



# The effect of refluxing on the alkoxide-based sodium potassium niobate sol–gel system: Thermal and spectroscopic studies

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## ABSTRACT

A study on the effects of prolonged heating under reflux conditions of up to 70 h on alkoxides of sodium, potassium and niobium dissolved in 2-methoxyethanol for the synthesis of sols of composition  $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$  (NKN) has been carried out using combined thermogravimetric–Fourier transform infrared spectroscopic analyses. Extended refluxing increases the homogeneity of the  $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$  (NKN) system. Spectroscopic analyses on the non-refluxed and 70 h refluxed NKN gels reveal the existence of inorganic hydrated carbonates and bicarbonates, which we propose arise from the hydration and carbonation of the samples on standing in air. The X-ray diffraction patterns of these two types of gels show orthorhombic NKN phase evolutions at higher temperatures.

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## 1. Introduction

Alkaline niobate ferroelectrics have attracted significant attention as lead-free ferroelectric compositions owing to their simple perovskite structure and high Curie temperature [1].  $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$  (NKN), which is a solid solution of ferroelectric  $\text{KNbO}_3$  and antiferroelectric  $\text{NaNbO}_3$ , has an orthorhombic phase at room temperature, and it is well known that it shows enhanced piezoelectric properties [2]. Recently, NKN and allied ceramic systems have been shown to have relatively good piezoelectric properties similar to those of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT)-based ceramics [3,4] and this has generated significant interest in the synthesis of compositions of sodium potassium niobate in both bulk and thin film forms.

A number of studies to synthesise dense NKN and allied ceramics has already been reported that utilise conventional mixed oxide routes using predominantly carbonates of Na and K as precursors [5,6]. However, due to the coarse particle sizes and issues of sinterability in these methods, it is difficult to obtain a homogeneous starting mixture at the molecular level by normal mixing techniques. Some synthetic difficulties can be mitigated by using chemical solution methods, such as the sol–gel process, which are suitable to fabricate complex oxide powders and thin films at lower temperatures, and which are also more effective at controlling the final composition. Tanaka et al. reported sol–gel  $\text{Li}_x(\text{Na}_{0.5}\text{K}_{0.5})_{1-x}\text{NbO}_3$  powder and thin films, in which the presence of secondary phases such as  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  and  $\text{K}_4\text{Nb}_6\text{O}_{17}$  were

observed [7]. Researchers have also reported the synthesis of NKN nano powders by sol–gel and Pechini methods and studied their phase formation and reactivity in an ambient atmosphere [8–10]. Wu et al. made NKN thin films with acetates of Na, K and niobium ethoxide [11]. Tanaka et al. have studied the effects of adding excess Na, K [12] and the effect of a Pt bottom layer [13] on the thermal processing of the alkoxy-derived precursor solutions of  $(\text{Na,K})\text{NbO}_3$  thin films. However, the electrical properties of these ferroelectric NKN films fell short of a saturated ferroelectric response. In all these cases, where  $P$ – $E$  loop measurements were carried out on the sol–gel NKN films, no evidence of ferroelectric hysteresis was observed [11,12]. Hence, there are significant difficulties in successfully applying sol–gel processing to these alkali niobate films and further work is required in this area.

In any sol–gel process, the stable sol primarily contains metal oligomeric chains formed by the reactions of the metal-organic precursor molecules that are subsequently pyrolysed and heated in thin layers to give the desired  $-\text{M}-\text{O}-\text{M}-$  chain links [14,15]. To ensure uniformity in the final sol–gel, and thus a single phase thin film, a uniform mixing of the individual precursors is necessary and the oligomerisation needs to be as complete as possible. In this context, we have recently reported the first evidence of phase heterogeneity existing in sol–gel NKN systems [16,17]. In these works, we investigated the phase formation during the thermal decomposition of alkoxide-based NKN sol–gel precursors and explained the potential reasons for the lack of ferroelectric behaviour in NKN thin films produced via the alkoxide sol–gel route. In a continuation of our detailed investigation into the sol–gel synthesis of NKN films, we herein report on the effect of prolonged refluxing of sol–gel NKN precursor solutions as shown

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through thermal, structural and spectroscopic characterisations of the dried gel system. The main focus of this paper is to investigate the refluxing event through the help of the combined TGA–FTIR technique.

## 2. Experimental procedure

Alkoxide sols of Na and K were prepared in a nitrogen filled glove box by magnetically stirring the metal in 2-methoxyethanol (Sigma–Aldrich) in a round bottomed flask followed by the addition of a calculated amount of niobium ethoxide in order to make a  $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$  sol of concentration 0.5 M. The sol was then refluxed under nitrogen for 24 or 70 h. The stock solution was slowly stirred in air at 60–70 °C for 4–5 h to obtain a dry NKN gel. The gels thus afforded showed a good reproducibility. A more detailed synthesis and sample preparation procedure has been described elsewhere [16].

The NKN gel was processed for combined Thermogravimetric analysis (TGA) — Fourier Transform Infrared (FTIR) spectroscopy. Thermogravimetric analysis (TGA) was conducted in air (Stanton & Redcroft TGA 1000, London, England). The TGA furnace temperature was increased at a rate of 20 °C  $\text{min}^{-1}$  until 950 °C. This was done to avoid significant levels of alkali metal evaporation and consequent damage to the apparatus. The sample was held at 950 °C for 20 min. The evolved gases from the sample at different time/temperature combinations were analysed by Fourier Transform Infrared (FTIR) spectroscopy (NICOLET FTIR 560 spectrometer, Madison, WI, USA) in the wavenumber range 4000–400  $\text{cm}^{-1}$ . Fourier transform infrared spectroscopy (FTIR) was carried out on NKN powder samples after calcination at different temperatures with a dwell time of 30 min at those final temperatures. Powder samples were placed in the diamond cell of a Perkin Elmer Spectrum One FTIR spectrometer. Spectra were recorded over the wavenumber range 4000–1000  $\text{cm}^{-1}$ . Phase analyses of the NKN gels were carried out at room temperature using an X-ray diffractometer with monochromic  $\text{CuK}\alpha$  radiation (Philips APD 1700, Almelo, The Netherlands,  $\lambda = 1.5418 \text{ \AA}$ ).

## 3. Results and discussion

### 3.1. Non-refluxed dried NKN gel

A standard TGA plot of the dried NKN precursor, non-refluxed gel heated in air to 950 °C, Fig. 1a, shows that the main weight loss steps occur below 600 °C, losing up to 19 mass % of the starting dried gel sample. The four main weight losses occur in the 50–130 °C, 130–480 °C and the 480–530 °C temperature ranges. A slow, gradual change can be observed from 670 to 800 °C (1%).

The corresponding Gram–Schmidt plot, showing the variation in the total absorbance of evolved gases as a function of time/temperature, Fig. 2a, has peaks at 128, 204, 526 and 950 °C. The peak around 526 °C spreads beyond 800 °C and ends with a crest at 950 °C. The FTIR spectra of the vapours evolved at temperatures corresponding to the peaks on the Gram–Schmidt plot are presented in Fig. 3 and the principal features are also described below. Peak assignments are carried out with reference to standard texts [18–20] and to instrument software (Nicolet Vapour Phase Library, Madison, WI).

An FTIR spectrum for the first Gram–Schmidt peak temperature at 128 °C (Fig. 3a) indicates the  $\text{CO}_2$  formation, with peaks at 2360 and 2310  $\text{cm}^{-1}$  (stretching mode) and around 670  $\text{cm}^{-1}$  (bending mode). There is also a suggestion of some carbon monoxide evolution (faint peaks at 2180 and 2110  $\text{cm}^{-1}$ ). Absorbance in the range  $\sim 3620\text{--}3730 \text{ cm}^{-1}$  is consistent with an O–H stretch of

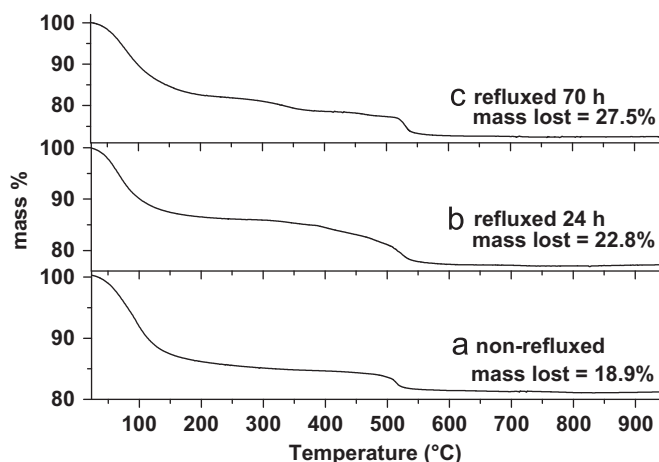


Fig. 1. TGA plots for the NKN dried gels obtained under different refluxing conditions. The rate of heating in this case was 20 °C  $\text{min}^{-1}$ .

$\text{H}_2\text{O}$ . The peak at 1060  $\text{cm}^{-1}$  is indicative of the presence of residual alcohols (both primary and secondary). The FTIR spectrum recorded at a temperature of 204 °C (Fig. 3b) is similar to that for 128 °C.

The vapour sample corresponding to the third Gram–Schmidt peak, at 526 °C (Fig. 3c), shows the most intense  $\text{CO}_2$  and water IR absorbances of any spectrum; no organic vapours were detected. The plot for 950 °C (Fig. 3d) is similar to that for 526 °C. These observations suggest that residual carbonaceous materials remain in the system at very high temperatures ( $\geq 800 \text{ °C}$ ).

### 3.2. Dried NKN gel refluxed for 24 h

The TGA plot of the dried NKN precursor gel refluxed for 24 h, Fig. 1b, shows a mass loss up to 23 wt% of the starting dried gel sample. The main weight losses occur in the 40–160 °C, 350–570 °C and a slow gradual change 650–750 °C.

The corresponding Gram–Schmidt plot, Fig. 2b, shows peaks at 108 °C, 450 °C (shoulder), 536 °C and a faint peak at 730 °C. The low temperature peak at 108 °C is less intense and has less spread compared to a similar peak observed for the non-refluxed sample. The FTIR spectra of the vapours evolved at temperatures corresponding to the peaks on the Gram–Schmidt plot are presented in Fig. 4.

The FTIR plot at 108 °C (Fig. 4a) shows an evolution of methoxyethanol and  $\text{CO}_2$  and water. The moderately strong peaks at 2920, 1130 and 1060  $\text{cm}^{-1}$  are typical of a standard methoxyethanol spectrum as obtained from the Nicolet Vapour Phase Library for the C–H stretching (2920  $\text{cm}^{-1}$ ) and C–O(H) stretching vibrations (1130 and 1060  $\text{cm}^{-1}$ ) of methoxyethanol. Water (asymmetric stretch at 3500–3730 and bending at 1510–1710  $\text{cm}^{-1}$ ) and  $\text{CO}_2$  (stretching vibrations at 2350 and 2305  $\text{cm}^{-1}$  and bending at 670  $\text{cm}^{-1}$ ) peaks can also be identified. This trend continues to higher temperatures and, finally, at 246 °C (Fig. 4b) only  $\text{CO}_2$  and water are seen, indicating that the evolution of methoxyethanol is complete around this temperature range.

All other plots (Fig. 4c–e) show the evolution of  $\text{CO}_2$  in various proportions. Gaseous evolution reaches a maximum at 536 °C. A trace amount of  $\text{CO}_2$  is evident for the 730 °C plot (Fig. 4e) and corresponds well with the Gram–Schmidt peak at 730 °C.

### 3.3. Dried NKN gel refluxed for 70 h

The TGA plot of the dried NKN precursor gel refluxed for 70 h, Fig. 1c, shows that the main weight loss steps occur below 600 °C, losing up to 28 wt% of the starting dried gel sample.

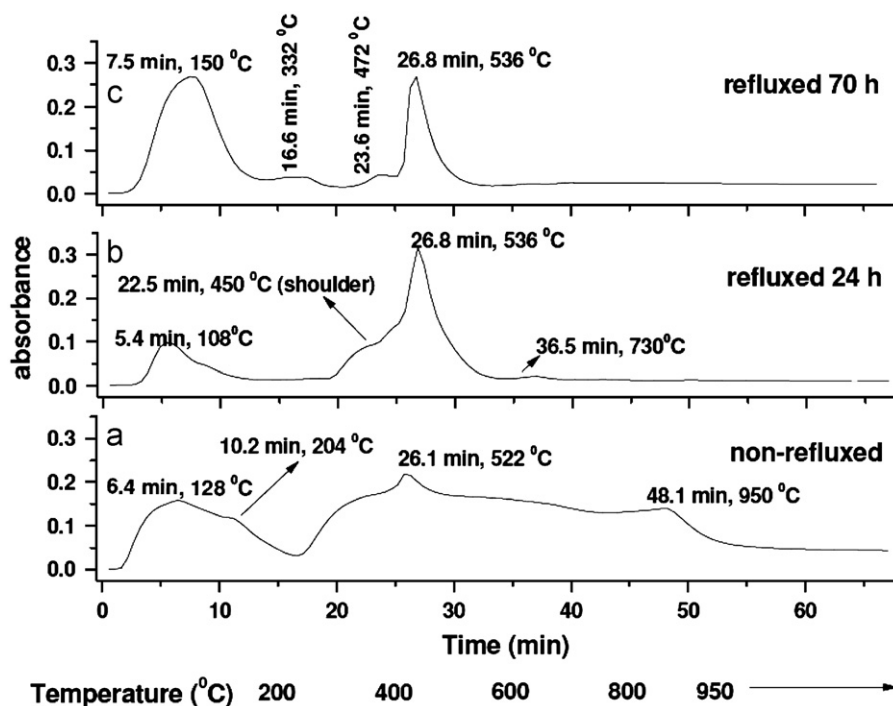


Fig. 2. Gram-Schmidt plots for the NKN dried gels obtained under different refluxing conditions.

The corresponding Gram-Schmidt plot, Fig. 2c, show peaks at 150 (more intense than in Fig. 2a and b and spread up to 240), 332, 472 and 536 °C. The FTIR spectra of the vapours evolved at temperatures corresponding to the peaks on the Gram-Schmidt plot are presented in Fig. 5. The plot at 150 °C (Fig. 5a) shows an evolution of methoxyethanol predominantly. The spectrum exhibits O–H stretching at  $3645\text{ cm}^{-1}$ . Two C–H deformation modes appear at  $1465$  and  $1365\text{ cm}^{-1}$ . The solvent also shows two C–O stretching modes, one at  $1135\text{ cm}^{-1}$  characteristic of a  $-\text{CH}_2\text{O}-\text{CH}_2-$  ether moiety and another at  $1065\text{ cm}^{-1}$  characteristic of a primary alcohol [21]. All these peaks match standard 2-methoxyethanol spectra very closely; a standard spectrum for methoxyethanol as obtained from the Nicolet Vapour Phase Library is shown in Fig. 6 for comparison. The evolution of methoxyethanol is complete after  $\sim 330\text{ °C}$  (Fig. 5b). Beyond this temperature all the peaks show an evidence of  $\text{CO}_2$  and water in various intensities. In other words, we can assume that the first broad Gram-Schmidt peak which ends around  $\sim 320\text{ °C}$  (Fig. 2c) may be predominantly attributed to the methoxyethanol vapours.

All the other FTIR plots (Fig. 5c–e) show an evolution of water and  $\text{CO}_2$  in various proportions; the wavenumbers of the peaks have been already discussed. The evolution of gases reaches a maximum at  $536\text{ °C}$  (Fig. 5d). A trace amount of  $\text{CO}_2$  is noted in the  $612\text{ °C}$  (Fig. 5e) plot; this might be a carry-over of the previous decomposition at  $536\text{ °C}$ .

The non-refluxed dried gel shows a smaller weight loss (19%) compared to the refluxed powders (respectively, 23% and 28% for the 24 and 70 h refluxed gel dried powders); a fact that may be correlated with the extent of cross-linking promoted by the prolonged hours of refluxing.

#### 3.4. FTIR analyses of NKN dried gels

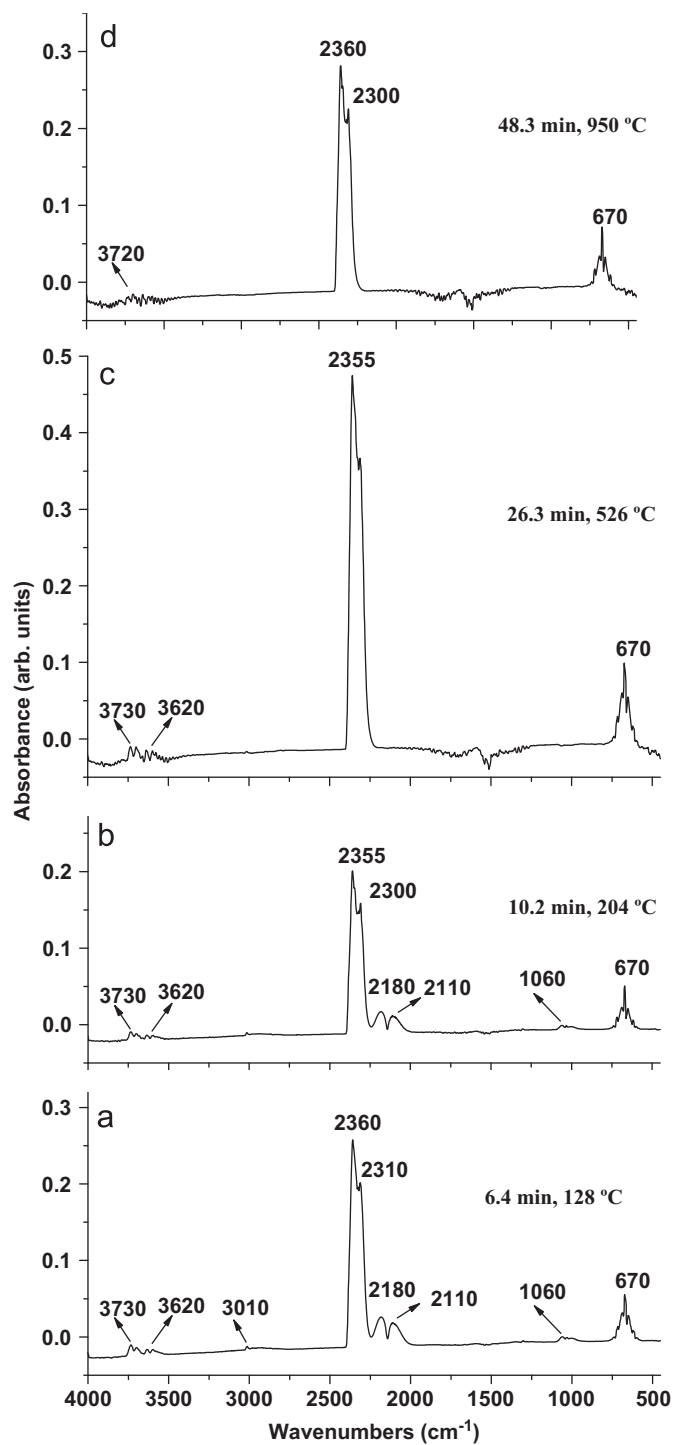
Following the identification of the vapours eliminated from the gels during heating, the gel residues were also analysed by an FTIR Figs. 7 and 8. Peaks were assigned with reference to standard texts [18,19]. The 24 h refluxed sol shows intermediate characteristics

and therefore further discussion is generally directed towards the 0 and 70 h samples. It is noteworthy to mention that the temperatures of gas evolution for these two sets of gel varied over a range;  $120\text{--}150\text{ °C}$  for the first broad peak and  $520\text{--}540\text{ °C}$  for the second peak. We therefore decided to investigate the gradual structural change, if any, over a fixed step division of temperature ( $100\text{ °C}$ ). A summary of wavenumbers and their assignments for key peaks is shown in Table 1.

Mostly, organic residues remain in the non-refluxed gel sample calcined at  $250\text{ °C}$ , Fig. 7. However in the range  $350\text{--}450\text{ °C}$ , the FTIR peaks indicate the formation of intermediate carbonate/s. Sharp peaks at  $1630\text{--}1640\text{ cm}^{-1}$  (C=O bending),  $1420\text{--}1440\text{ cm}^{-1}$  ( $\text{CO}_3^{2-}$  bending),  $1350\text{ cm}^{-1}$  ( $\text{COO}^-$  stretching) and  $1050\text{ cm}^{-1}$  ( $\text{COO}^-$  stretching,  $\text{CO}_3^{2-}$  stretching) signify the presence of non-coordinated and bidentate carbonates [22].

At the higher temperature range  $550\text{--}750\text{ °C}$ , the emergence of a new peak at  $1220\text{ cm}^{-1}$  together with peaks around  $1650$  and  $1440\text{ cm}^{-1}$  suggest the presence of bicarbonates (acid carbonates), although carbonates formed at lower temperatures might also be present with these bicarbonates. The combination of peaks at  $1620$ ,  $1430$  and  $1220\text{ cm}^{-1}$  have been previously [23] assigned to bicarbonate species. Pairs of bands of around  $1650\text{--}1370\text{ cm}^{-1}$  and  $1450\text{--}1415\text{ cm}^{-1}$  have also been attributed to a bidentate carbonate species and a nearly symmetrical carbonate species, respectively [22,24]. Peaks around  $1630\text{ cm}^{-1}$  have also been correlated to the presence of bound or adsorbed water [25]. This may be due to moisture absorbed by NKN samples during FTIR experiment and/or after furnace treatment and it underscores the hygroscopic nature of the of these NKN gels.

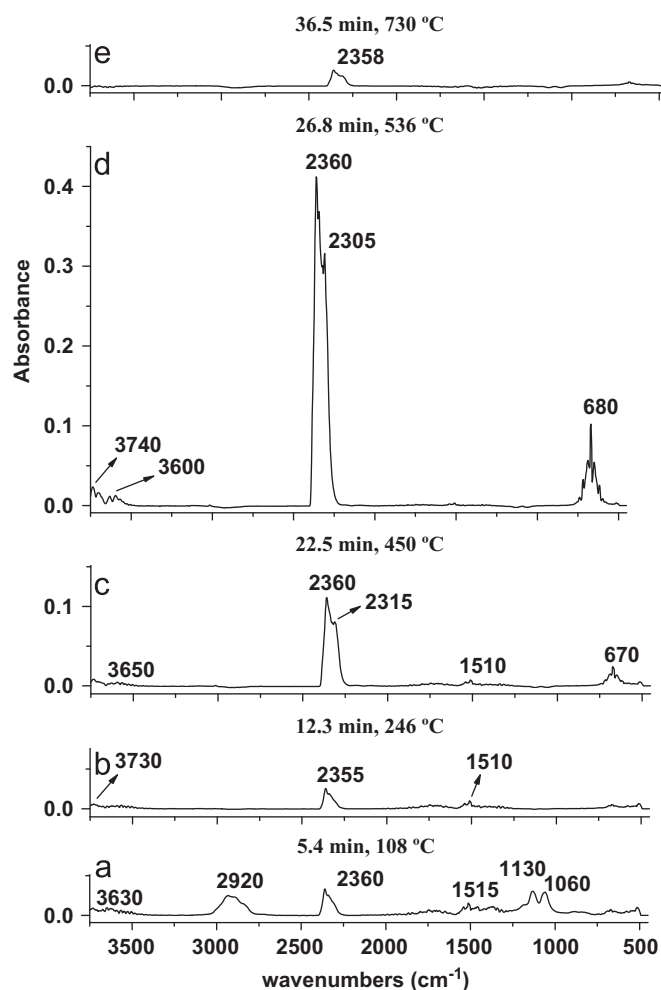
The peak at  $1750\text{ cm}^{-1}$ , which is always present in these plots up to  $850\text{ °C}$ , possibly indicates the existence of some free Na/K carbonate. Similar evidence has been reported for the presence of carbonate groups in our previous work [8]. The evidence suggests that free carbonate material persists in the sample, resulting in the phase segregation within the gel. At  $950\text{ °C}$ , the peaks at  $1420$  and  $1220\text{ cm}^{-1}$  are still prominent. However, the peak around  $1650\text{ cm}^{-1}$  becomes faint.



**Fig. 3.** FTIR spectrum of the evolved gases from the non-refluxed dried NKN gel during the TGA experiment at different time/temperatures. The relative intensity of absorbance between the spectra represents the approximate amount of the evolved gases.

For the 70 h refluxed NKN gel, an IR spectra (Fig. 8) are mostly in good agreement with the non-refluxed samples (Fig. 7). The significant differences are:

- From 550 to 750 °C, two major broad peaks are evident around 1640–1650 and 1350–1380  $\text{cm}^{-1}$ . A close inspection reveals small peaks at around 1520 and 1430  $\text{cm}^{-1}$ , which may be due to the presence of monodentate carbonate and adsorbed



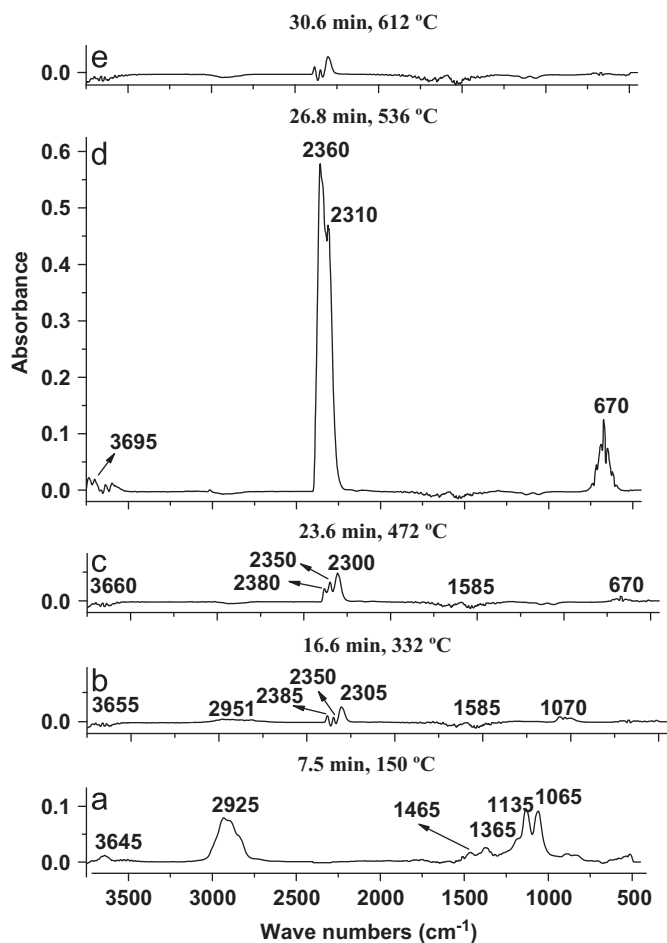
**Fig. 4.** FTIR spectrum of the evolved gases from the dried NKN gel (refluxed 24 h) during the TGA experiment at different time/temperatures. The relative intensity of absorbance between the spectra represents the approximate amount of the evolved gases.

carboxylate ( $\text{CO}_2^-$ ) ions [26]. These peaks become faint after 750 °C, indicating only a marginal presence of these compounds at higher temperatures.

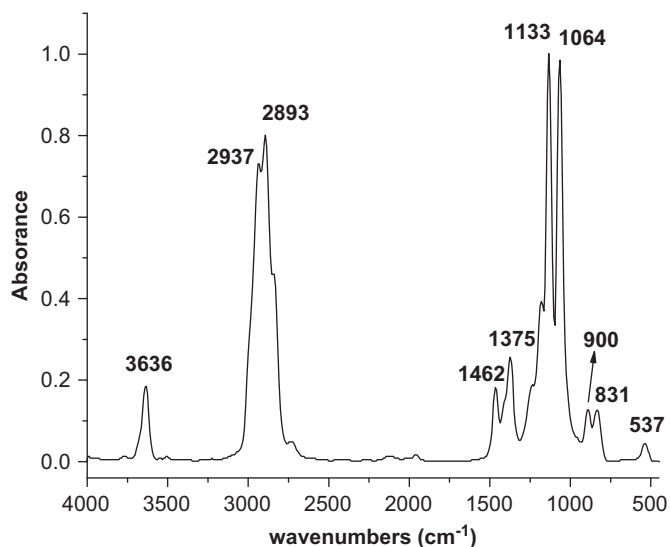
- Compared to the case of non-refluxed dried gel, two significant absences can be noted here; the peaks at 1220  $\text{cm}^{-1}$  (observed at higher temperatures) and 1750  $\text{cm}^{-1}$  as found in the case of the non-refluxed dried gel (250–850 °C), Fig. 7.

Using the information obtained from the FTIR in combination with that from the TGA, a comparative analysis can be made on the non-refluxed and 70 h refluxed dried NKN gel. In both cases, the major organic decomposition events are complete by 350 °C. The intermediate carbonates start forming at 350 °C and decompose at around 750 °C. For non-refluxed NKN gel, bicarbonate species are detected from 550 up to 950 °C. It is reasonable that these bicarbonate compounds form via the participation of surface hydroxyl groups or in combination with moisture in the atmosphere. It is feasible that, beyond 750 °C, the FTIR peaks indicating bicarbonates are not due to an intrinsic contribution from the sample, but arise from the interaction with the ambient environment during storage and handling of the sample prior to recording the FTIR spectra. We have dealt with this point explicitly in our previous work [16].

The presence of some free Na/K carbonate is evident up to 950 °C, which again points towards the phase segregation in the non-refluxed dried NKN gel. The absence of the peak at 1750  $\text{cm}^{-1}$

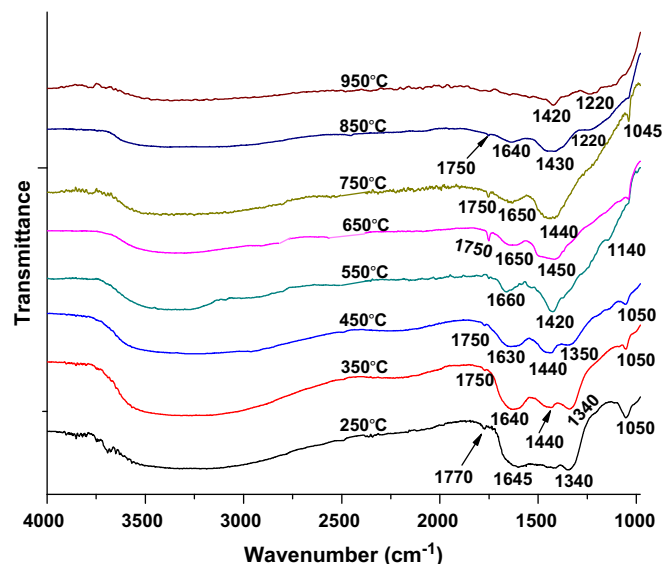


**Fig. 5.** FTIR spectrum of the evolved gases from the dried NKN gel (refluxed 70 h), during the TGA experiment, at different time/temperatures. The relative intensity of an absorbance between the spectra represents the approximate amount of the evolved gases.

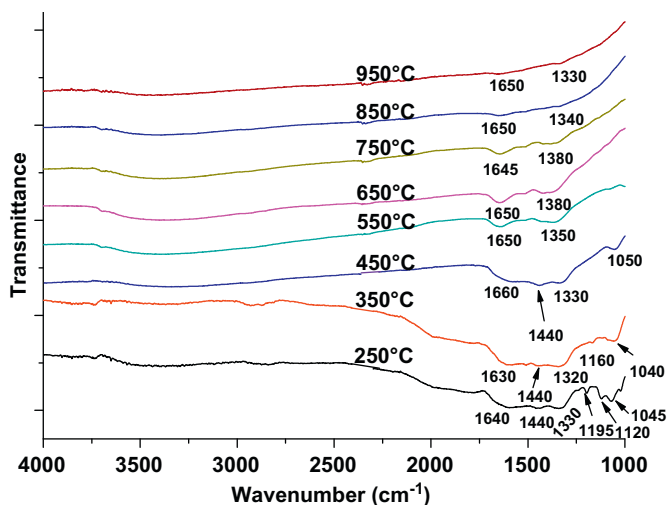


**Fig. 6.** FTIR spectrum of 2-methoxyethanol from the Nicolet Vapour Phase Library.

in the 70 h refluxed gel suggests a minimal presence of free carbonates in the sample. This observation supports our initial hypothesis mentioned in Section 1 that longer refluxing would promote more complete exchange reactions in the sol.



**Fig. 7.** FTIR plots for the NKN dried gels (non-refluxed) heated at various temperatures.



**Fig. 8.** FTIR plots for the NKN dried gels (refluxed 70 h) heated at various temperatures.

**Table 1**  
Infrared wavenumbers and their assignments for key peaks in the spectra shown in Figs. 7 and 8.

Peak assignment	Wavenumber/wavenumber range (cm <sup>-1</sup> )	Reference
C=O bending	1630–1640	[18,19]
CO <sub>3</sub> <sup>2-</sup> bending	1420–1440	[18,19]
COO <sup>-</sup> stretching	1350	[18,19]
COO <sup>-</sup> stretching, CO <sub>3</sub> <sup>2-</sup> stretching	1050	[18,19]
Inorganic hydrogen carbonate	Combination of peaks at 1620, 1430 and 1220	[23]
Inorganic bidentate carbonate species	Pairs around 1650–1370 and 1450–1415	[22]
Bending vibration for bound/adsorbed water	1630	[25]
C=O stretching (for metal carbonate formation)	1750	[8,18,19]
Monodentate carbonate and adsorbed carboxylate (COO <sup>-</sup> ) ions	Combination of peaks at 1520 and 1430	[26]

Unlike the case for the non-refluxed dried gel, no evidence for any bicarbonate/s ( $\text{HCO}_3^-$ ) can be seen in the 70 h refluxed NKN gel. The peaks observed in this case (for  $> 550^\circ\text{C}$ ) may be attributed to adsorbed carboxylate species ( $\text{M}^n+\text{COO}^-$ ). According to Davydov [26], there can be several carbonates with different structures simultaneously present on the oxide surface. This was established from the spectra obtained during and after the thermal desorption [26]. In that report, it was found that adsorbed species showed no contribution/s from the hydroxyl ( $-\text{OH}$ ) groups.

### 3.5. XRD analyses of NKN dried gels

XRD plots of the calcined non-refluxed and 70 h refluxed NKN powders are shown in Figs. 9 and 10, respectively. There is little evidence of crystallisation in the  $350^\circ\text{C}$  powder for either sample (the broad background hump is due to the glass sample holder).

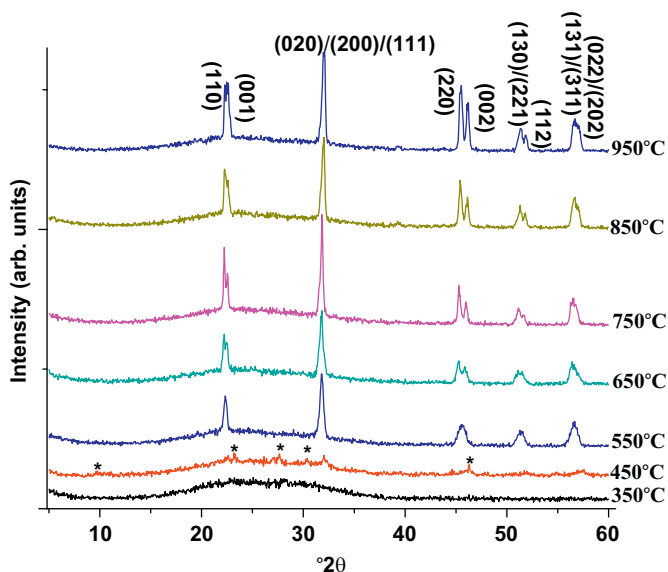


Fig. 9. X-ray diffraction plots for the NKN dried gels (non-refluxed) heated at various temperatures; the "\*" symbol depicts the extra phases in the  $450^\circ\text{C}$  sample.

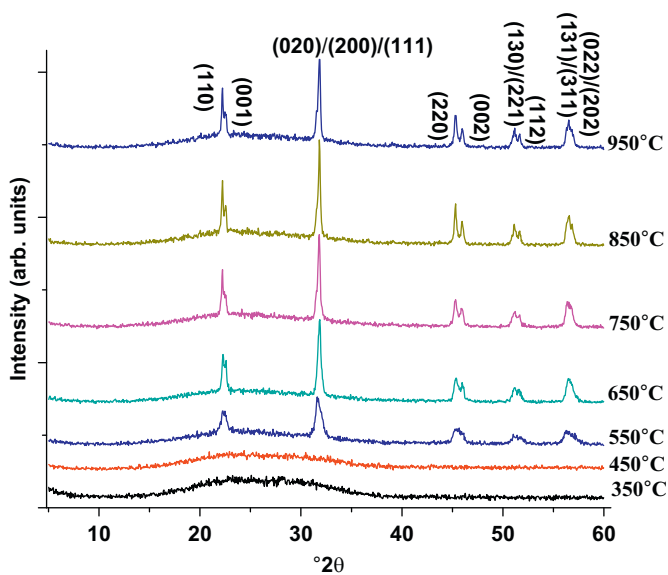


Fig. 10. X-ray diffraction plots for the NKN dried gels (refluxed 70 h) heated at various temperatures.

However, close inspection of a non-refluxed NKN sample heated at  $450^\circ\text{C}$  (for 30 min) reveals faint extra peaks at  $9.7$ ,  $23.2$ ,  $27.6$ ,  $30.4$  and  $46.3^\circ 2\theta$ , in addition to the NKN peaks. The extra XRD peaks most likely originated from a mixed influence of  $\text{K}_8\text{Nb}_6\text{O}_{19} \cdot 10\text{H}_2\text{O}$  (JCPDS file No. 14-0288) and/or  $\text{K}_2\text{Nb}_4\text{O}_{11}$  (JCPDS file No. 31-1059). The 70 h refluxed NKN gel shows no extra peak at  $450^\circ\text{C}$ . The first appearance of a crystalline, pseudo cubic XRD pattern is noted at  $550^\circ\text{C}$ . For samples heated at  $\geq 550^\circ\text{C}$ , no extra XRD peaks are evident. However, the hydrated carbonate phase(s) may be present at a level below the XRD detection limit (a few wt%), or are present in an amorphous form.

It should also be noted here that the evidence from an XRD is not sufficient to ascertain the formation of crystalline  $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ . In our previous work, we have already shown that due to the phase segregation in the NKN system, mixed niobates (of Na and/or K) could also be formed [16]. The formation at  $450^\circ\text{C}$  of a K-rich phase in the non-refluxed system could be related to the possible presence of Na or/and K rich niobate cluster region/s in the precursor solution. However, these phases, if formed, would generate similar set of peaks and therefore, from the ordinary XRD analysis, it would be extremely difficult to differentiate between composite mixed phase and the NKN phase on the atomic scale. Thus, in the future it would be of interest to carry out a detailed phase analysis of these sol-gel based NKN systems using other characterisation tools such as neutron diffraction, etc., in order to shed more light on the complex phase formation of these systems.

## 4. Discussion

### 4.1. Effect of refluxing on the sol-gel NKN system

Prolonged hours of refluxing are a common practice in the sol-gel chemistry and, as reported previously for different oxide systems [27,28]; it is believed to encourage a uniform mixing of the precursor chemicals. In this work, a rationalisation of the different thermal history for the refluxed and non-refluxed NKN gels may be made from a consideration of the structural chemistry of the individual alkoxide precursors. The changes in the final thermochemistry of the gels have been interpreted on the basis of the thermal analyses on the gels refluxed for different durations. The presence of methoxyethanol in the pre-calcined gel may be one of the components that leads to a higher level of carbonate formation in the calcined product, and thus refluxing improves the oligomer cross-linking and reduces the amount of entrained solvent in the gel. For the case of partially refluxed sols, the oligomeric  $-\text{M}-\text{O}-\text{M}-$  chain link formation mentioned in Section 1 is probably incomplete for the following reasons:

- In the non-refluxed case the individual binary end member (Na and K niobate gels) units persist, but with Na and/or K rich niobate regions in clusters.
- A small but significant amount of the precursor chemicals may remain individually as Na/K methoxyethoxides in the solution.

Both of these factors could lead to heterogeneity and segregation in the parent sol. As observed from the combined TGA-FTIR experiments, the relative change in the amount of evolved methoxyethanol vapours serves as a good metric for comparison. The methoxyethanol solvent may have evaporated significantly during the drying process of the non-refluxed sol, thus giving rise to FTIR plots showing predominantly water and  $\text{CO}_2$  even at the lower temperature of  $128^\circ\text{C}$  (Fig. 3a). However, the refluxing process helps a uniform mixing of the precursors at the molecular level. Data from Fig. 4a, showing the 24 h refluxed gel dried powdered samples, suggest that the fraction of  $-\text{M}-\text{O}-\text{M}-$  chain link

formation has improved, whereas, for the 70 h refluxed gel dried powdered samples, the evolution of pure 2-methoxyethanol at a lower temperature (Fig. 5a) indicates a much improved level of transformation of the –M–O–M– chains in the sol.

The main difference among the solutions obtained after reflux of 0, 24 and 70 h lies on the improved cross-linked network developed as the refluxing time is increased. Despite this, the amounts of reagents present in these solutions should be the same, independent of being more or less intimately involved in the network. At temperatures close to 900 °C, it is expected that the elimination of all the organic compounds of the system (again, independent of being more or less intimately involved in the network) would consequently lead to the formation of the final oxide phase. The difference in weight loss observed in the TGA analyses of these gels could likely come from the previous gel drying process at 60–70 °C (mainly, due to evolved species during drying).

It should be mentioned that the gel formation process (gelation) is also significant in the sol–gel systems. The conditions of the gel preparation are usually varied in bulk ceramic systems in order to ensure a final homogeneous gel. However, for the case of thin films, refluxing serves the same purpose in ensuring the formation of a homogeneous sol. In this work, as we did not get good ferroelectric properties, even after 70 h of refluxing [16], the obvious next step was to dry the NKN sol as it is to investigate the thermochemistry.

Furthermore, it should be noted that a combined DTA–TGA–MS experiment carried out on the same series of NKN gels [16] has also shown this point, i.e., simultaneous thermogravimetric analysis mass spectrometry peaks featured a gradual intensification of the peak for methoxyethanol fragment at ~110 °C, as the refluxing hours for the NKN systems were increased from zero to 70 h. No methoxyethanol evolution was recorded for the non-refluxed NKN gel and there was an order of magnitude difference between the evolved methoxyethanol species from the 24 h refluxed NKN compared to the sample refluxed for 70 h. However, the combined DTA–TGA–MS experiment showed moderate CO<sub>2</sub> and H<sub>2</sub>O peaks and a very strong methoxyethanol peak at 110 °C making it clear that the process of CO<sub>2</sub> evolution at low temperature (< 200 °C), as observed for 0 and 24 h refluxed samples, had not finished, and hence, even 70 h of refluxing is insufficient for the completion of –M–O–M– exchange reactions in this alkoxide based sol–gel NKN system. This fact also points towards the limitation of the sensitivity of the TGA–FTIR instrument, as it showed predominantly methoxyethanol vapours (Fig. 5a).

#### 4.2. Spectroscopic and structural analyses on NKN gels calcined at different temperatures

The FTIR analyses on the gels (non-refluxed and refluxed for 70 h) showed two types of hydration and carbonation reactions: intrinsic (constituents within the sample) and extrinsic (contributions from the ambient atmosphere, during storage and handling of the sample). Together with inorganic carbonates, evidence for the presence of bicarbonates and/or hydroxycarbonates is also confirmed. As expected, the series for the non-refluxed dried gels (Fig. 7) appears to be more due to the intrinsic contributions, whereas the series plot for 70 h refluxed NKN gels (Fig. 8) is much cleaner with mostly an extrinsic contribution/s.

Information obtained from the XRD patterns of the two series of samples does not bring out any significant information about the NKN system. The only change seen for the non-refluxed samples, where a few extra peaks occur in the 450 °C sample (Fig. 9), indicates that the extra phase could be related to some potassium rich systems. However, a precise identification of the phase will require further investigation. The most likely reason for the extra peaks is that they arise from the presence of an extra phase that

may be either below the XRD detection limit or in an amorphous form undetectable by an XRD. A further possible explanation for the apparent similarity of the zero and 70 h refluxed gels could be that any new peaks overlap with those for the dominant and strong NKN peaks.

## 5. Conclusion

Alkoxide-based NKN gels made by using in-house alkoxide precursors have been refluxed for 0, 24 and 70 h. The effect of an increased refluxing time supports our initial hypothesis that the ligand exchange reaction taking place in the sol–gel solution requires to be driven to completion, and this is illustrated by the combined TGA–FTIR experiments, where it is found that prolonged hours of refluxing (from 0 to 70 h) makes the NKN system more homogenous. FTIR studies on dried gels calcined at different temperatures (250–950 °C) show the existence of different (hydrated) carbonate/s with the 70 h refluxed series being relatively less carbonated. The XRD of the gels did not show any noteworthy changes, but pointed towards the existence of the mixed phases in this alkoxide-based NKN sol–gel system.

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## References

- [1] B. Jaffe, W.R. Cook Jr., H. Jaffe, *Piezoelectric Ceramics*, Academic Press, New York, 1971.
- [2] A. Moulson, J. Herbert, *Electroceramics*, second ed., John Wiley & Sons Ltd., Chichester, West Sussex, 2003.
- [3] Y. Guo, K.-i. Kakimoto, H. Ohsato, *Mater. Lett.* 59 (2004) 241–244.
- [4] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, *Nature* 432 (2004) 84–87.
- [5] D. Lin, K.W. Kwok, K.H. Lam, H.L.W. Chan, *J. Appl. Phys.* 101 (2007) 074111/1–074111/6.
- [6] R. Zuo, J. Roedel, R. Chen, L. Li, *J. Am. Ceram. Soc.* 89 (2006) 2010–2015.
- [7] K. Tanaka, K.-i. Kakimoto, H. Ohsato, T. Iijima, *Ferroelectrics* 358 (2007) 175–180.
- [8] A. Chowdhury, J. Bould, Y. Zhang, C. James, S. Milne, *J. Nanopart. Res.* 12 (2010) 209–215.
- [9] A. Chowdhury, S. O'Callaghan, T.A. Skidmore, C. James, S.J. Milne, *J. Am. Ceram. Soc.* 92 (2009) 758–761.
- [10] S.A. O'Callaghan, K.M. Knowles, *Mater. Sci. Technol.* 25 (2009) 1302–1306.
- [11] X. Wu, L. Wang, W. Ren, X. Yan, P. Shi, X. Chen, X. Yao, *Ferroelectrics* 367 (2008) 61–66.
- [12] K. Tanaka, H. Hayashi, K.-i. Kakimoto, H. Ohsato, T. Iijima, *Jpn. J. Appl. Phys.* 1 (46) (2007) 6964–6970.
- [13] K. Tanaka, K.-i. Kakimoto, H. Ohsato, T. Iijima, *Jpn. J. Appl. Phys.* 1 (46) (2007) 1094–1099.
- [14] C.J. Brinker, C.S. Ashley, R.A. Cairncross, K.S. Chen, A.J. Hurd, S.T. Reed, J. Samuel, P.R. Schunk, R.W. Schwartz, C.S. Scotto, *Metall. Ceram. Prot. Coat.* (1996) 112–151.
- [15] C.J. Brinker, G.W. Scherer, *The Physics and Chemistry of Sol–Gel Processing*, Academic Press, London, 1990.
- [16] A. Chowdhury, J. Bould, M.G.S. Londesborough, S.J. Milne, *Chem. Mater.* 22 (2010) 3862–3874.
- [17] A. Chowdhury, J. Bould, M.G.S. Londesborough, E. Vecerníková, S.J. Milne, *Mater. Chem. Phys.* 124 (2010) 159–162.
- [18] R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, sixth ed., New York, 1997.
- [19] G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, third ed., 2004.
- [20] D.H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, fourth ed., McGraw-Hill, London, 1990.

- [21] C. Guha, J.M. Chakraborty, S. Karanjai, B. Das, *J. Phys. Chem. B* 107 (2003) 12814–12819.
- [22] C. Gensse, T.F. Anderson, J.J. Fripiat, *J. Phys. Chem.* 84 (1980) 3562–3567.
- [23] K. Tomishige, Y. Ikeda, T. Sakaijori, K. Fujimoto, *J. Catal.* 192 (2000) 355–362.
- [24] M.B. Cerfontain, J.A. Moulijn, *Fuel* 65 (1986) 1349–1355.
- [25] J.L. Bandfield, T.D. Glotch, P.R. Christensen, *Science* 301 (2003) 1084–1087.
- [26] A. Davydov, *Molecular Spectroscopy of Oxide Catalyst Surfaces*, John Wiley & Sons, 2003, pp. 133–139.
- [27] C.D.E. Lakeman, D.A. Payne, *J. Am. Ceram. Soc.* 75 (1992) 3091–3096.
- [28] M. Thammachart, V. Meeyoo, T. Risksomboon, S. Osuwan, *Catal. Today* 68 (2001) 53–61.