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Effect of alkali carbonates excess on the properties of sodium potassium niobates ceramics

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Abstract

Nowadays, lead-free materials have been urgently demanded from the viewpoint of environmental protection. One of the promising candidates to replace the lead containing materials is sodium potassium niobate. In present work, sodium-potassium niobate ($(Na_{0.5}K_{0.5})NbO_3$; NKN) ceramics with excess of alkali carbonate starting powders (0, 0.01, 0.03 and 0.05 mol) were prepared by solid – state reaction. The results showed that the amount of K_2CO_3 and Na_2CO_3 excess affected significantly to sintering temperature, bulk density, microstructure and dielectric property. Whereas, the XRD result showed the orthorhombic phase and there was no secondary phase formed in all samples. The highest dielectric constant value was found to be 1707 for sample with excess of 0.01 mol when sintered at 1100 °C. This is believed that the uniform microstructure and smaller in grain size were obtained.

Keywords: Powders: solid state reaction, Dielectric properties, Niobates, Microstructure-final

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1. Introduction

Lead oxide based ferroelectrics such as lead zirconate titanate [$Pb(Zr,Ti)O_3$ or PZT] are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [1-2]. Because of the detrimental effects of lead on human health, and because of European Union legislation it is important that Pb-free ferroelectric and piezoelectric materials are developed. The new environmentally acceptable and biocompatible materials should exhibit electrical properties comparable to those of Pb-based ferroelectrics, which have been developed over several decades.

Sodium-potassium niobate, [$Na_{1-x}K_xNbO_3$ or NKN], based ceramics are one of the most promising alternative systems to PZT [1, 3]. The $Na_{1-x}K_xNbO_3$ solid solution system, between ferroelectric $KNbO_3$ and antiferroelectric $NaNbO_3$, forms several morphotropic phase boundaries (MPB), one of which exists between two orthorhombic phases near the composition x = 0.5 [1,4-5]. Although the piezoelectric properties of NKN solid solutions improve close to this MPB, they are still substantially inferior to PZT. However it has been shown by Saito et al. that Li and Ta ion substitution of the base $Na_{0.5}K_{0.5}NbO_3$ composition, together with <001> grain-orientation, results in piezoelectric d_{33} charge coefficients of ~ 400 pC/N. These values are very competitive

with PZT [6]. For randomly oriented $(K_{0.5}Na_{0.5})_{1-x}Li_x(Nb_{1-y}Ta_y)O_3$ ceramics, d_{33} coefficients are ~ 200-250 pC/N [6-7]. Guo et al. have studied the more simple binary $Na_{0.5}K_{0.5}NbO_3$ – $LiTaO_3$ system, and for compositions at a MPB between tetragonal and orthorhombic phases, d_{33} values of ~ 200 pC/N are reported for conventional, non-oriented, ceramic samples [3].

Specialist fabrication routes, including hot-pressing and spark-plasma sintering, have been investigated in-order to overcome difficulties which have been encountered in fabricating high density NKN-based ceramics [5, 8-9]. However there are also reports that high density alkali niobate ceramics may be obtained by normal sintering methods, particularly if efficient milling is used prior to compaction [9, 10-12]. Whichever densification method is employed, the most cost-effective means of producing a starting powder is by a mixed-oxide solid state reaction route. The Nb_2O_5 starting component is relatively refractory, with a melting point of 1520 °C, whereas Na_2CO_3 and K_2CO_3 have much lower melting points, 851 °C and 891 °C, respectively [13]. The alkali components therefore become volatile at moderate calcination or sintering temperatures, and this combination of properties in the starting reagents makes it potentially difficult to prepare chemically homogeneous, single-phase alkali niobate powders by the mixed-oxide route. Variability in the starting powders may in-part be responsible for some of the reported discrepancies in the densification characteristics of NKN- based ceramics.

The present work, the effects of introducing excess alkali carbonates to the starting mixture as a function of sintering conditions, in order to compensate for probable alkali oxide losses during calcination or sintering on phase development and the properties in $Na_{0.5}K_{0.5}NbO_3$ ceramics were investigated.

2. Experimental procedure

Samples containing excess of Na_2CO_3 and K_2CO_3 at levels of 0, 1, 3 and 5 mol% were prepared by the conventional mixed-oxide process using K_2CO_3 (Aldrich Chemical Company, Inc., ≥ 99.0% purity), Na_2CO_3 and Nb_2O_5 (Aldrich Chemical Company, Inc., 99.9+% purity). This type of approach is often used for PZT powders by adding excess PbO to compensate for the volatility of PbO (losses during subsequent sintering can be addressed by using an 'atmosphere' powder). In the present work, powder samples were made with an equimolar ratio of Na_2CO_3 and K_2CO_3. This two carbonate powders are moisture-sensitive; thermogravimetric analysis indicates that dehydration is completed at ~ 200 °C, therefore to avoid compositional errors when weighing out the $Na_{0.5}K_{0.5}NbO_3$ precursor mixture, the starting reagents were dehydrated in an oven for 24 h prior to use. Dried powders were allowed to cool to room temperature under reduced pressure in a dessicator, and all powders were stored in the dessicator until immediately prior to weighing in the correct proportions. The mixed starting materials were transferred to a plastic jar containing 10 mm-diameter alumina grinding balls. Ball-milling was carried out for 24 h using ethanol as the liquid medium; this was followed by drying at 120 °C for 24 h, prior to grinding with an alumina mortar and pestle. The mixtures were calcined in alumina crucibles at 900 °C, exempt sample with 5 mol% excess was calcined at 800 °C, for 2 h with loosely fitting lids. The calcined powder was ball-milled in ethanol again for 24 h. After drying, it was mixed thoroughly with a PVA binder solution and uniaxially pressed at 100 MPa into disk samples with a diameter of 15 mm. The disk samples were then sintered in air at temperature ranging from 1075 - 1160 °C for 2 h, using heating and cooling rates of 5 °C/min.

Phase formation in the polished surfaces of sintered samples was examined at room temperature using X-ray powder diffraction (XRD; Philips X' Pert MPD, Ni-filtered CuK_α radiation). The geometric density of samples was calculated by mass and volume. The microstructures of the as-sintered surfaces of the samples were imaged directly, using scanning electron microscopy (SEM; Jeol : JSM-5800LV). To investigate dielectric property, capacitance and loss tangents (tan δ) of sample with silver paste electrode was measured at room temperature using a LCR meter (HP 4263B) on the basis of frequency, and the relative permittivity (ε_r) was then calculated.

3. Results and Discussion

The XRD patterns of samples with different alkali carbonate starting powders sintered at 1140 °C for 2 h are shown in Fig 1. The diffracted peaks are identified to perovskite phase with orthorhombic structure, formed without secondary phase in all samples. An excess of 5 mol% Na_2CO_3 and K_2CO_3 was found to have a significant effect on phase development, but 1-3 mol % produced similar results to the non-excess samples. This is confirmed that the increase of diffraction peak intensities was obtained. The addition of excess alkali carbonates had no measurable effect on d-spacings, with estimated lattice parameters: a = 5.59, b = 15.73 and c = 5.67 Å for all sample-types. These values are similar to those reported in the literature [14].

The density of samples as a function of amount of alkali carbonate and sintering temperature is shown in Fig. 2. The density of non-excess sample decreased significantly with increasing of sintering temperature. This is due to the loss of alkali oxide during sintering. After introducing excess alkali carbonates, the maximum density was reach to

4.14 g/cm^3 for the sample containing 0.03 mol% of alkali carbonate powders at sintering temperature of 1140 °C. The density values represent an increase from ~ 89 % to 92 % theoretical density (assuming a theoretical value of 4.51 g/cm^3 [10]) through adding 3 mol % excess alkali carbonates to the initial powder mixture. At sintering temperature of 1100 °C, the density decreased with increasing the excess alkali carbonate content. This is due to an adding with high content of excess Na_2CO_3 and K_2CO_3 (5 mol %) showed significantly larger agglomerated cuboid particles, are potentially more difficult to mill into a sinter active powder resulting in increases its porosity. At higher sintering temperature, the presence of Na_2CO_3 and K_2CO_3 rich liquid phase usually helps higher densification in sintering. Further increasing of sintering temperature to 1160 °C makes too high for sintering NKN ceramics and causes the density decrease. The limiting sintered geometric density for the optimum level of excess carbonates is around 3 % lower than Archimedes density values reported for NKN ceramics made from (non-excess) powders prepared using conventional planetary milling [10]. In part this may be due to differences in measurement techniques as at these porosity levels geometric densities are often lower than corresponding values measured by water displacement.

The dependence of microstructure on the level of excess alkali carbonate and sintering temperature is shown in Figs 3-4. By using the intercept method, the average grain sizes at 1100 °C were 4.41 ± 2.51, 0.85 ± 0.07 and 1.37 ± 0.32 μm for samples with the excess alkali carbonates of 0, 1 and 3 mol%; whereas at 1140 °C they were 4.25 ± 0.87, 3.77 ± 1.65, 4.07 ± 2.25 and 5.56 ± 1.09 μm for samples with the excess alkali carbonates of 0, 1, 3, and 5 mol%, respectively. This result showed that the grain size was strongly dependent on sintering temperature and addition of excess alkali carbonates,

especially at lower sintering temperature of 1100 °C. Inhomogeneous grain was observed in non-excess NKN samples, while homogeneous and smaller in grain size was obtained for excess-sample. This is directly attributed to the addition of excess alkali carbonate suppressed grain growth with sensitive to sintering temperature. After sintering at 1140 °C, grain structure of non-excess sample was more uniform than that of the samples contained alkali carbonates -excess. This is suggested that the higher liquid phase in excess-sample promoted an inhomogeneous grain growth at higher sintering temperature.

The dependence of dielectric property (ε_r and tanδ) on frequency for both of non-excess and excess-samples was investigated. It was found that the ε_r and tanδ decreased with increase of frequency. The ε_r and tanδ at 1 kHz as a function of amounts of excess alkali carbonates and sintering temperature at room temperature is shown in Fig 5. The amounts of excess alkali carbonates and sintering temperature were found to have a significant effect on the relative permittivity. The results showed an increase in relative permittivity up to a maximum of 1707 in the 1 mol% excess alkali carbonates contained sample. This is contributed to the more uniform and much smaller in this sample. However, at the higher alkali carbonates contained the relative permittivity decreased at lower sintering temperature (1100 °C). This result attributed to the lowering of density at the higher alkali carbonates, which causes the high porosity. The ε_r decreased continuously and tan δ increased with increase of excess alkali carbonates content at higher sintering temperature of 1140 °C. This is due to the inhomogeneous grain structure and low densities were observed.

4. Conclusions

$Na_{0.5}K_{0.5}NbO_3$ ceramics were prepared by a mixed-oxide route under various sintering conditions and amount of excess alkali carbonates starting powders. Evidence gained from XRD revealed that an orthorhombic single-phase product, with adding excess of Na_2CO_3 and K_2CO_3 up to 5 mol %. Maximum sintered density was achieved for 3 mol %, of the combined additive; this is attributed to an optimized liquid phase amount to promote densification and compensation of probable alkali oxides losses. An excess-sample showed a much smaller and uniform grain size than that of non-excess sample when sintered at low temperature of 1100 °C. This is resulting in the highest relative permittivity of 1707 for 1 mol%-excess sample.

Acknowledgments

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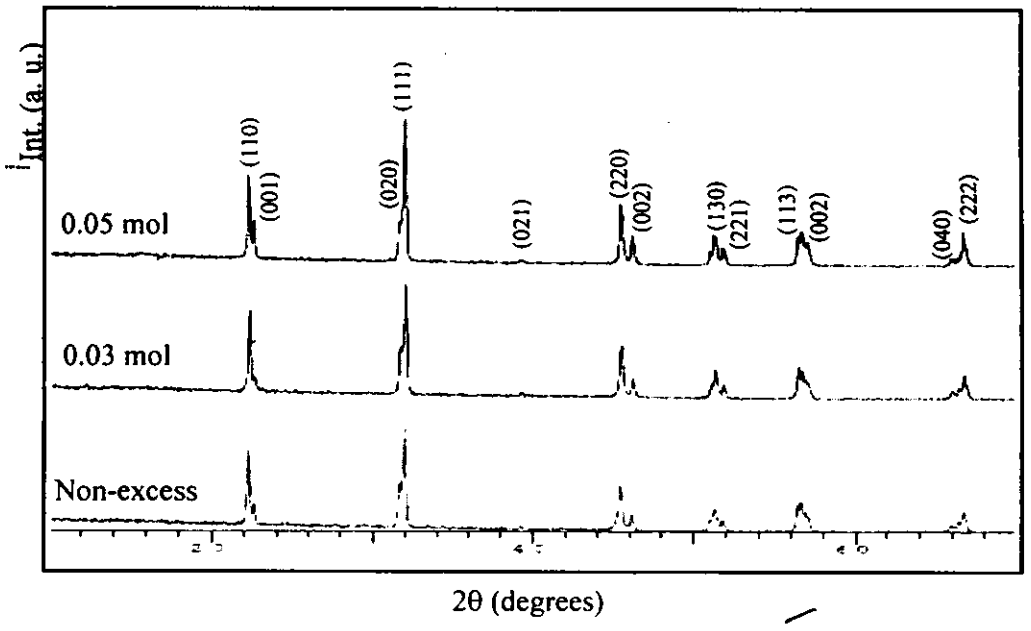

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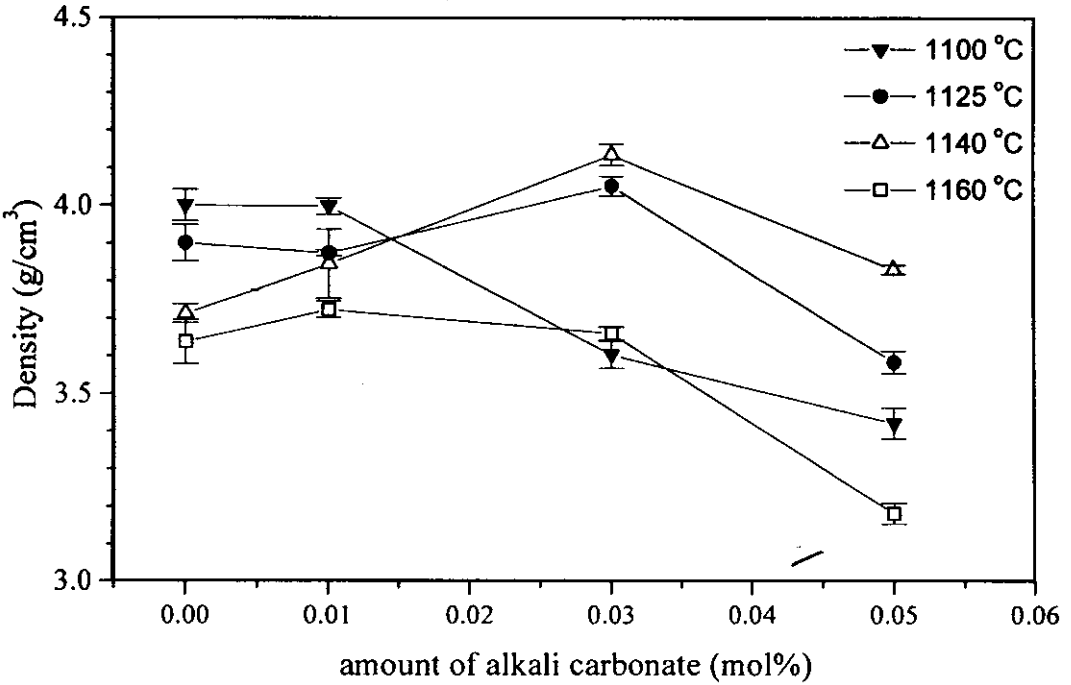

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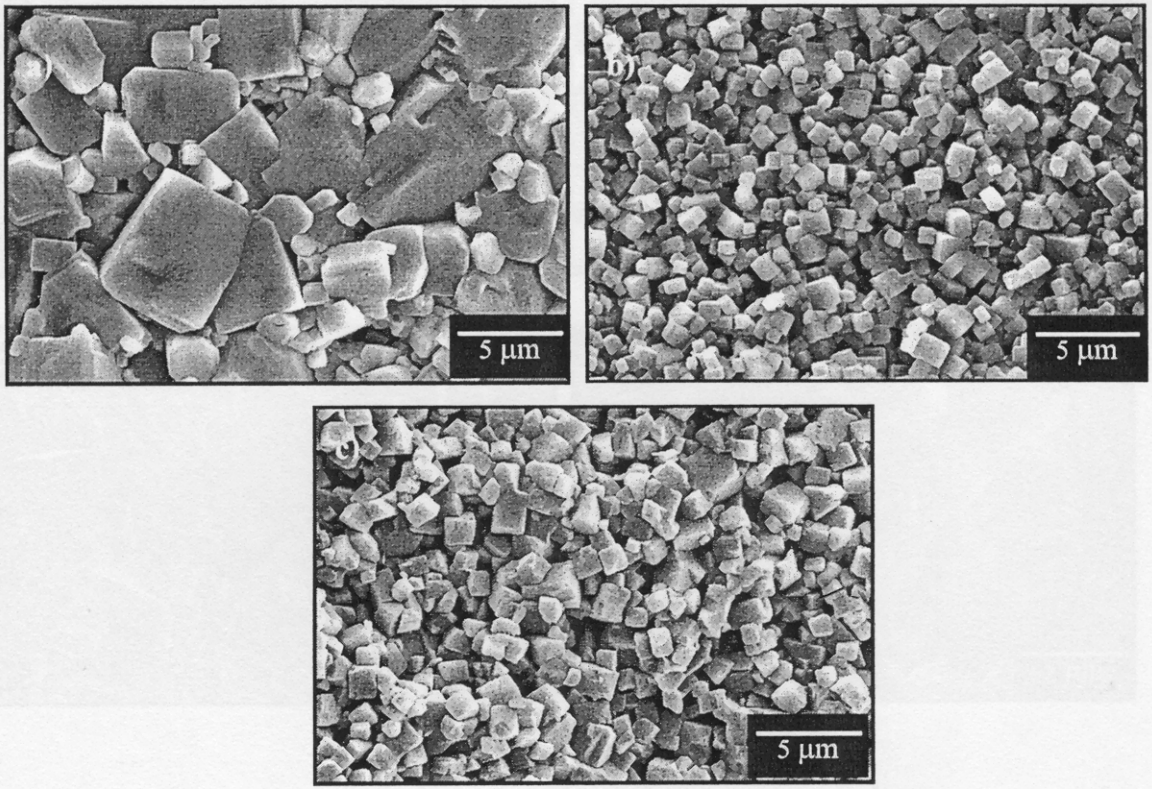

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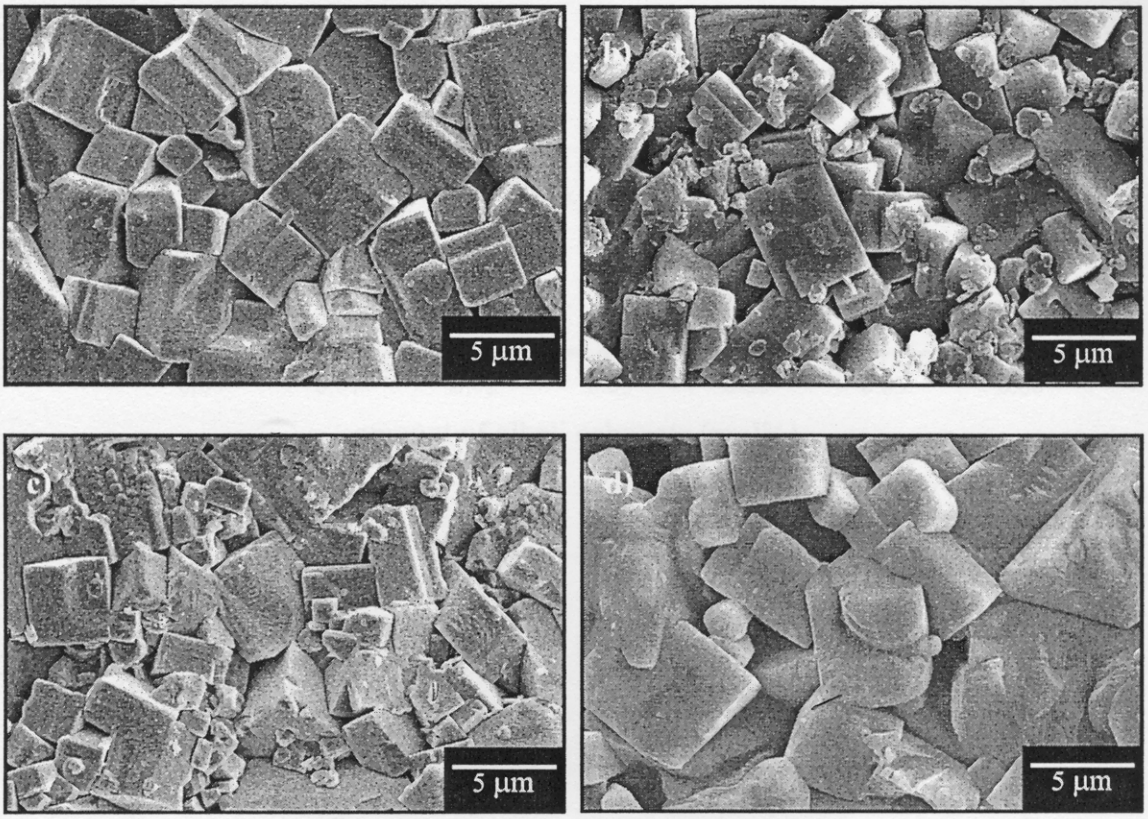

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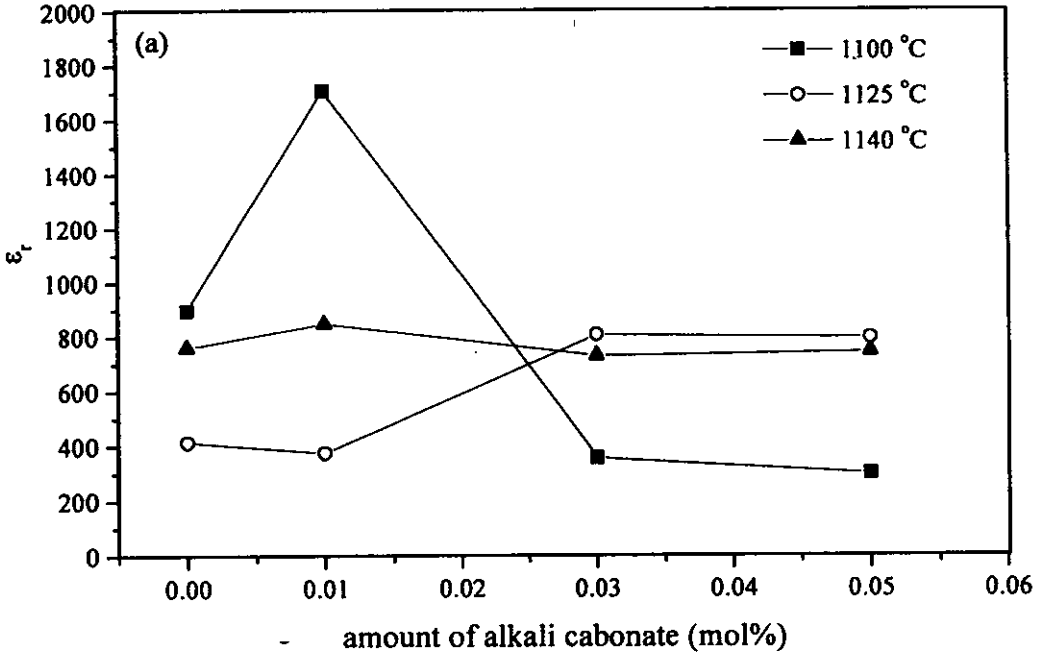

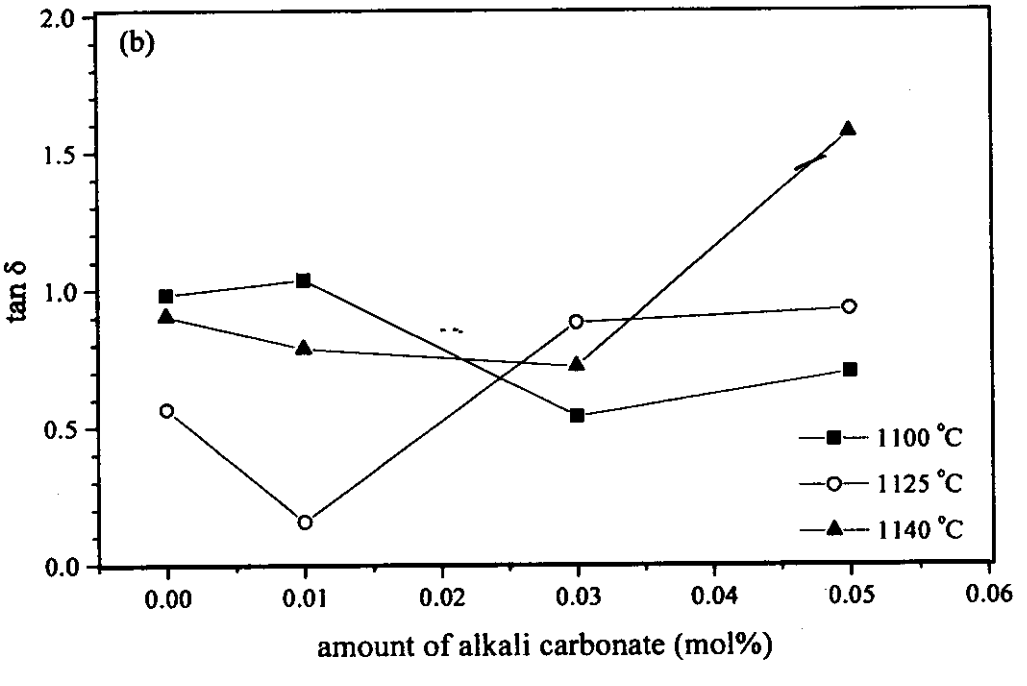

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