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Effect of lithium salts addition on sintering temperature, cationic ordering and dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic

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The effect of different lithium salts (LiF, Li_2CO_3, $LiNO_3$) addition on sintering temperature, cationic ordering and dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic has been investigated. This perovskite was synthesised by solid state reaction from $BaCO_3$, MgO and Ta_2O_5. It was shown that, by addition of $LiNO_3$, the sintering temperature was decreased to 1300°C (versus 1550°C–1600°C for the pure $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramic) without altering dielectric properties at 1 MHz. A cationic ordering was also observed. Sintering with co-fired nickel electrodes in Ar/H_2 atmosphere was also successfully performed for Multi Layer Ceramic Capacitors applications.

1. Introduction

$Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is a well-known perovskite material used at microwave frequencies as a dielectric resonator device [1, 2]. This material exhibits a medium dielectric constant ($\varepsilon = 25$), very low dielectric losses ($\tan(\delta) < 10 \times 10^{-4}$) and a low temperature coefficient of the resonant frequency ($\tau_f < 50$ ppm/°C). The crystallographic structure of the ($AB'_{1/3}B''_{2/3}O_3$) materials is the cubic perovskite one (ABO_3) when B'^{2+} and B''^{5+} cations are randomly distributed in the B-site. In this case, $Ba(Mg_{1/3}Ta_{2/3})O_3$ structure is described with Pm3m space group [3]. An hexagonal superstructure appears if an ordering of the cations Mg^{2+} and Ta^{5+} occurs along the [111] direction of the cubic lattice (space group P-3 ml) [4]. In this case, the lattice of BMT is described by infinite BaO_3 layers and infinite layers of either Ta^{5+} and Mg^{2+} in octahedral sites in the proportion 2/3:1/3 respectively along the [111] direction of the parent perovskite cubic lattice. It is well known that dielectric losses depend on the degree of the B-site ordering since the hexagonal superstructure modifies the mode of the lattice vibration that lowers the dielectric losses [5]. This parameter depends also on the different microstructural factors such as the porosity, the secondary phases and the crystal imperfections in the ceramic [6–12]. Unfortunately, a very high temperature (>1550°C) and a long sintering time are necessary to obtain both cationic ordering and a satisfactory density [6–9, 11, 12].

Our purpose is to decrease the sintering temperature of BMT material without altering dielectric properties. This aspect is of primary importance in order to use the BMT ceramic as a dielectric material for Base Metals Multi-Layer Ceramic Capacitor (BME-MLCC). The dielectric constant of BMT with its linear dependence versus temperature is suitable for the manufacturing of type I MLCC components. Moreover, their low dielectric losses should permit to process high performance capacitors. In order to use cheaper internal electrodes than the usual ones made of Ag/Pd alloy, the use of Base Metal is also envisaged (Ni or Cu). It involves to reach (for Ni electrodes) a sintering temperature lower than 1453°C (Nickel Melting Point) and to use a reductive atmosphere in order to avoid the electrodes oxidation. Studies have already reported that lithium salts additions are beneficial for lowering the sintering temperature of some perovskites [13–15]. These compounds have been then tested to decrease the sintering temperature of BMT. In the first part, the effect of the lithium salts (LiF, Li_2CO_3, $LiNO_3$) additions on the sintering temperature, the cationic ordering and the dielectric properties of BMT is investigated (in static air). In the second part, the sintering in a reductive atmosphere and the final properties of the best composition are presented. Finally, a BMT-nickel co-sintering is performed to validate the feasibility of manufacturing BME-MLCC.

2. Experimental procedure

A mixture of $BaCO_3$ (Diopma, 99.99% purity), MgO (Cerac, 99.95% purity) and Ta_2O_5 (Cerac, 99.99% purity) was thoroughly mixed by attrition grinding in a teflon container using ZrO_2 balls in ethanol during 2 h. Precursors are previously weighted according to the stoichiometric composition. The perovskite phase $Ba(Mg_{1/3}Ta_{2/3})O_3$ was subsequently synthesised

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by solid state reaction at 1300°C during two hours in air (heating rate = 2.5 K/min). This powder was ground using the same process than before the calcination step. X-ray diffraction (SEIFERT diffractometer—Cu K_α radiation) was used to determine the phase purity. Lithium salt additives (LiF, Li_2CO_3, $LiNO_3$, Prolabo, 99% purity) and BMT material were wet ball milled in an agate mortar. This powder was uniaxially pressed to cylindrical pellets of $\varnothing = 6.36$ mm for dilatometric measurements and $\varnothing = 8.07$ mm for sintering.

The shrinkage curves versus temperature was obtained by Thermo-Mechanical Analysis in air (SETARAM TMA-92). Sintered samples were subsequently characterised by X-ray Diffraction (XRD Philips, X'Pert) using the Cu K_α X-ray line. Samples microstructures were observed by Scanning Electron Microscopy (SEM Phillips XL'30 FEG) and dielectric properties (permitivitty and losses factor) versus temperature were measured at 1 MHz using an LRC bridge (Flucke PM6306).

Both faces of a $\varnothing = 8.07$ mm disc sample were painted with a mixture composed of nickel and organic linker to investigate the co-sintering. A mixture of 90% Ar/10% H_2 moister saturated was used as a reductive atmosphere during the sintering to avoid the metal oxidation. The thermal cycle used for this co-sintering was 1300°C during 2 h (heating rate = 2.5 K/min).

3. Results

3.1. Lithium salts addition

The amount of lithium was chosen with respect to an addition of 1 wt% of LiF (12.2% mol) based on the material weight. Thus, Li_2CO_3 and $LiNO_3$ additions were respectively 1.43 wt% of and 2.66 wt%. The shrinkage curves and final samples apparent densities are presented on Fig. 1. The addition of lithium salts allows undoubtedly to decrease the sintering temperature. However, a low final shrinkage value is obtained for the LiF added pellet (about 10%). The Li_2CO_3 addition involves a two steps sintering and a final sintering temperature upper than 1400°C. The lower sintering temperature is obtained owing to the addition of 2.66 wt% of $LiNO_3$. The decrease of the sintering temperature may be explained by the sintering in presence of a liquid phase.

Taking into account this result, different amounts of $LiNO_3$ have been tested. The pure BMT material is named BMT_0 and $x$$LiNO_3$ molar% added materials are called LiNx. Fig. 2 depicts shrinkage curves for

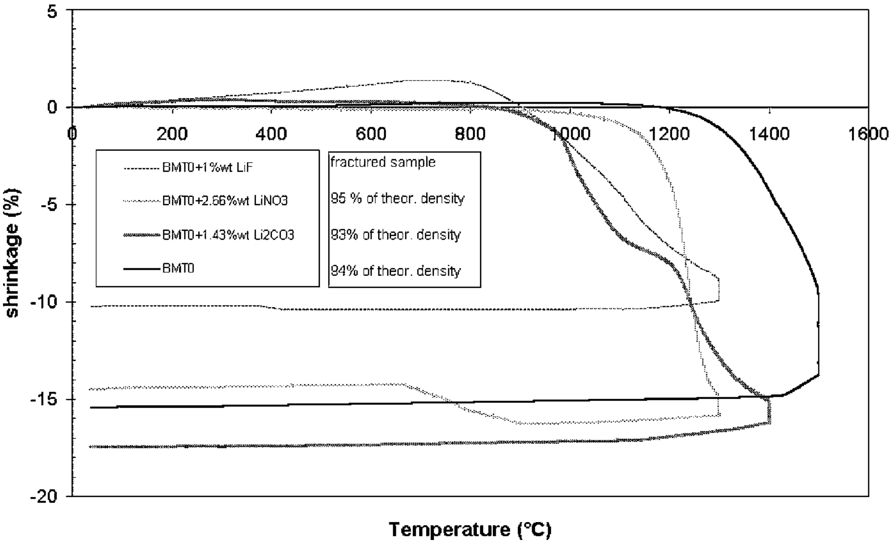


Figure 1 Dilatometric curves and final samples apparent densities for BMT_0 and samples with lithium salts additions.

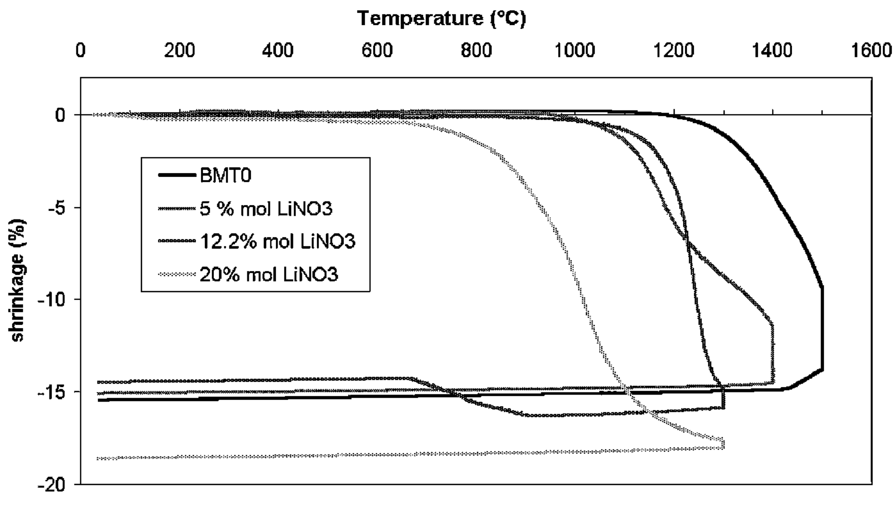
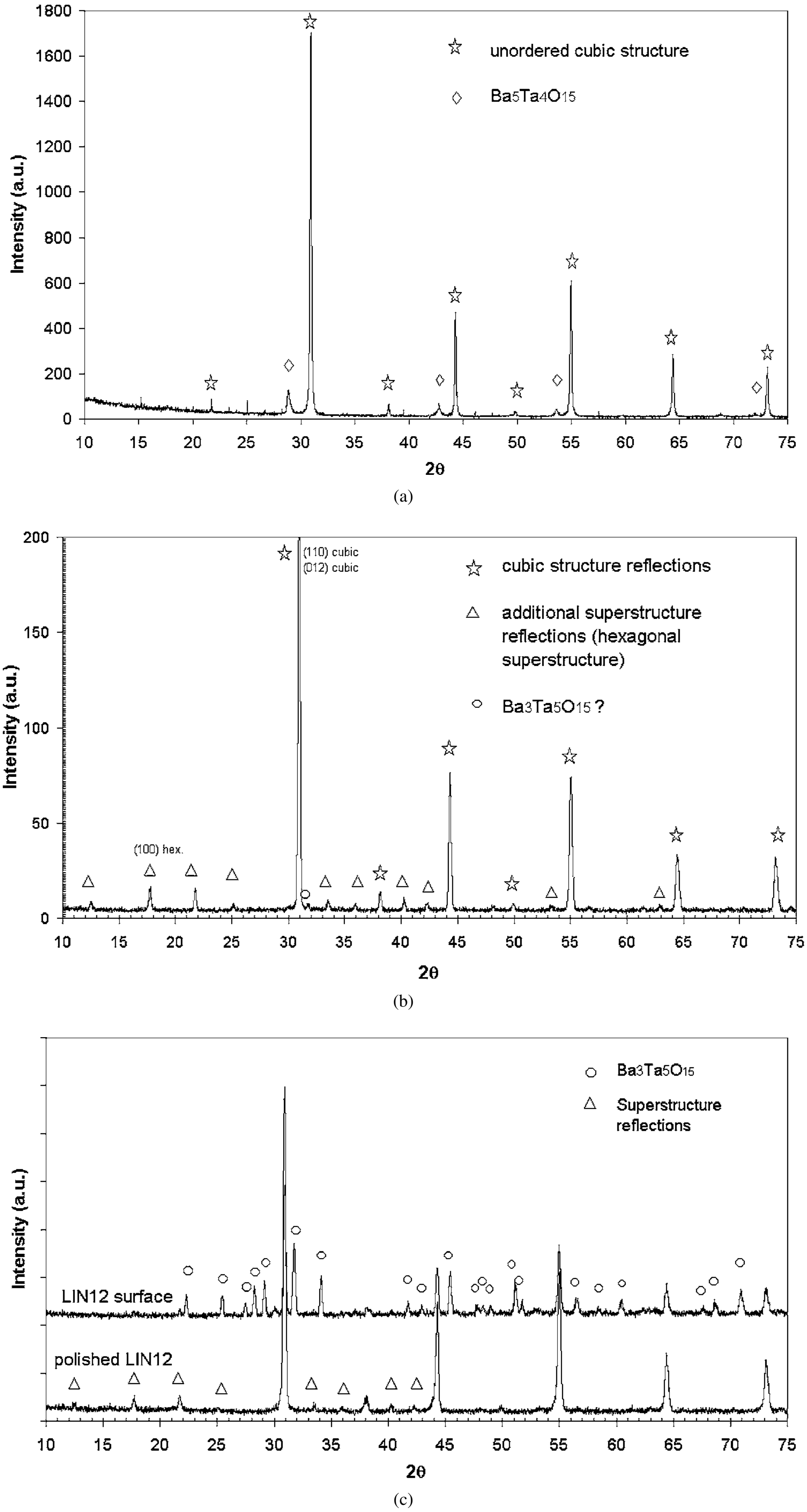


Figure 2 Dilatometric measurements for BMT_0, LiN5, LiN12 and LiN20.



(a)

(b)

(c)

Figure 3 (a) X-ray diffraction patterns of BMT_0 powder after calcination (1300°C/2 h). (b) X-ray diffraction patterns of BMT_0 sintered at 1550°C during 10 h. (c) X-ray diffraction patterns of LiN12 surface and core.

all the compositions. LiN5 sample exhibits a sintering in two steps which is insufficient to significantly lower the sintering temperature. LiN20 sample could be sintered below 1200°C but an attempt to sinter this sample at 1150°C failed (the final density was only 66% of theoretical density). Our first aim being to reduce the sintering temperature without affecting dielectric properties, the study was turned into LiN12 which probably corresponds to a compromise between the lowest sintering temperature and the lowest $LiNO_3$ content.

To validate the beneficial effect of the $LiNO_3$ addition on the sintering temperature of BMT, BMT_0 and LiN12 were sintered respectively at 1550°C during 10 h and at 1300°C during 2 h in air atmosphere and both samples properties were compared. Fig. 3a presents XRD patterns of BMT_0 powder after calcination. The unordered cubic structure (Pm3m) is observed as well as the usual secondary phase $Ba_5Ta_4O_{15}$.

After the sintering stage (Fig. 3b), the $Ba_5Ta_4O_{15}$ peaks disappear and additional superstructure reflections are observed on the sample surface, revealing the presence of ordered domains in BMT_0 structure. Traces of a secondary phase which could be the $Ba_3Ta_5O_{15}$ one are also detected. XRD patterns are identical in the bulk sample.

On the LiN12 sample surface, the $Ba_3Ta_5O_{15}$ phase is present (Fig. 3c). Nevertheless, this phase is not observable on the bulk of the sample. In addition, superstructures reflections are seen.

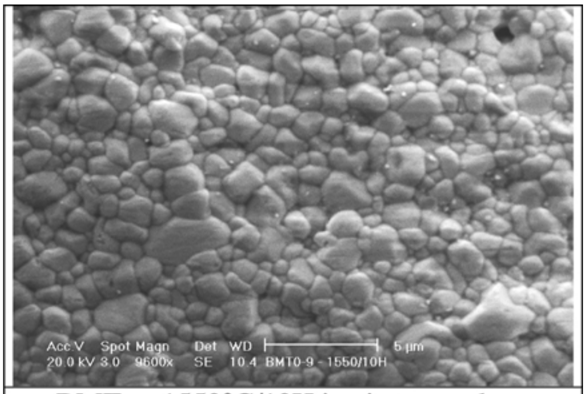
The B-site ordering parameter (S) was calculated from the (100) superstructure reflection using Equation 1.

Ordering parameter (S) [16]:

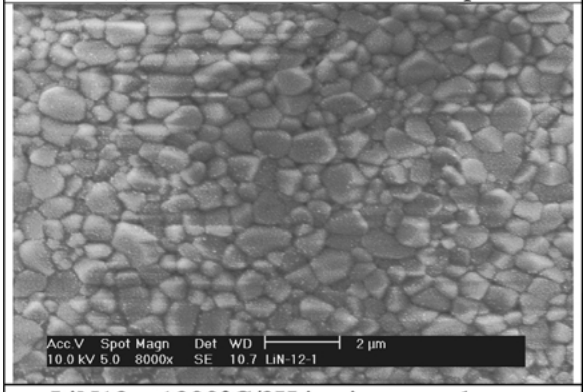
$$S = \left[\frac{\left(\frac{I_{100}}{I_{110,012}}\right)_{\text{obs}}}{\left(\frac{I_{100}}{I_{110,012}}\right)_{\text{ord}}} \right]^{1/2} \qquad (1)$$

where $(I_{100}/I_{110,012})_{\text{obs}}$ is the observed intensity ratio of the (100) superstructure reflection intensity and the (110) and (012) fundamental structure reflection intensity. For a completely ordered structure, an intensity ratio of 8.3% $(I_{100}/I_{110,012})_{\text{order}}$ was computed using the software CARINE 3.1. For LiN12, S was estimated to 70% versus 80% for BMT_0.

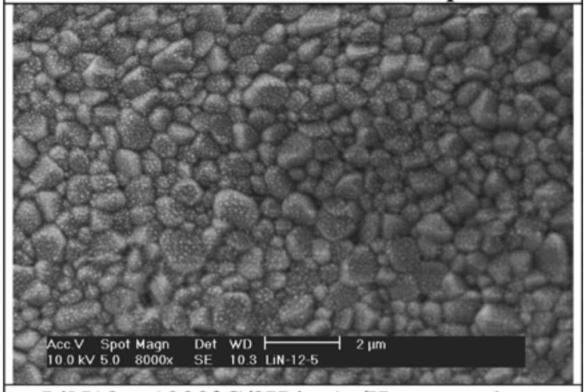
SEM observations performed on the BMT_0 and LiN12 are shown on Fig. 4. Both present full dense microstructures. However, it appears that the mean grain size is higher for BMT_0 (<2 μm) than for LiN12 (<1 μm). This grain growth can be attributed to the high temperature and the long dwell time imposed to BMT_0.



BMT_0 – 1550°C/10H in air atmosphere



LiN12 – 1300°C/2H in air atmosphere –



LiN12 – 1300°C/2H in Ar/H_2 atmosphere

Figure 4 SEM observations performed on BMT_0 and LiN12.

Dielectric properties were also measured for both samples at 1 MHz between −60°C and 180°C. Results are indicated in Table I. $LiNO_3$ addition does not modify significantly the dielectric constant (ε) neither the temperature coefficient (τ_ε) of BMT_0 ($\tau_\varepsilon = \frac{\Delta\varepsilon}{\varepsilon_{25}\cdot\Delta T}$).

These results underline the fact that, using $LiNO_3$,

(i) high dense BMT ceramic can be obtained at low sintering temperature (1300°C),

(ii) despite this relatively low sintering temperature, a partial ordered structure can be observed,

TABLE I Global results for all tested compositions

					1 MHz		
Composition	Sintering temp. (°C)	Secondary phases	Density (%)	S	ε	Q	$\tau\varepsilon$ (ppm/°C)
BMT_0	1550/10 h		93	0.8	25	>1000	−40
LiN12	1300/2 h	$Ba_3Ta_5O_{15}$ on periphery	93	0.7	25	>1000	−35
LiN12 (Ar/H_2)	1300/2 h	$Ba_3Ta_5O_{15}$ on periphery	94	0.7	25	>1000	−30

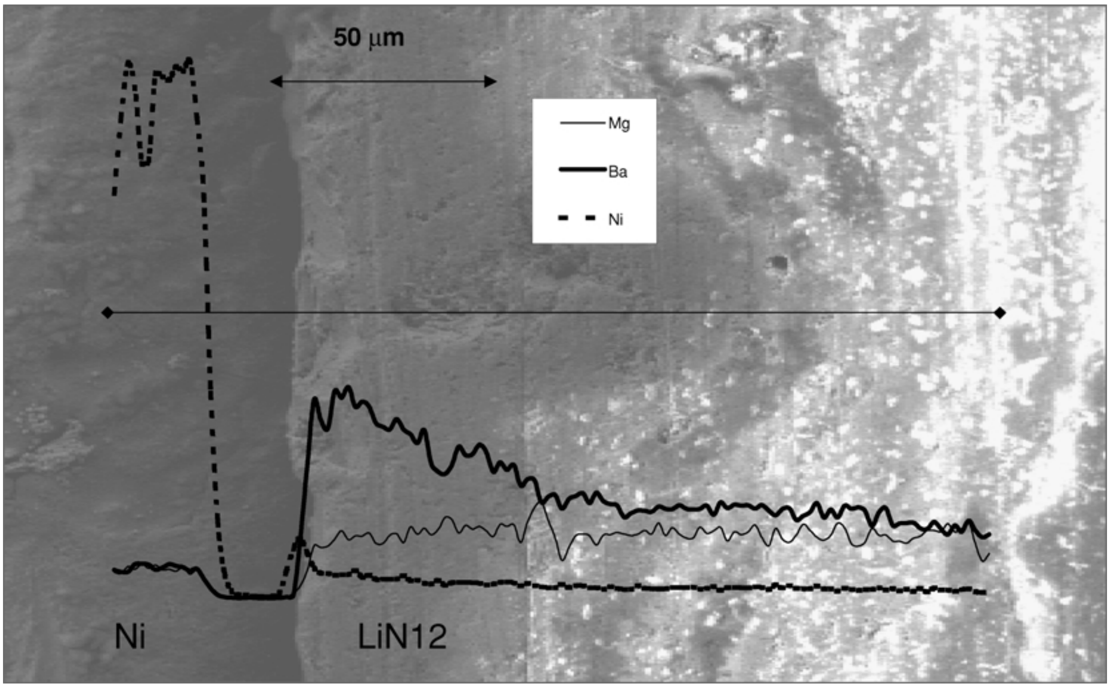


Figure 5 SEM observation and EDS analysis performed on a line for the Ni electrode-LiN12 interface.

(iii) the BMT$_0$ dielectric properties are maintained at 1 MHz.

3.2. MLCC application with nickel metal electrodes

It is important to determine the LiN12 sample behaviour when sintering is performed in a reductive atmosphere (90%Ar/10%H$_2$). Results are summarised in Table I and the sample microstructure is presented on Fig. 4. Sample is well sintered and the same secondary phase (Ba$_3$Ta$_5$O$_{15}$) is observed at the sample surface but not in the sample bulk. Moreover, final density, *S* parameter and dielectric properties are not changed compared to those previously obtained. The reductive atmosphere used seems to be not detrimental for the BMT dielectric properties showing that our material is not altered by this treatment. Being given this result, the sintering with co-fired Ni electrodes has been done. The sintered and the co-fired sample exhibit quite the same dielectric properties ($\varepsilon = 25$, $\tau_\varepsilon = -28$ ppm/°C, $Q > 1000$ at 1 MHz) than the sintered sample in air (cf. Table I). This data testifies that nickel electrodes are well co-fired with the LiN12 pellet and confirms the satisfying stability of BMT regarding the reductive atmosphere.

The interface between the metal and the ceramic has also been investigated using Energy Dispersive Spectroscopy performed along a line crossing this interface (Fig. 5). These measurements account for the absence of diffusion between both layers. The gap (nearly 20 μm) observed on the analysis curves which appears in the vicinity of the interface is due to the polishing which has slightly removed the electrode material from the sample. This low adherence between the two materials accounts for the poor affinity between the ceramic and the nickel. This observation shows that MLCC application can be envisaged with the LiN12 composition and the nickel electrodes.

4. Conclusion

This study has shown that an addition of LiNO$_3$ (12.2% mol) is efficient to decrease the BMT sintering temperature to 1300°C without altering dielectric properties measured at 1 MHz ($\varepsilon = 25$, $Q > 1000$). The Ba$_3$Ta$_5$O$_{15}$ secondary phase is observed only on the surface of the LiNO$_3$ doped sample and a partial ordered structure is obtained in the bulk. This observation is remarkable since it is well established that cationic ordering takes place only when using high temperature and a long dwell time.

The sintering temperature being reduced to 1300°C, the co-sintering with Ni electrodes has been successfully demonstrated. The co-sintered sample exhibits the same dielectric properties than the sintered sample in air and no diffusion of nickel in BMT is observed showing that MLCC application can be envisaged with the given composition.

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