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# Densification and dielectric properties of $SrO–Al_2O_3–B_2O_3$ ceramic bodies

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**Abstract. The influence of SrO (0·0–5·0 wt%) on partial substitution of alpha alumina (corundum) in ceramic composition (95 $Al_2O_3$–5$B_2O_3$) have been studied by co-precipitated process and their phase composition, microstructure, microchemistry and microwave dielectric properties were studied. Phase composition was revealed by XRD, while microstructure and microchemistry were investigated by electron-probe microanalysis (EPMA). The dielectric properties by means of dielectric constant ($\varepsilon_r$), quality factor ($Q \times f$) and temperature coefficient of resonant frequency ($\tau_f$) were measured in the microwave frequency region using a network analyser by the resonance method. The addition of $B_2O_3$ and SrO significantly reduced the sintering temperature of alumina ceramic bodies to 1600 °C with optimum density ($\sim$ 4 g/cm$^3$) as compared with pure alumina powders recycled from Al dross (3·55 g/cm$^3$ sintered at 1700 °C).**

**The sintered ceramic bodies show different ranges for the dielectric properties. Dielectric constant exists between 24 and 29, quality factor ($Q \times f$) is ranging between 15,236 and 22,020 GHz with a slight increase than those recorded with commercial alumina (10,000 – 20,000 GHz) and temperature coefficient of resonant frequency ($\tau_f$) in the –69 to –83 ppm/°C range. The addition of SrO up to 5 wt% leads to a maximum ($\varepsilon_r$) value (29) due to relatively higher ionic polarizability of $Sr^{2+}$ than that of the $Al^{3+}$ and $B^{3+}$ ions. On the other hand, changing chemical and phase composition with the formation of platelets of Sr-hexaluminate phase ($SrAl_{12}O_{19}$) results in maximizing value of ($Q \times f$) up to 22,020 GHz at $\approx$ 8 GHz and large negative charge of ($\tau_f$) to –83 ppm/°C.**

**Keywords. Ceramic; microwave; SrO; alpha alumina; $B_2O_3$; dielectric properties.**

## 1. Introduction

Remarkable progress has been made in the development of new dielectric ceramics, especially for electronic applications including wireless communication and memory devices. There is a continuing trend toward miniaturization and higher frequency ranges (1–100GHz).

Alumina is a well known ceramic material for dielectric applications, such as substrates, dielectric resonators and patch antennas. Although it is not a practical material for most applications due to its low dielectric constant, $\varepsilon_r = 10$, and high temperature coefficient of resonant frequency (TCF) −60 ppm/K, alumina ($Al_2O_3$) is of interest for several reasons. Firstly, in its single crystal form (sapphire) it is the microwave material with the lowest known loss. This makes it useful for very high $Q$ resonators needed for low noise oscillators. Secondly, its simplicity and low loss makes it an ideal material for the study of the causes of dielectric loss. The very low intrinsic loss of $Al_2O_3$ makes it very sensitive to causes of extrinsic loss (Alford and Penn 1996; Huang *et al* 2005, 2008; Vishista and Gnanam 2006). However, a very high sintering temperature at about 1750 °C is needed to obtain dense alumina bodies. Chemical processing of small-sized particles as starting materials, and adding glass or other low-melting materials effectively lower firing temperature with improvement in dielectric properties of the aluminous bodies (Cutler *et al* 1991; Chen and Chen 1992; Alford and Penn 1996; Erkalfa *et al* 1996; Liu *et al* 2001; Ota *et al* 2004; Huang *et al* 2005; Huang and Chen 2006; Vishista and Gnanam 2006; Lim *et al* 2007; Kargin *et al* 2008; Abdel Aziz *et al* 2009). The properties of alumina ceramic bodies are significantly affected by the liquid sintering temperature due to the development of microstructure at low sintering temperature or the reaction between the host materials.

Strontia (SrO) was added to $Al_2O_3$ ceramic bodies to improve their physical and mechanical properties (Cutler *et al* 1991; Vishista and Gnanam 2006; Kargin *et al* 2008). Vishista and Gnanam (2006) studied the effect of strontia content (5–20 wt%) on the properties of sol–gel alumina bodies. They concluded that addition of SrO up to 5 wt% to the alumina bodies, sintered for 6 h between 1400 and 1600 °C gave increased density values from 3–3·80 g/cm$^3$ due to formation of excessive amount of liquid phase. While, addition of SrO content above 5 wt% showed slight decrease

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in density, owing to the formation of strontium hexaluminate plate-like grains. However, Cutler *et al* (1991) and Chen and Chen (1992) found that the plate-like grains of strontium hexaluminate ($SrAl_{12}O_{19}$) are supposed to increase the mechanical properties of alumina ceramics.

Many authors have concluded that the $B_2O_3$ (6 and 8 wt%) added ceramics are often used for lowering the sintering temperature (Chen and Chen 1992; Erkalfa *et al* 1996; Liu *et al* 2001; Ota *et al* 2004; Huang and Chen 2006). So, Liu *et al* (2001) found that addition of $B_2O_3$ powder with 2·0–20·0 wt% to Ca ($Li_{1/3}Nd_{2/3}$) $O_{3-\delta}$ ceramic bodies reduces sintering temperature from 1423–1263 °C without deteriorating the microwave dielectric properties. Abdel Aziz *et al* (2009) also concluded that $0{\cdot}5Li_2O$–$0{\cdot}5B_2O_3$ can be added as a sintering aid in the form of raw oxides (LBR) and a pre-reacted glass (LBG). 0·5 wt% LBR is the most effective in reducing the temperature to achieve optimum density by 50 °C with no significant effect on microwave properties.

The present work aims to study the influence of Sr (0·0–5·0 wt%) addition in partial substitution of fine $\alpha$-$Al_2O_3$ recycled from Egyptian Al Dross on the densification and microwave dielectric properties of co-precipitated 95 $Al_2O_3$–$5B_2O_3$ ceramic bodies. The relationship among the developed crystalline phase and the microwave dielectric properties of $95Al_2O_3$–$5B_2O_3$ ceramics are also investigated.

## 2. Experimental

Table 1 shows the chemical analysis of the Al dross. After leaching Al dross (from the Aluminum Company of Egypt) by dilute hydrochloric acid, 5 wt% solid boric acid ($H_3BO_3$) as constant for all batches and 0·0, 1·0, 2·0, 3·0, 4·0 and 5·0 wt% strontium carbonate ($SrCO_3$) were added in partial substitution of $Al_2O_3$ in the composition $95Al_2O_3$–$5B_2O_3$ (AB) with continuous stirring till complete dissolution. Thereafter,

**Table 1.** Chemical analysis of the Egypt alum fine Al dross (Serry *et al* 2006).

| Oxide | Mass% |
|---|---|
| $SiO_2$ | 5·40 |
| $Al_2O_3$ | 85·79 |
| $Fe_2O_3$ | 0·84 |
| CaO | 1·06 |
| MgO | 3·71 |
| $Na_2O$ | 2·05 |
| $K_2O$ | 0·93 |
| L.O.I | 0·29 |
| $Cl^-$ | 0·95 |
| $SO_3$ | 0·40 |

a gel was co-precipitated by adding commercial ammonia solution ($NH_4OH$) with stirring for 2 h up to pH = 7. The gel was then filtered and washed by distilled water till free from chlorides, aged for three days in a dryer at 110°C and subsequently calcined for 2 h at 1000°C. The co-precipitated batches were referred to as AB, ABS1, ABS2, ABS3, ABS4 and ABS5. The dried samples were ground in zirconium mill for 15 min at 230 rpm and subsequently dry pressed into pellets with 10 mm diameter and ∼5 mm thickness under a pressure of 200 MPa. The shaped pellets were sintered for 6 h at temperatures ranging between 1450 and 1600 °C and then investigated for their bulk density using the Archimedes method.

Crystalline phases of the sintered pellets were identified by X-ray powder diffraction (XRD) analysis using Cu-K$\alpha$ radiation at 2$\theta$ from 20 to 60°. Microstructure and microchemistry of polished and thermally etched pellet surfaces were examined using a Electron Probe Microanalyser (EPMA), Japan, equipped with an X-ray energy-dispersive spectrometer EDAX (INCAX-sight, OXFORD) (Model JEOL 6400). Microwave dielectric resonance measurements were examined using a network analyser (Model ADVANTEST R3767CH), in the frequency range 40MHz–8GHz.

## 3. Results and discussion

Figure 1 (a and b) shows the bulk density as a function of sintering temperature of the ceramic bodies with different concentrations of Sr sintered at 1450–1600 °C for 6h. In the previous work, Ahmed (1998) found the pure alpha alumina powders (corundum) recycled from Egyptian Al dross sintered at 1700 °C for 1h with a density of 3·55 g/cm$^3$ and an apparent porosity of 6·5 %. In the present study, it is shown that the addition of SrO (0·0–5·0 wt %) in partial substitution of alpha alumina (corundum) in ceramic composition (95 $Al_2O_3$–$5B_2O_3$) has significant effect on reducing the temperature to achieve optimum density temperature by about 100 °C. Figure 4(a) shows that the bulk density is comparatively small at low sintering temperature but it is increased with increasing sintering temperature. This is due to the insufficient amount of liquid phase at temperatures between 1450 and 1500 °C with appreciable percentage of porosity as seen in figure 1 (b). With increasing sintering temperature up to 1600 °C, the density is increased to maximum values of ≈ 4·00 g/cm$^3$ with reducing apparent porosity (0·1 – 0·7 %) in addition to grain growth, as seen in figures 1 (b) and 2, respectively. These results are in agreement with results reported by Huang *et al* (2005).

Figure 2 shows the XRD patterns of the AB bodies containing (0·0–5·0 wt %) SrO sintered for 6h at the maximum temperature (1600 °C). It shows that corundum ($\alpha$-$Al_2O_3$) is the major crystalline phase in the hexagonal

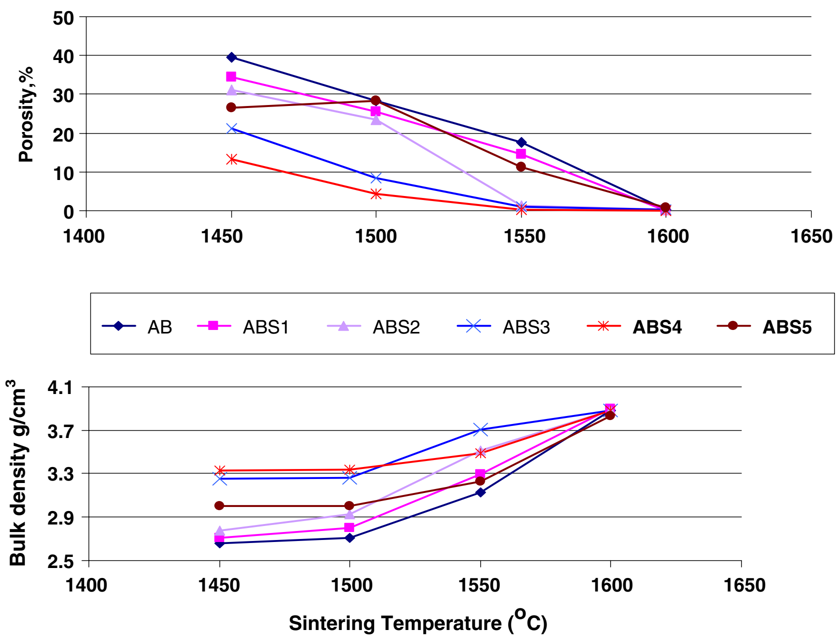



**Figure 1.** Physical properties of aluminous bodies as a function of sintering temperature.

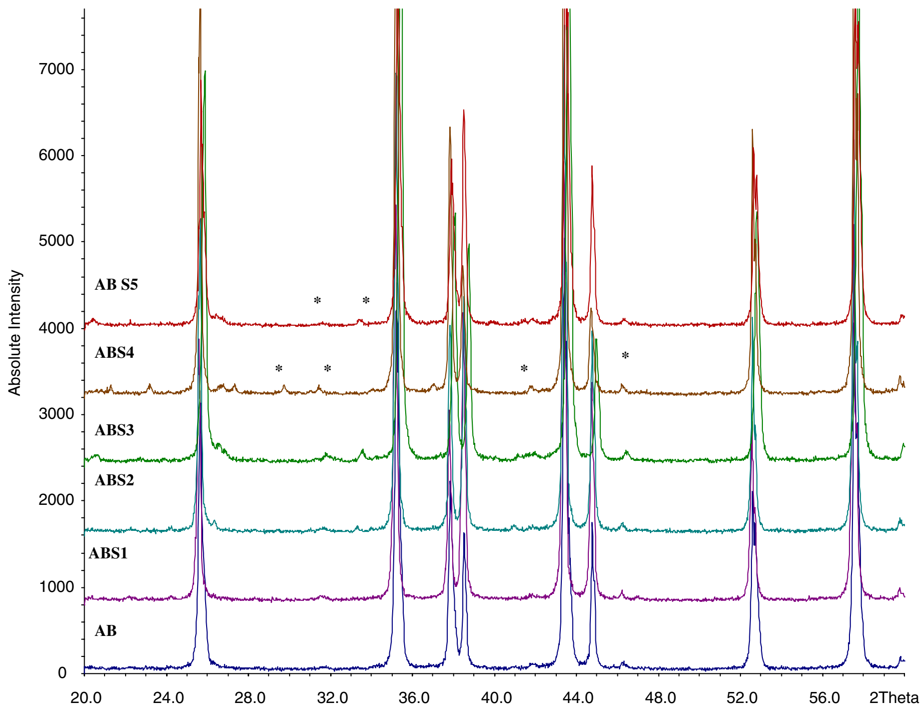



**Figure 2.** XRD of (AB) $95Al_2O_3$–$5B_2O_3$ ceramic bodies with different strontium contents sintered at 1600 °C (* strontium hexaluminate).

structure (JCPDS # 82-1468). For $B_2O_3$ added $Al_2O_3$ ceramics, no $Al_2O_3$–$B_2O_3$ phases were observed at 1600 °C. It has been reported that $B_2O_3$-bearing alumina bodies were sintered above 1200°C; boron oxide assists in liquid phase sintering and then evaporates (Ota *et al* 2004; Lim *et al* 2007; Kargin *et al* 2008). According to the $Al_2O_3$–$B_2O_3$ phase diagram (Grente *et al* 2003), the reactions of $Al_2O_3$–$B_2O_3$ powders can be expressed as follows:

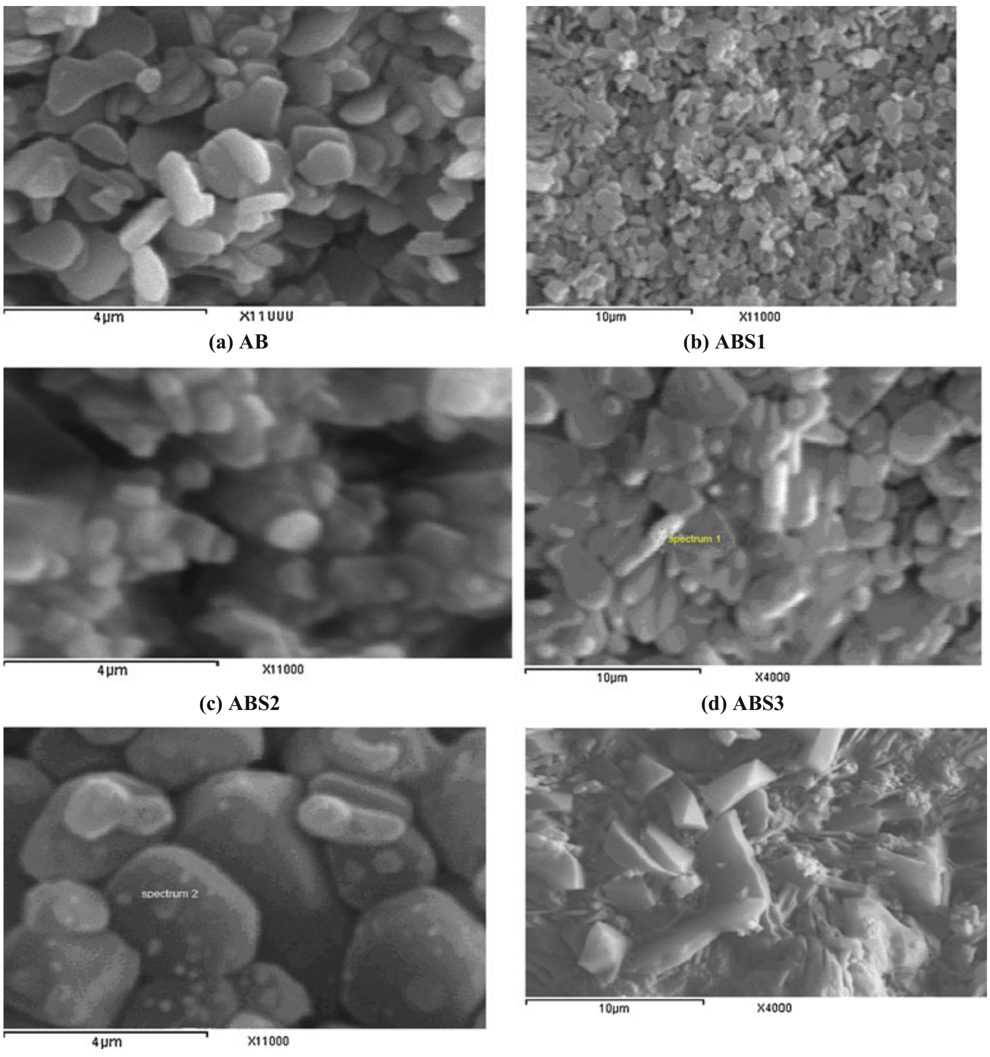
$$Al_2O_3 + B_2O_3 \xrightarrow{700-900°C} 2Al_2O_3 \cdot B_2O_3 + \alpha\text{-}Al_2O_3, \quad (1)$$

$$2Al_2O_3 \cdot B_2O_{3(s)} \xrightarrow{900-1200°C} 9Al_2O_3 \cdot 2B_2O_{3(s)} + \alpha\text{-}Al_2O_3 + \text{liquid}, \quad (2)$$

$$9Al_2O_3 \cdot 2B_2O_{3(s)} + \text{liquid} \xrightarrow{1200-1400°C} \alpha\text{-}Al_2O_3 \text{ (corundum)} + \text{liquid}. \quad (3)$$

The addition of Sr up to 2 wt% has no significant effect on the crystalline phases which may indicate to some solid solutions. The increase of Sr addition from 3 to 5 wt% results in appearance of a new second phase of strontium hexaluminate ($SrO{\cdot}6Al_2O_3$) with very weak intensity peaks, indicating that the solubility limit has been exceeded (Vishista and Gnanam 2006). It is worthy to note here that diffraction lines, observed at about $2\theta = 38{\cdot}5°$ and 45°, are mainly due to the aluminum holder.

The microstructure of thermally etched surfaces of the ceramic bodies sintered at 1600 °C is shown in figure 3. AB body with no SrO shows that most of the $Al_2O_3$ rounded platy grains have angular shape with different sizes at $\geq 2$ μm, as shown in figure 3 (a). When (1wt %) SrO is added in (ABS1) (figure 3 (b)), uniform grained microstructure is shown with a slight decrease in grain size $\sim\geq 1$ μm, as compared with the pure body (AB). As the amount of SrO is increased to 2 wt%, the size of matrix grains grows with a




(a) AB (b) ABS1 (c) ABS2 (d) ABS3 (e) ABS4 (f) ABS5

**Figure 3.** SEM of sintered aluminous bodies containing different concentrations of strontium.

slow grain growth rate (figure 3 (c)). At the level of 3 to 4 wt% SrO (figure 3 (d and e)), the grain growth rapidly increases with increasing strontia content. However, increase in the amount of SrO up to 5 wt%, degradation in grain uniformity as well as abnormal grain growth are observed (figure 3 (f)).

The microstructure investigations also show that the strontia added above 1wt% leads to large grains with (platelet) a plate-like morphology as a second phase ($SrO_6 \cdot Al_2O_3$) (figure 3 (c-f) which supports XRD data in figure 2). The formation of these is related to the increased growth rate of $Al_2O_3$ grains caused by the diffusion of Sr ions through the surface of $Al_2O_3$ more than through the bulk. It is clear that addition of SrO to alumina is dissolved into its structure (Song and Coble 1990; Riu *et al* 2000; Goswami *et al* 2001). These results are confirmed by the energy dispersive X-ray analysis (EDAX) carried out for the platelet grains of the ABS3 (figure 4 (a)) and ABS4 (figure 4 (b)) specimens. As a result, the EDAX analysis illustrates that the concentration of Al, Sr and O elements suggests that strontium hexaluminate is the major component of the second phase, as shown in table 2.

Figure 5 shows the variation of dielectric constant ($\varepsilon_r$), quality factor ($Q \times f$) and temperature coefficient of resonant frequency ($\tau_f$) values with various SrO contents for the ceramic bodies sintered at 1600 °C. It is evident that addition of SrO to aluminous ceramic bodies has significant effect on the microwave dielectric properties measured above 7 GHz. The $\varepsilon_r$ values of the ceramic bodies increased from 24–29 with increasing SrO content (figure 5 (a)). This is referred to the ionic polarizability of $Sr^{2+}$ ($\alpha D = 4{\cdot}24$ Å$^3$) which is higher than that of $Al^{3+}$ ($\alpha D = 0{\cdot}97$ Å$^3$) and $B^{3+}$ ($\alpha D = 0{\cdot}05$ Å$^3$).

Figure 5 (b) shows $Q \times f$ values, which also increased from 15,236 to 22,020 GHz with increasing strontium content as compared with commercial alumina which has $Q \times f$ values around 10,000–20,000 GHz (Huang *et al* 2008). The increase of the $Q \times f$ with increasing strontium content may be attributed to the presence of $SrAl_{12}O_{19}$ phase in large and plate like grains as observed in SEM micrographs (figure 2). Similar results were reported by Lin *et al* (2005), who found that the shape of grains (large and plate like grains) in ceramic bodies played an important role for enhancing microwave property.

Figure 5(c) shows the temperature coefficient of resonant frequency ($\tau_f$) values being sensitive to the partial substitution of $Al_2O_3$ by SrO and varied from −69 to −83 ppm/°C. In general, ($\tau_f$) is related to the chemical and phase composition of the ceramic bodies.

According to the above results, a maximum $\varepsilon_r$ (29), $Q \times f$ (22,020 GHz at $\sim$ 8GHz) and large negative ($\tau_f$) value (−83 ppm/°C) are recorded with 5 wt% SrO in the (ABS5) $90Al_2O_3–5B_2O_3–5SrO$ ceramic body.

Meanwhile, the present study shows that the addition of SrO and $B_2O_3$ to the alpha alumina prepared from Al dross

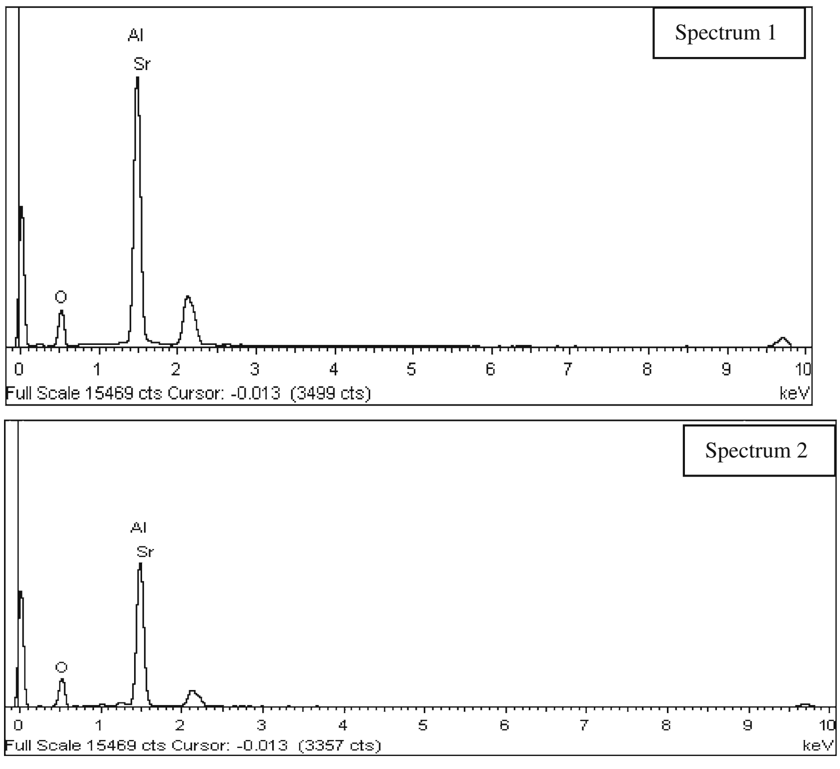



**Figure 4.** Energy dispersive X-ray analysis of (ABS3) $92Al_2O_3–5B_2O_5–3SrO$ and (ABS4) $91Al_2O_3–5B_2O_5–4SrO$ samples.

enhanced the densification properties of ceramic bodies sintered at 1600 °C for 6h with deteriorating microwave dielectric properties compared with high purity (99·99%) alumina which produced a quality factor, 42,000 at 9 GHz (Penn *et al* 1997). This may be attributed to the presence of some impurities in alumina recycled from Al dross (McN Alford and Penn 1996) as shown in table 1. Anyway the values of $Q \times f$ (15,236–22,020 GHz) which was obtained from this study showed a slight increase than those recorded with commercial alumina (10,000 – 20,000 GHz) and it can be used in the electronic applications such as wireless communication and memory devices.

**Table 2.** EDX data of samples for spectra 1 and 2 as shown in figure 4.

| | Atomic (%) | | |
|---|---|---|---|
| Spectra | Al K | SrL | OK |
| 1 | 42·67 | 0·03 | 57·30 |
| 2 | 37·37 | 0·9 | 62·53 |

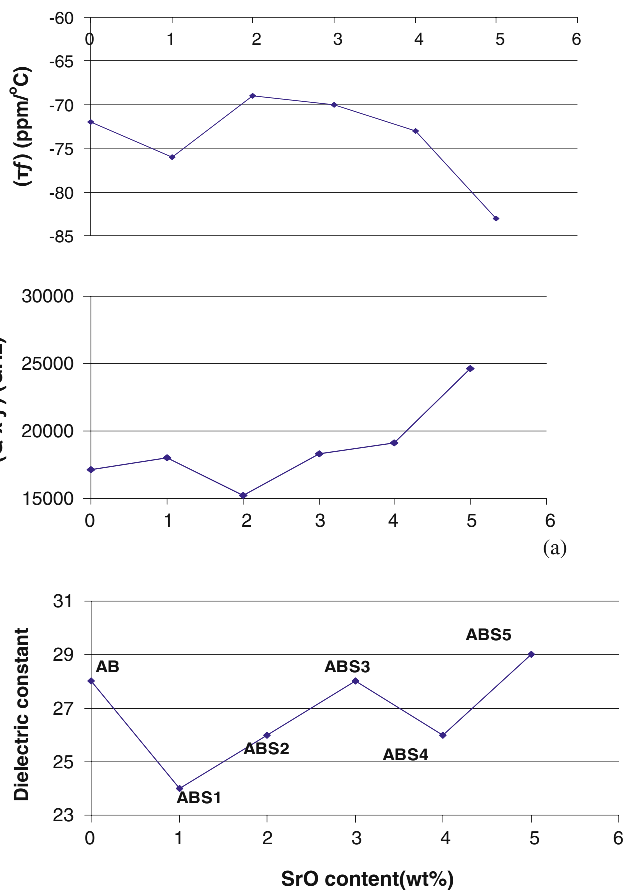



**Figure 5.** Dielectric properties of alumina bodies with different SrO contents.

## 4. Conclusions

The addition of SrO (0·0–5·0 wt %) in partial substitution of alpha alumina (corundum) in ceramic composition (95 $Al_2O_3$–$5B_2O_3$) has significant effect on reducing the temperature to achieve optimum density temperature by about 100 °C as compared with pure alpha alumina ceramic bodies. The sintered ceramic bodies show different ranges for the dielectric properties. Dielectric constant exists between 24 and 29, quality factor is ranging between ($Q \times f$) 15,236 and 22,020 GHz, and temperature coefficient of resonant frequency ($\tau_f$) in the −69 to −83 ppm/°C range. It is concluded that increasing SrO addition up to 5 wt% SrO leads to maximum ($\varepsilon_r$) value (29) due to relatively higher ionic polarizability of $Sr^{2+}$ than that of $Al^{3+}$ and $B^{3+}$ ions. On the other hand, changing chemical and phase composition with the formation of platelets of Sr hexaluminate phase ($SrAl_{12}O_{19}$) results in maximizing values of ($Q \times f$) up to 22,020 GHz at ≈ 8 GHz and minimizing that of ($\tau_f$) to −83 ppm/°C.

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