2Ox_3 \cdot nH_2O$ in air are all indicative of trivalent europium, and do not provide evidence for a divalent intermediate. A divalent intermediate would have been indicated by the broad band emission of Eu^{2+} which is centered around $\approx 18\,000\ \mathrm{cm}^{-1}$. Figure 4 shows luminescence spectra obtained for the corresponding decomposition of a europium oxalate sample which had been sealed-off under vacuum. Although a pressure of $\approx 10^4$ Pa of the gaseous decomposition products (H_2O, CO_2 and CO) was generated inside the sealed capillary, the conditions were not oxidizing, in contrast to the air decomposition experiments. These particular spectra are of somewhat inferior quality but there is again no indication of any divalent intermediate, at least up to ≈450°C, above which temperature the spectral resolution deteriorated substantially. Whereas our inert-atmosphere DTA results were similar to those reported by Nagase et al. [9], we were not able to confirm their report of a divalent intermediate occurring in a non-oxidizing atmosphere at ≈300–400°C. Although it is undoubtedly possible to decompose europium sesquioxalate to a divalent product, e.g., EuO, under adequately reducing conditions, it is doubtful that thermal decomposition of a trivalent compound to a trivalent product should occur via a divalent intermediate. Our findings substantiate this intuition.

The Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ luminescence lifetimes (τ) measured for one of the

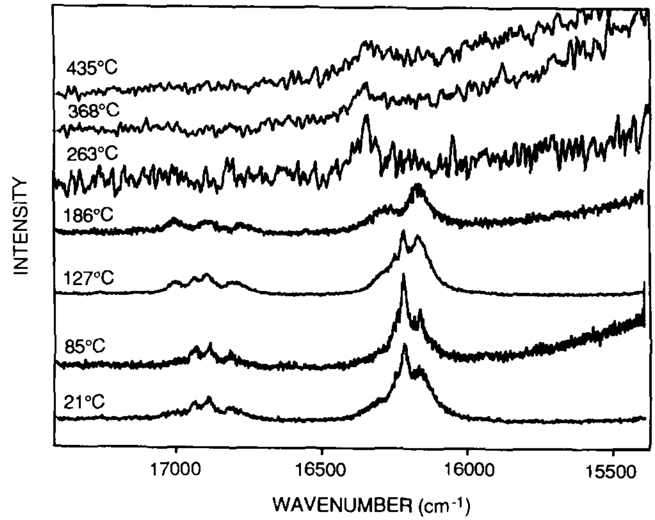

Fig. 4. Luminescence spectra for $Eu_2Ox_3 \cdot nH_2O$ decomposing under a partial vacuum. The dominant feature in the region 16 500–16 000 cm^{-1} is due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}.

europium oxalate samples during the decomposition process are given in Table 1. In the absence of coordination changes for Eu^{3+}, a gradual decrease in the luminescence lifetime with increasing temperature would be expected due to the shorter lifetimes associated with the higher-lying electronic levels which are thermally accessible [14]. Following such a gradual decrease up to ≈150°C, the abrupt drop in τ at ≈200°C is presumably associated with complete dehydration. A second abrupt decrease around ≈350°C may be associated with the first step in the decomposition process. No clear break in τ versus T could be assigned to a second decomposition intermediate (formed around ≈600°C), but the resolution of the measurements was ≈20 μs and any such effect may have been difficult to detect. Finally, there is a noticeable increase in τ above ≈650°C, suggesting a longer lifetime for the sesquioxide product.

TABLE 1

Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ fluorescence lifetime during $Eu_2Ox_3 \cdot nH_2O$ decomposition

T/°C	τ/μs	T/°C	τ/μs
18	226	375	35
50	220	433	38
80	194	499	34
141	189	617	29
206	95	680	48
302	78		

CONCLUSIONS

The value of the complementary structural and electronic probes of Raman and luminescence spectroscopies for assisting in the interpretation of thermal analytical measurements has been demonstrated. In particular, this investigation has served to further illuminate the mechanism associated with the thermal decomposition of hydrated europium sesquioxalate to europium sesquioxide. The luminescence results are consistent with the occurrence of two trivalent decomposition intermediates; evidence for a divalent intermediate was not obtained. The Raman spectra suggest that the dominant vibrational mode of both intermediates occurs at an energy close to that found for pure europium carbonate. A likely explanation of these observations is the decomposition mechanism postulated by Shyamala et al. [7] whereby monoxy-dicarbonate and dioxy-monocarbonate intermediates are formed sequentially prior to final decomposition to the sesquioxide.

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REFERENCES

1 D. Dollimore, J. Therm. Anal., 11 (1977) 185.
2 E. Birnbaum, Gmelin Handbook of Inorganic Chemistry, Rare Earth Main Vol. D5, Springer-Verlag, New York, 8th edn., 1984, pp. 112–139.
3 M.J. Fuller and J. Pinkstone, J. Less-Common Metals, 70 (1980) 127.
4 A. Glasner, E. Levy and M. Steinberg, J. Inorg. Nucl. Chem., 25 (1963) 1415.
5 A. Glasner, E. Levy, M. Steinberg and W. Bodenheimer, Talanta, 11 (1964) 405.
6 P.K. Gallagher, F. Schrey and B. Prescott, Inorg. Chem., 9 (1970) 215.
7 M. Shyamala, S.R. Dharwadkar and M.S. Chandrasekharaiah, Thermochim. Acta, 56 (1982) 135.
8 V.A. Sharov and G.V. Bezdenezhnykh, Z. Neorg. Khim., 32 (1987) 809.
9 K. Nagase, H. Yokobayashi, K. Muraishi and M. Kikuchi, Thermochim. Acta, 177 (1991) 273.
10 G. Chen, R.G. Haire and J.R. Peterson, Appl. Spectrosc., 46 (1992) 273.
11 J.K. Gibson and R.G. Haire, Thermochim. Acta, 207 (1992) 65.
12 D.E. Morris and D.E. Hobart, J. Raman Spectrosc., 19 (1988) 231.
13 K.O. Hartman and I.C. Hisatsune, J. Phys. Chem., 71 (1967) 392.
14 G. Chen, N.A. Stump, R.G. Haire and J.R. Peterson, Appl. Spectrosc., 46 (1992) 1198.