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A R T I C U L O

Drastic decrease of $Ba(Zn_{1/3}Ta_{2/3})O_3$ sintering temperature by lithium salts and glass phase addition

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The complex perovskite oxide $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) has been studied for its attractive dielectric properties which make this material interesting for applications such as multilayer ceramics capacitors or hyperfrequency resonators. Nevertheless, BZT ceramic requires high temperature to be correctly sintered (≅1450°C), that is too high to envisage a silver co-sintering (T_f(Ag) = 961°C). For this reason, the lowering of the sintering temperature of BZT by glass phase's additions has been investigated. This material is sinterable at low temperature with combined glass phase –lithium salt additions, and exhibits, at 1MHz very low dielectric losses combined with relatively high dielectric constant and a good stability of this later versus temperature. The 5 wt% of $ZnO\text{-}SiO_2\text{-}B_2O_3$ glass phase and 1 wt% of LiF added BZT sample sintered at 900°C exhibits a relative density higher than 95% and attractive dielectric properties: a dielectric constant ε_r of 32, low dielectrics losses (tan (δ)< 10^{-3}) and a temperature coefficient of permittivity τ_ε of -10ppm/°C. Their good dielectric properties and their compatibility with silver electrodes, make these ceramics suitable for L.T.C.C applications.

Keywords: ceramics, glass, sintering, $Ba(Zn_{1/3}Ta_{2/3})O_3$, dielectric properties, low sintering temperature.

Disminución drástica de la temperatura de sinterización del Ba $(Zn_{1/3}Ta_{2/3})$ O_3 mediante la adición de una fase vítrea y sales de litio.

Se ha estudiado el óxido complejo con estructura tipo perovskita Ba $(Zn_{1/3}Ta_{2/3})$ O_3 (BZT). Sus atractivas propiedades dieléctricas le hacen muy interesante para aplicaciones como condensadores cerámicos multicapa o resonadores de microondas. No obstante, los cerámicos de BZT requieren temperaturas de sinterización superiores a 1450 ° C, que es muy alta para abordar un proceso de co-sinterización con electrodos de plata (T_f(Ag) = 961 ° C). Para ello, se ha estudiado la bajada de la temperatura de sinterización del BZT mediante la adición de una fase vítrea. La suma combinada de la fase vítrea y la sal de litio lleva la sinterización de este material a temperaturas bajas. Las propiedades dieléctricas presentan pérdidas muy bajas, constante dieléctrica relativamente alta a 1MHz y buena estabilidad frente a la temperatura. La adición del 5% en peso de una fase vítrea de $ZnO\text{-}B_2O_3\text{-}SiO_2$ y el 1% en peso de LiF disminuye la temperatura de sinterización del BZT hasta 900° C presentando una densidad relativamente alta (> 95%) y las propiedades dieléctricas de interés: la constante dieléctrica de 32, bajas pérdidas dieléctricas (tan (δ) <10^{-3}) y un coeficiente de temperatura de la permitividad τ_ε de -10ppm / ° C. Las propiedades dieléctricas obtenidas y la compatibilidad con los electrodos de plata hacen esta cerámica adecuada para su aplicación como LTTC.

Palabras clave: Cerámica, vidrio , sinterización, Ba $(Zn_{1/3}Ta_{2/3})O_3$, propiedades dieléctricas, temperatura de sinterización baja.

1. INTRODUCTION

The miniaturization of microwave dielectric components implies the use of multilayer devices such as multilayer ceramic capacitors or LTCC module etc … [1,2]. In such devices, the metallic electrodes are preferentially made of silver due to its high stability at high temperatures in oxidant atmosphere. In addition, the silver is highly conductive and relatively cheap. However, the silver melting temperature is 961°C. Such temperature implies to develop dielectric ceramics which can be sintered at temperatures lower than this critical value. Another point is that the silver co-sintering must be feasible, keeping in mind that reaction between ceramic and metal must be avoided.

It is well established that complex perovskite ceramics, with the general formula $Ba(B'_{1/3}B''_{2/3})O_3$ (B'=Mg, Zn; B''=Ta, Nb), exhibit very good dielectric properties at MHz range as well as GHz [3, 4]. The $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) compound is a perovskite type material exhibiting attractive dielectric properties namely, a low losses factor (tan(δ) < 10^{-3}), a relatively high permittivity (ε_r around 30) and a low temperature coefficient of the permittivity at high frequencies (from MHz to GHz) ($|\tau\varepsilon| < 100$ ppm/°C [5–8]). These properties make it attractive for fabricating type I multilayer chip capacitors. Nevertheless, BZT ceramic is usually sintered at around 1450°C to get well dense material. This latter temperature prevents it from co-sintering with silver. The goal is hence to lower the sintering temperature of BZT using appropriate sintering agent addition in order to be able to sinter BZT in presence of silver as electrodes while preserving its dielectric

properties. The glass materials addition is known to reduce the sintering temperature of several dielectric system, e.g. $(Zr,Sn)TiO_4$ [9], $BaTi_4O_9$ [10], $(Ca,Mg)TiO_3$ [11], $MgO–SiO_2–TiO_2$ [12]. These sintering aids melt at high temperatures enabling to get an inter-granular liquid phase during the sintering. The diffusion mechanisms are subsequently accelerated and the final sintering temperature could be lowered. In order to accelerate the atomic diffusion, another type of additives can also be used and they operate in slightly modifying the host structure, creating either a small amount of anionic vacancies or cationic ones. A typical example is the MgO addition to alumina to promote its densification. In this case, Mg partially substitutes for alumina that creates some anionic vacancies as summarised by this following equation:

$$MgO \xrightarrow{Al_2O_3} Mg'_{Al} + \frac{1}{2}V_0^{oo}$$

The anionic vacancies increase the oxygen diffusion and hence the sintering temperature decreases, especially when diffusion is limited by the oxygen mobility. The lithium salts are well known to act as sintering aid via this peculiar mechanism. For example, in barium titanate, LiF addition enables to decrease its sintering temperature by 300°C [13]. This result is attributed to the creation of anionic vacancies through partial substitution Ti – Li and / or F– O as schematically shown by this following equation:

$$LiF \xrightarrow{BaTiO_3} Li'''_{Ti} + F_O^o + V_0^{oo}$$

In our work, the different types of sintering aids (glass phase combined or not with lithium salts) have been investigated in order to decrease the BZT sintering temperature below the silver melting point. Four glass phases based on the SiO_2-ZnO-B_2O_3 system have been chosen for their previous interesting effects as sintering aid [9-12] whereas LiF has been selected as the second type of sintering agent. The effects of these additions on sintering temperature, microstructure, composition, and dielectric properties of BZT will be investigated.

2. EXPERIMENTAL PROCEDURE

The $Ba(Zn_{1/3}Tab_{2/3})O_3$ compound was prepared by solid state reaction using reagent grades powders of $BaCO_3$, ZnO and Ta_2O_5 (purity >99%). The precursors were appropriately weighted according to the $Ba(Zn_{1/3}Ta_{2/3})O_3$ stoichiometry . The mixing was performed in an ammoniac solution at pH=11 using zircon balls in a Teflon jar for 2 hours. These conditions were found to be optimal to obtain very well-dispersed slurry [14]. The slurry was subsequently dried under infra-red lamps and the powder was manually reground and heat treated at 1200°C for 2 hours in air [14]. The powder was finally reground using the same process than before in ammoniac solution at pH=11 for 1 hour. The molar compositions of the various glass phases are listed table 1.

For each glass compound, the ZnO (crystallised, purity >99%), SiO_2 (crystallised, purity >99%) and H_3BO_3 (amorphous, purity >99%) precursors were appropriately weighted according to the various compositions and mixed in deionised water using zircon balls in a Teflon jar for 2 hours. The mixtures were then melted at 1100 °C for one hour in a platinum crucible and quenched at room temperature in deionised water. These glasses were grinded in a planetary grinder for 45 minutes to obtain a fine powder. Ceramic powders and glass powders were mixed in a planetary grinder for 45 minutes in absolute ethanol. $Ba(Zn_{1/3}Tab_{2/3})O_3$+ x wt.% ZSB glass + y wt.% LiF (for (x,y) = (2,1), (2,2), (2,3), (5,1), (5,2)), mixtures were prepared by mixing the powders in a planetary grinder for 45 min in absolute ethanol. To fabricate pellets, an organic binder (Polyvinyl alcohol at 5 volume %) was manually added to the powder and disks (8 or 6 mm in diameter, 2 mm thick) were shaped by uni-axial pressing with a force of 21 kN. The green samples were finally sintered in air in a tubular furnace for two hours at a dwell temperature determined by TMA (Thermo-Mechanical analysis Setaram TMA 92), with heating and cooling rates of 150°C/h. The densities of the sintered samples were characterised using a He pycnometer (Accupyc 1330). The dielectric properties were determined using a RLC bridge (PM6306) versus temperature (from -60°C to 160°C). The crystallised phase composition has been identified by X-ray diffraction (XRD) technique using the Cu kα X-ray radiation (Philips X' Pert) and the microstructures were observed using a Scanning Electron Microscopy (SEM Philips XL'30).

TABLE 1: TABLE DEPICTING THE COMPOSITION AND THE ASSOCIATED SYMBOL OF THE GLASS PHASES

Symbol → Composition mol %	ZSB	ZB11	ZB32	ZB52
ZnO	60	50	60	71
SiO_2	30	0	0	0
B_2O_3	10	50	40	29

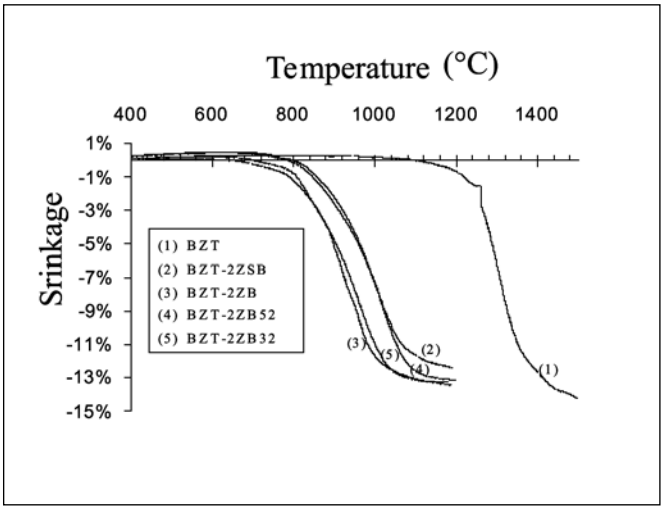

Figure 1: Shrinkage curves versus temperature of BZT ceramics

3. RESULTS AND DISCUSSION

3.1 Addition of glass phases

The figure 1 shows the shrinkage curves of glass phases added BZT. It can be clearly seen that all glass added sample can be sintered between 1100°C and 1150°C whereas the pure BZT sample requires 1450 ºC to achieve a high density. The mixtures ZB and ZB32 are the most efficient additives among those investigated since they authorise a sintering temperature of 1100°C. The others glass added samples require 1150°C to be well sintered.

These different formulations were sintered at the temperatures previously. After sintering, all samples exhibit a density higher than 94% of the theoretical value.

The XRD patterns sintered samples are given Fig.2 .They show that none crystallised secondary phases are present and that BZT has the disordered cubic structure.

Table 2 summarizes the dielectric properties of the different formulations. It is interesting to note that the permittivity is practically independent with the temperature. First of all, all glass added samples have a higher ε_r that pure BZT. This is partially explained by the fact that glass added samples have a higher density. All samples exhibit low losses factor (Tan $\delta < 10^{-3}$), high resistivity ($10^{13}\Omega$.cm), but the τ_ε value highly depends on the glass phase added. However, the τ_ε value tends to increases for BZT with glass phase added passing from negative to positive values. This behaviour is very pronounced for BZT-2ZB32, a sample in which the temperature coefficient becomes higher than 200ppm/°C. This high and positive value of $\tau\varepsilon$ for BZT with glass phase added, could be attributed to the dielectric properties of the glass phase addition. It is indeed well known that these phases generally have a high and positive value of $\tau\varepsilon$ [15].

3.2 Combined effects of glass phase and lithium salt additions (ZSB-LiF)

This combined addition already showed the important role on the reduction of the sintering temperature of BZN [16]. For it, we were tested this addition on the BZT material.

The combined additions used are: 2%ZSB+1%LiF noted 2Z1LF, 2%ZSB+2%LiF noted 2Z2LF, 2%ZSB+3%LiF noted 2Z3LF, 5%ZSB+1%LiF noted 5Z1LF and 5%ZSB+2%LiF noted 5Z2LF.

The figure 3 presents the dilatométric results of different compositions. The variation of the quantities ZSB and LiF in the ZSB-LiF combined addition affects the sintering temperature of BZT. The 5Z1LF and 5Z2LF additions shows a very gain in term of sintering temperature, the withdrawal of this additions ends at 900°C.This temperature is compatible to achieve BZT co-sintering with silver. The effect of other additions permits to decrease the sintering temperature, but their values are elevated, between 950°C and 1050°C.

The BZT-5Z1LF and BZT-5Z2LF formulations have been sintered at 900°C during 2hours. The obtained densities are superior to 95% of the theoretical one.

The disks so sintered have been grounded, and characterized by XRD diffraction. We notice that the additions don't modify the materials structure, the patterns present only BZT peaks of the perovskite structure (figure 2).

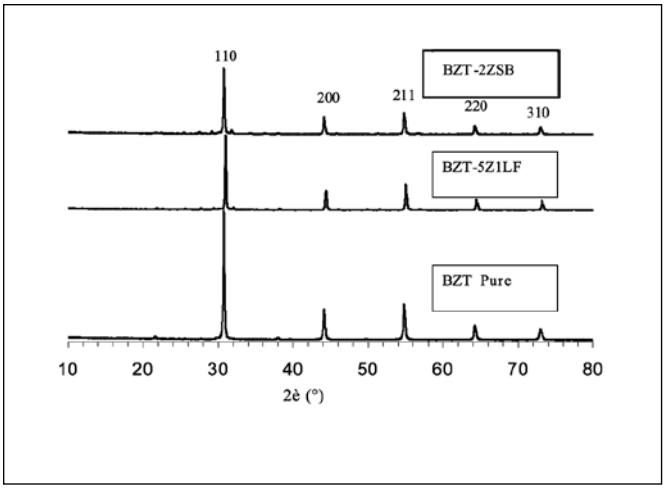

Figure 2: XRD patterns of sintered samples

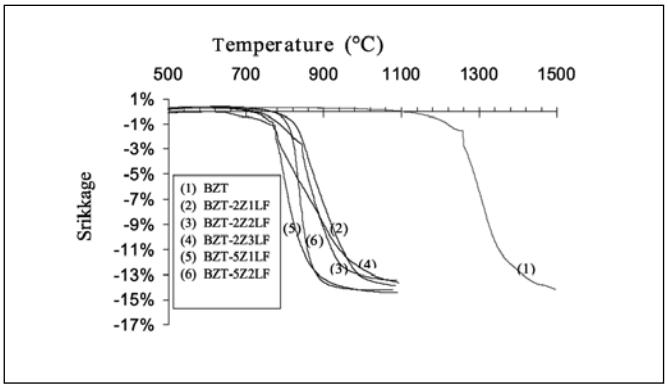

Figure 3: Shrinkage curves versus temperature of BZT with combined ZSB-lithium salt added

TABLE 2: DIELECTRIC PROPERTIES AND DENSITY OF THE SINTERED CERAMICS AT 1 MHZ

Samples	Sintering temperture (°C)	Relative density % of the teorical one	ε_r	Tan (δ)	τ_ε (ppm/°C)	$\rho_{i\,(\Omega.Cm)}$
BZT	1450	94	25	<10⁻³	-45	>10¹³
BZT-2ZB	1100	>95	31		69	
BZT-2ZSB	1150		32		33	
BZT-2ZB32	1100		29		280	
BZT-2ZB52	1150		34		66	

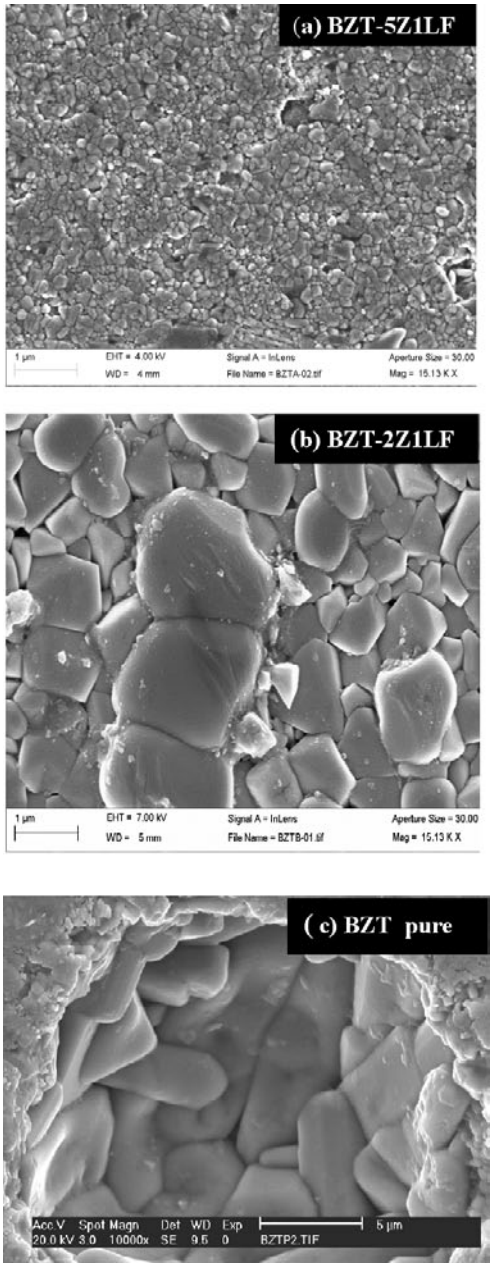

Figure 4: Scanning electron micrographs (SEM) of sintered samples: (a) BZT-5Z1LF sintered at 900°C, (b) BZT-2Z1LF sintered at 950°C, and (c)BZT pure sintered at 1450°C.

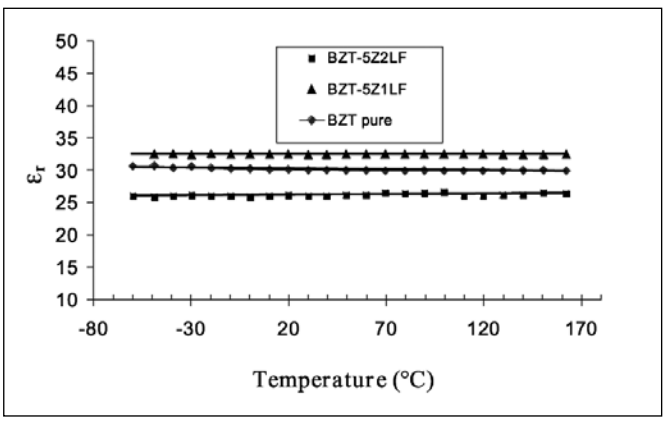

Figure 5: Relative permittivity of the samples versus temperature

TABLE 3: DIELECTRIC PROPERTIES OF SAMPLES CO-FIRED WITH AG

Samples	Sintering temperture (°C)	ε_r	Tan (δ)	τ_ε (ppm/°C)	$\rho_{i\ (\Omega.Cm)}$
BZT-5Z1LF	900°C	30	$<10^{-3}$	-39	$>10^{12}$
BZT-5Z2LF	900°C	28		-46	

The MEB observation of the sample BZT-5Z1LF sintered at 900°C show a well dense microstructure, the grains sizes are in order of 500nm (figure 4 (a)). However, BZT without added sintered at 1450°C shows the grains size higher than 5μm (figure 4 (c)). In the case of the BZT-5Z2LF system sintered at 950°C, the microstructure reveals the presence a big grains, their middle size can reach 2μm (figure 4(b)). This elevated grains size can be justified by the increased sintering temperature which promotes the grains growth in the presence of the liquid phase.

The dielectric properties of BZT-5Z1LF and BZT-5Z2LF formulations are very interesting. The values of the permittivity are not degraded, are in order of 32 and 26, respectively. They vary linearly with the temperature (figure 5), the obtained values of the temperatures coefficients are: τ_ε = -10ppm/°C and τ_ε = 69ppm/°C respectively. These compositions present also a lower dielectric losses and an elevated isolation resistivity: Tan $\delta < 10^{-3}$ and $\rho_i > 10^{13}\Omega$.cm.

The results obtained of the BZT-5Z1LF and BZT-5Z2LF compositions reveals the good dielectrics properties and the sintering temperature obtained is 900°C, this temperature is compatible for BZT co-sintered with silver.

3.4 Properties of silver co-sintered samples

The samples BZT-5Z1LF and BZT-5Z2LF samples were co-sintered with silver in air in a tubular furnace at 900 °C during 2 h. The dielectrics properties of these compositions are very promising, with a high dielectric constant ($\varepsilon_r \approx 37$)

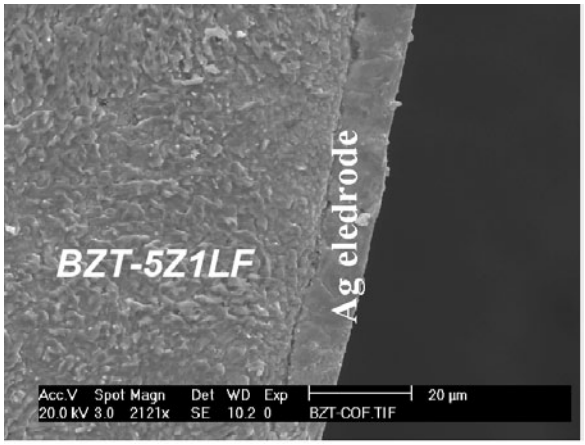

Figure 6: Scanning electron micrographs of BZN-5Z1LF samples co-fired with Ag at 900°C for 2hs.

and good temperature stability (τ_ε = -39 ppm/°C and τ_ε = -46ppm/°C) respectively (table 3). The dielectric losses are not degraded are lower than 10^{-3}. The isolation resistivity also remain elevated, $\rho_i > 10^{13}$ Ω.cm. The Figure 6 shows the morphology of the interface Ag/ BZT-5Z1LF ceramics. It puts in evidence a good adherence of silver and the ceramics with absence of silver diffusion to the ceramic. It is coherent with the good obtained dielectric properties. This composition is compatible for co-sintered at low temperature with silver and respect all requirements fixed previously in ours object.

Therefore, it can be used to achieve multilayered dielectric structures with a good dielectric properties and low cost.

4. CONCLUSION

In this paper we studied BZT perovskite, in the objective to decrease their densification temperature to reach a temperature close to 900°C. This last is recommended to fabricate multilayer structure dielectrics co-sintered with silver.

For it, several types of sintering agents have been tested on BZT in the optics to decrease their sintering temperature. The combined addition between the ZSB phase, and the lithium salt showed a good efficiency on the sintering temperature of this material. It permits a gain of 500°C of the sintering temperature compared to the BZT without addition. The combined addition of (5% in weight of ZSB and 1% in weight of LiF) to BZT conducted an important lowering of sintering temperature. The BZT-5Z1LF formulation was sintered at 900°C and exhibits good dielectric properties: ε_r=32, τ_ε=-10ppm/°C, Tan $\delta < 10^{-3}$ and $\rho_i > 10^{13}$Ω.cm.

The dielectric properties of the BZT-5Z1LF co-sintered with silver show also the acceptable values, which justifies a good compatibility between the silver electrodes and the BZT ceramic.

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El presente libro aparece por la necesidad actual de fomentar y difundir el conocimiento de los Biomateriales, debido a su gran importancia económica y sanitaria, así como por su gran repercusión social.

Su contenido está basado en los cursos internacionales impartidos por la Red CYTED VIII.J, para estudiantes de Ciencia de Materiales, Ingeniería, Biología, Odontología, Medicina, etc., así como para profesionales de dichas disciplinas.

El libro cubre, de una manera condensada y didáctica y con amplia bibliografía, las principales familias de los materiales actualmente empleados como Biomateriales así como aquellas aplicaciones más representativas de los mismos.

El carácter multidisciplinar de los Biomateriales justifica que en su elaboración hayan participado destacados especialistas: (físicos, químicos, biólogos, ingenieros, traumatólogos, odontólogos, patólogos, etc.), lo que contribuye a una visión amplia y actual de la problemática de dichos materiales.

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