Journal of Electroceramics, 13, 277–280, 2004

Al_2O_3-MgO-ReO_x (Re: Rare Earth)-Based LTCC and its Application to Multilayer Non-Shrinkage Substrate for Microwave Devices

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Submitted February 7, 2003; Revised November 24, 2003; Accepted January 8, 2004

Abstract. We studied the dielectric properties of Al_2O_3-MgO-ReO_x (Re: rare earth) systems in the microwave region and found that the magnetoplumbite phases in the MgO-poor regions of $MgReAl_{11}O_{19}$ (Re: La ∼ Tb) compositions had positive TCF (temperature coefficient of resonance frequency) values in spite of having low dielectric constants of under 20. By mixing a lead-free glass with the above system, a novel LTCC (which we term an AMSG) was obtained that was characterized by a low dielectric constant (<10), a near zero TCF, and high bending strength. When firing these AMSG green sheets inserted between HTCC alumina or magnesia green sheets that cannot be sintered at the AMSG sintering temperature, the AMSG sheets were seen to shrink not in the x-y directions but in the z direction due to the constraining effects of the HTCC layers. The obtained non-shrinkage substrate had precise dimensions and a high degree of flatness. The AMSG and the non-shrinking techniques have potential for application to integrated RF modules in mobile communications equipment.

Keywords: LTCC, microwave device, dielectric property, green sheet

1. Introduction

RF devices using LTCCs (low temperature cofired ceramics) are increasingly being used in mobile communications equipment [1]. However, the temperature coefficients of the resonance frequency (TCF) of many LTCC materials composed of Al_2O_3-glass systems show large negative values of around -50 ppm/K, since Al_2O_3 has a negative TCF. Worse, the x-y shrinkage of LTCCs during the conventional process is a very high 20%, making the precise mounting of small components or semiconductors on the LTCC very difficult.

In this paper, we describe a ternary system composed of Al_2O_3-MgO-ReO_x (Re: rare earth) with a positive TCF value in spite of having a low dielectric constant of under 20. Next we report on the characteristics of a LTCC (AMSG) with a near-zero TCF composed of the Al_2O_3-MgO-Sm_2O_3 system plus a lead-free glass [2]. Furthermore, we describe the non-shrinkage substrate [3] obtained by firing the AMSG green sheets inserted between HTCC green sheets made of materials such as alumina.

2. Produced Phases and Dielectric Properties of the Al_2O_3-MgO-ReO_x System

The specimens were fabricated using a conventional ceramic process. Al_2O_3, MgO and ReO_x were weighed and mixed in a ball mill. The mixture was then dried, calcined at 1300°C, and crushed again in the ball mill. The crushed powder was then granulated, made into disks, and sintered at 1650–1680°C. The dielectric properties were measured using a resonator metod [4]. The temperature coefficient of resonance frequency was determined from the values at 20 and 85°C.

Figure 1 shows the relationship between the composition and produced phases of a ternary system when Re was Sm. Samarium was selected as a typical rare earth, since the atomic number of Sm lies towards the middle of the rare earth elements. When using the composition of the magnetoplumbite phase reported in the formula $MgReAl_{11}O_{19}$ [5], a spinel phase ($MgAl_2O_4$) was produced in addition to a magnetoplumbite phase. A pure magnetoplumbite phase, however, was obtained by using the MgO-poor composition $Mg_3Re_4Al_{44}O_x$.

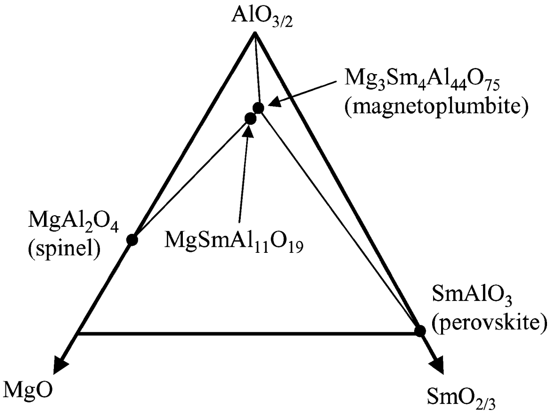

Fig. 1. Crystalline phases sintered at 1650–1680°C in the Al_2O_3-MgO-Sm_2O_3 system.

Table 1. Crystalline phases in the composition of $Mg_3Re_4Al_{44}O_{75}$ sintered at 1650–1680°C.

Re	Primary phases	Other phases
La	MP	PE, uk
Ce	MP	uk
Pr	MP	uk
Nd	MP	uk
Sm	MP	uk
Eu	MP	uk
Gd	MP	uk
Tb	MP	uk
Dy	GN	α-alumina, SP, MP
Yb	GN	α-alumina, SP

MP: magunetoplumbite, PE: perovskite, GN: garnet, SP: spinel, uk: unknown phase.

Sufficient equilibrium may not have been reached under our sintering conditions. We presume that the magnetoplumbite phase can be readily obtained under poor-MgO conditions or that the stoichiometric composition of the magnetoplumbite phase is shifted away from that for $MgReAl_{11}O_{19}$.

The produced phase of the compositions $Mg_3Re_4Al_{44}O_x$, which was an almost entirely single phase, was further examined using a different Re. The results are summarized in Table 1. The structure produced using La through Tb in order of atomic number was primarily a magnetoplumbite phase. When Dy and Yb were used in the place of Re, the primary structure was garnet phase ($Re_3Al_5O_{12}$), which was a mixture of Al_2O_3 and spinel phase ($MgAl_2O_4$). Interestingly, the magnetoplumbite phase was generated as a primary structure when a perovskite phase ($ReAlO_3$) was present in an Al_2O_3-ReO_x system. The X-ray diffraction pattern of the magnetoplumbite phase we obtained is shown in Fig. 2. The peaks in the pattern could be identified for the most part as those for $MgNdAl_{11}O_{19}$. Analysis of the detailed stoichiometric composition of the magnetoplumbite phase and its crystalline structure will be left for future study.

The microwave dielectric characteristics of $Mg_3Re_4Al_{44}O_x$-based materials are shown in Table 2. A comparison with Table 1 shows that when the magnetoplumbite phase is the primary structure, both the dielectric constant and the temperature coefficient of resonance frequency increase with increasing atomic number of Re. With increased atomic number of Re, the ionic radius of the Re decreases and the Re ion moves more easily in response to the electric

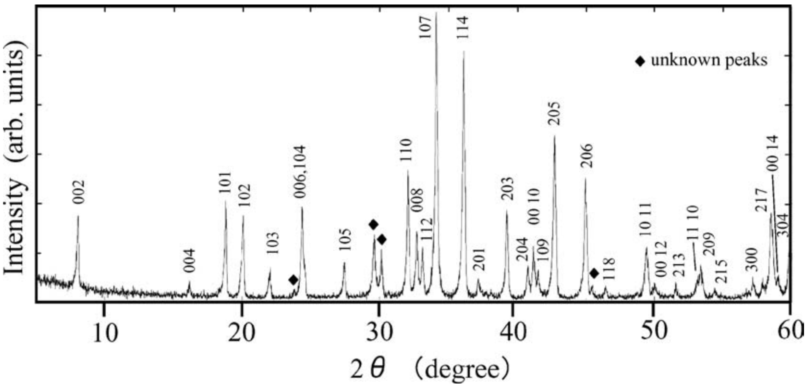

Fig. 2. XRD pattern of $Mg_3Sm_4Al_{44}O_{75}$ composition.

Table 2. Microwave Dielectric Characteristics of $Mg_3Re_4Al_{44}O_{75}$ ceramics.

Re	ε_r	Q_f (GHz)	TCF(ppm/°C)
La	13.0	7700	+3
Ce	14.0	9000	+11
Pr	14.5	10000	+23
Nd	15.0	11000	+35
Sm	16.5	11000	+93
Eu	17.3	11000	+147
Gd	18.3	4800	+175
Tb	18.3	5900	+200
Dy	10.3	28000	−49
Yb	10.3	41000	−57

field in the magnetoplumbite lattice. The charge of the Re also increases. Consequently, the dielectric constant increases. This material is significantly different from well-known compounds in that its TCF value has a high positive number in spite of its dielectric constant being below 20. Compounds with a magnetoplumbite structure have only rarely been studied as dielectric materials, but new compounds with unique temperature coefficients may now be found based on the compositions investigated in this study.

3. Characteristics of LTCC Based on the Al_2O_3-MgO-Sm_2O_3 System

We attempted to reduce the sintering temperature of the Al_2O_3-MgO-ReO_3 by adding lead-free glass with the composition of SiO_2-Al_2O_3-B_2O_3. Samarium was selected as the Re for reasons of *Q* value and cost. This material needs to be sufficiently sintered at approximately 900°C to allow the LTCC to be cofired with silver. The base material composition was determined to be $Mg_3Sm_4Al_{44}O_{75}$, and the oxide mixture of the base material was calcined at 1500°C. This base material and the glass were mixed in equal quantities. A sintering body was produced by the same method mentioned above and its characteristics were evaluated. The LTCC produced will hereafter be termed AMSG. The characteristics of AMSG are shown in Table 3 in comparison with those of a conventional Al_2O_3-glass-based LTCC. It can be seen from Table 3 that AMSG matches the characteristics of conventional LTCCs with respect to relative dielectric constant, *Q* value, bending strength, etc., but has a near-zero TCF. As for the reason of the near-zero TCF, we think that the AMSG is made from a mixture of $Mg_3Sm_4Al_{44}O_{75}$ with a positive TCF and glass with a negative TCF. By taking advantage of its good temperature characteristics, future applications of this material are likely to include highly integrated RF modules, including narrow-band devices such as band-pass filters and notch filters.

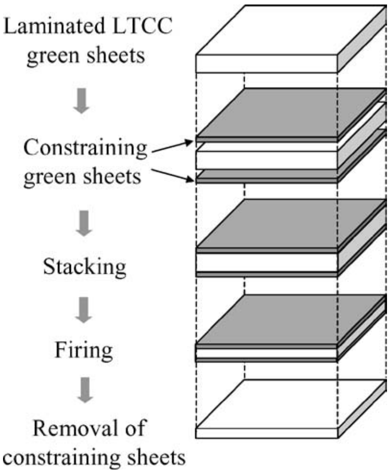

Fig. 3. Process of non-shrinkage substrate.

4. Non-Shrinkage Substrate Using AMSG

Non-shrinkage LTCC substrates were obtained by firing a glass ceramic laminated with HTCC alumina or magnesia green sheets on both sides and then removing the non-sintered HTCC, as shown in Fig. 3. The glass ceramic green sheets shrink in the *z* direction, not in

Table 3. Characteristics of "AMSG".

Materal code	Composition	ε_r	Q_f (GHz)	TCF(ppm/°C)	Thermal exp. coeff. (ppm/°C)	Bending strength (MPa)
AMSG	$Mg_3Sm_4Al_{44}O_{75}$ + B—Si—O glass	7.8	10000	+6	+11	250
Conventional	Al_2O_3-glass	7.8	10000	−55	+6	250

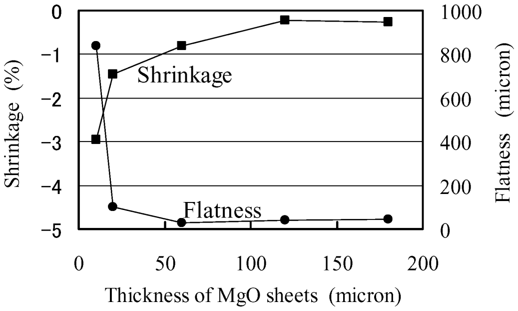

Fig. 4. Relationship between the shrinkage and the flatness versus the thickness of MgO sheets.

the x-y directions, due to the constraining effects of the HTCC layer. Figure 4 shows the relationship between the x-y shrinkage and the thickness of the constraining magnesia sheets. The above AMSGs were used as the LTCC sheets with a thickness of 1.4 and 25 mm square. Sufficient shrinkage of the LTCC occurred in the z direction when it was fired at 920°C. Under these conditions, non-shrinkage substrates (with a shrinkage of below 1%) were obtained when the constraining sheets were over 50 μm thick. The flatness was good at within 60 μm. The use of AMSGs combined with our non-shrinking technique will enable the manufacture of more highly integrated RF-LTCC devices.

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