EFFECT OF CaO, CuO AND V_2O_5 ON BARIUM ZINC TANTALATE (BZT) DIELECTRIC PROPERTIES

by

HIDAYANI BT JAAFAR

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LIST OF ABBREVIATIONS

DR	Dielectric Resonators
GPS	Global Positioning Systems
BZT	$Ba(Zn_{1/3}Ta_{2/3})O_3$
BZN	$Ba(Zn_{1/3}Nb_{2/3})O_3$
BMT	$Ba(Mg_{1/3}Ta_{2/3})O_3$
FESEM	Field Emission Scanning Electron Microscopy
XRD	X-ray diffraction
RF	Radio frequency
UHF	Ultra high frequency
SHF	Super high frequency
EHF	Extremely high frequency
DRA	Dielectric resonator antenna
WLAN	Wireless local area network
Hz	Hertz
GHz	Giga hertz
MPa	Mega pascal
BW	Bandwidth
HELOS	Helium neon optical system
MPa	Mega pascal
DTA-TGA	Differential Thermal Analysis-Thermal Gravimetry Analysis

LIST OF SYMBOLS

ε_r	Dielectric constant
Q	Quality factor
c/a ratio	Lattice distortion
f	Resonance frequency
a	Radius
h	Height
ø	Azimuth
r	Radial
z	Axial
d	Thickness
w	Width
Ω	Ohms
R	Resistance
A	Cross sectional area
ρ	Volume resistance
I	Current
λ_d	Wavelength in dielectric
λ	Wavelength in air
t	Tolerance factor
V	Voltage

KESAN CaO, CuO DAN V_2O_5 TERHADAP SIFAT-SIFAT DIELEKTRIK BARIUM ZINK TANTALAT (BZT)

ABSTRAK

BZT mempunyai pemalar dielektrik ($\varepsilon_{r)}$ yang tinggi dan lesapan dielektrik (tan δ) yang rendah. Walau bagaimanapun, suhu pensinteraan yang tinggi diperlukan untuk menghasilkan BZT yang mempunyai sifat-sifat dielektrik yang cemerlang. Oleh itu, bagi mengatasi masalah tersebut, pendopan dilakukan ke atas BZT dan mengkaji kesan pengurangan suhu pensinteran berdasarkan pendopan CaO CuO dan V_2O_5 ke atas BZT. CaO dipilih kerana penggantian Ca menghasilkan struktur baru dan mengelakkan pengurangan sifat-sifat dielektrik pada julat frekuensi yang tinggi. Manakala, penambahan CuO dapat mengelakkan peruapan Zn yang menyebabkan pengurangan sifat-sifat dielektrik. Pemilihan V_2O_5 sebagai bahan dop kerana mempunyai suhu leburan yang rendah. Dalam kajian ini, rekabentuk eksperimen dibahagi kepada tiga bahagian. Bahagian pertama, eksperimen dijalankan bagi menghasilkan fasa tunggal BZT pada suhu yang terendah dan 1150°C menghasilkan keputusan yang terbaik. Fasa kedua, BZT yang terhasil daripada fasa pertama dibahagikan kepada dua, bahan asal BZT yang disinter pada suhu 1350°C dan BZT yang didop, (0.1 hingga 2.5 mol%) dan disinter pada 1250°C. Sampel yang disediakan dianalisis menggunakan analisis XRD, FESEM, ketumpatan dan pengecutan. Fasa ketiga, sifat-sifat dielektrik terhadap kesan pendopan daripada fasa kedua dikaji. BZT + *x*CaO bertindakbalas menghasilkan BCZT dan menukarkan struktur heksagonal ke kubik. Manakala, BZT yang didop dengan CuO dan V_2O_5 tidak memberi kesan kepada struktur asal. Penambahan mol% bahan daripada 0.1 sehingga 0.5 mol% menghasilkan struktur yang lebih padat. Setiap sampel menunjukkan hasil yang berbeza bergantung kepada mol% bahan didop dimana frekuensi salunan adalah dari 10.3 hingga 14.8 GHz dan kebertelusan dalam julat 26.29 hingga 75.9 serta kehilangan tangen dalam linkungan 0.04 hingga 0.159.

EFFECT OF CaO, CuO AND V_2O_5 ON BARIUM ZINC TANTALATE (BZT) DIELECTRIC PROPERTIES

ABSTRACT

BZT has high dielectric constant (ε_r) and low dielectric loss (tan δ). However, the formation of BZT using solid state method required high sintering temperature to produce excellent dielectric properties. Therefore, to overcome these problems, other elements were added in BZT and investigate the effect of reducing sintering temperature of BZT by doping with by CaO, CuO and V_2O_5 respectively. CaO was selected as a doping compound because the Ca substitution form a new structured and avoid deteriorated dielectric properties in high frequency range. Meanwhile, adding CuO can avoid Zn evaporation problem which lower the dielectric properties. The selection of V_2O_5 as a doping compound is to improve BZT dielectric since V_2O_5 has a relatively low melting point. In this study, the experimental design is divided into three phases. In the first phase, the experiment was designed to produce the lowest calcination temperature that form single phase of BZT and 1150°C give the best result. For the second phase, BZT produced from the first phase was divided into; pure BZT sintered at 1350°C and doped BZT, (0.1 to 2.5 mol%) sintered at 1250°C. The samples produced were characterized using XRD, FESEM density and shrinkage analysis. In the third phase, the effects of dopants from second phase were investigated on dielectric properties of doped BZT. BZT + *x*CaO appeared to react to form BCZT and turn from hexagonal to cubic structure. While for BZT doped with CuO and V_2O_5, the structure remains unchanged. Increasing the mol% of dopants from 0.1 to 0.5 mol% produced more compacted structure. Each samples showed a resonance frequency from 10.3 to14.8 GHz and dielectric constants in the range of 26.29-75.9 and the dielectric loss is 0.04-0.159 depending on the mol% of dopant.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Microwave dielectric materials play an important part in the developing of the satellite communication including Global Positioning Systems (GPS) to environmental monitoring via satellites (Sebastian et al., 2008). The widely research that is related to microwave telecommunication, satellite broadcasting has resulted in an increasing demand for dielectric resonators (DR), which are low loss ceramics pucks used mainly in wireless communication devices (Sebastian et al., 2008). The development of high dielectric constant (ε_r), low dielectrics loss (tan δ) has enabled the production of miniaturized resonators and filters through the use of DR. A DR is an electromagnetic component that exhibits resonance with useful properties for a narrow range of frequencies (Pern et al., 1999). The properties that required for DR are suitable range of resonance frequency (*f*), low tan δ, and high ε_r. Low tan δ or high quality factor (Q) gives a smaller bandwidth (BW) at the *f*, a lower degree of noise, and less power loss (Muller et al., 2000). Thus, it is important to develop and study dielectrics with a high Q factor in the microwave regime.

Complex oxides are playing important role in the wireless communications and also in particular cellular phone. In the form of the ceramic DR they have had a great impact on the microwave-based wireless communications industry by reducing the size and cost of filter and oscillator components in products ranging from cellular telephones to GPS. Understanding more to the current materials in the aspects of their processing,

synthesis and structure property relationship is needed for further system miniaturization of new ceramics with higher ε_r and good temperature stability along with lower tan δ.

Before the development of complex perovskite take control in DR, Cohen et al. (1965) use TiO_2 as a DR. Although it has a high ε_r and low tan δ, it has poor stability of *f* that prevented its commercial exploitations. The earliest commercialization of DR was started in the early 1970 when the first temperature stable, low tan δ barium tetratitanate ($BaTi_4O_9$) ceramics were developed by Masse et al. (1971). Since then extensive theoretical and experimental work and development of DR materials has occurred.

$Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) is a ceramic composition that contained Ba, Zn, Ta and O elements. Dielectrics properties of complex perovskite compounds such as BZT and $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) have been extensively investigated for their use as DR for satellite communication systems at microwave frequencies >10 GHz (In et al., 1993). BZT is a well-known ceramic material having a high ε_r(ε_r ~29) and high Q (Q×*f*~80,000 - 150,000 GHz). BZT has a complex perovskite structure and belongs to the family of materials $A(B'_{1/3}\ B''_{2/3})O_3$ [A = Ba, $B'_{1/3}$ = Zn, $B''_{2/3}$= Ta] used in microwave communication system (Ioachim et al., 2007).

High sintering temperature above 1500°C or prolonged heat treatment will lead to volatilization of ZnO and the escape of ZnO loss will lead to poor densification near the surface of the samples (Reaney et al., 2003). The depletion of ZnO also will contribute to the second phase likes $Ba_3Ta_2O_8$ and $BaTa_2O_6$. The secondary phases that occur in BZT also the factor that causes the Q values factor decrements. The Zn loss during the processing also will decrease the dielectric properties and also play an important role in controlling the crystal structure. Kawashima et al. (1983) suggested

that the increase in Q values might be due to lattice distortion (c^*/a^* *ratio*) rather than ordering of Zn and Ta cations, porosity or grain size. Zn and Ta cations are ordered, BZT has a hexagonal crystal structure and the *c*/a* ratio* deviates from the value for an ideal hexagonal unit cell ($3^{1/2}/2^{1/2} = 1.2247$) which is called the *c*/a* ratio*. Meanwhile, Koga et al. (2006) said that the Q values of BZT system was found to depend not only on the ordering but also on their ceramic microstructure.

When Zn and Ta cations are disordered over the B-site, the crystal structure of BZT is cubic perovskite with Pm3m space group symmetry. When B-site cations order along the [111] direction of this simple perovskite compound, a hexagonal superlattice is formed with space group $P\bar{3}m1$. This ordering has been investigated for its effect on the microwave Q values. A strong relationship between ordering parameters and microwave Q values in BZT system was experimentally observed by Kawashima et al. (1983) under various heat conditions. They also reported that improvement of the microwave Q values in the BZT system by prolonged sintering and indicated that this Q values improvement corresponded with an increase in cation order of the structure.

Kawashima et al. (1993) reported that to achieve a perfect hexagonal structure at 1350°C takes at least 120 hours. However, Desu and O'Bryan (1985) pointed out that there is another factor at work during these long sintering times, the weight loss occur due to the loss of volatile ZnO. They noted that the *c*/a* ratio* and ordering do not occur simultaneously in the data of Kawashima et al. (1993) as would be expected if the only factor was ordering. They suggested that the continue *c*/a* ratio* after ordering is complete due to the loss of the ZnO. Loss of ZnO is greater on the surface compare with the bulk because slow diffusion rate of Zn through the dense ceramic.

However, BZT was a particular interest for microwave applications because it can be fabricated with exceptionally high Q values at microwave frequencies. The microwave dielectric properties of BZT is affected by it structure. The ordering of B site cations has been influence the Q values of BZT ceramics (Varma et al., 2005). For pure BZT, high temperature for sintering was needed to achieve high Q values but sintering at temperatures above 1500°C leads to volatilization of ZnO and also increase the cost of manufacturing. The escape of ZnO led to poor densification and decreases the dielectric properties of BZT (Sebastian et al., 2008). To overcome these problems, other elements were added in the pure BZT. The adding of new elements also increases the dielectric properties. It has been reported by Kim et al. (2004) that addition of small amount of 1 mol% TiO_2 and 0.75 mol% Al_2O_3 can improve the Q and ε_r values of the materials. Another study, Jeong et al. (2005), found that extra addition of 0.3 mol% Ta_2O_5 can also increase dielectric properties. For example, a small amount of Ta_2O_5 can improved the Q values and the 1:2 order structure still maintain without changing to 1:1 ordering. Lee et al. (1998) found that lanthanum (La) substitution at the A site in BZT decreased the 1:2 ordering and at higher concentrations transformed to 1:1 ordered phase. For all dopants, grain growth occurred. The increase in Q values for small amount of doping is attributed to increase in density and grain growth (Jeong et al., 2005). However, the large addition amount of dopants elements (>2mol %) can decrease the density and Q values of BZT (Daevies et al., 2008).

Varma et al. (2005) made an investigation on the effect of dopant addition in the BZT. They added several dopants of varying valencies, ionic size and concentrations and studied the variations in densification, and microwave dielectric properties. It was

found that the Q values increased when the ionic radii of the dopant is close to that of B-site ions (Zn or Ta). The Q values increased when the ionic radii of the dopant is close to that of Zn (0.74 Å) or to that of Ta (0.64 Å). An amount of 0.5 mol% of Mg, Ni, Cr, In, Ga, Sn, Zr, Ce, Mn, and Sb improved the Q. values When the amount of dopant was increased to 1 mol%, the Q values were found to increase only for Cr, Ga, Zr, Ce, and Sn. The highest Q values were found for doping with Zr, Cr and Ce. In the doped samples the Q values are very much improved although the order parameter is decreased. Since these dopants having ionic radii close to that of the B-site ions improve Q values, it implies that these dopants are substituting for Zn or Ta in BZT.

There are many methods that producing the electroceramic powder like BZT. Generally, powder mixing method selection are depends on manufacturing cost, technical needed and the ability of the choosing method to achieve the needed properties. Mclaren et al. (1999) was prepared the BZT by hydrothermal methods. Varma et al. (2006) prepared BZT nanopowder by the decomposition of a citrate precursor gel. However, the sinterability of BZT ceramics that made from nanopowder was very poor and on the sintering at high temperatures cause depletion of ZnO and form second phase of BZT, $BaTa_2O_6$. Varma et al. (2006) succeed in sintering BZT ceramics from nanopowder by using solid state method. Therefore, the solid state method is the cheapest method to produce this dielectric material. It is because this method is the cheapest manufacturing cost and simple procedure compare with sol gel and hydrothermal synthesis. Even though sol gel and hydrothermal synthesis can solve the high processing temperature problem but the quantity that produce is in small volume and the cost for these methods also expensive. Kong et al. (2007) stated that the

weakness of using sol gel is due to expensive alkoxide metal as a starting material and very sensitive with environment such as heat, light and moisture. Moisture sensitivity means the experiment must be conducted in vacuum room. So, the final product in a big amount is difficult to produce (Warikh et al., 2008).

1.2 Problem Statement

Complex perovskites $Ba(B'_{1/3}B''_{2/3})O_3$ compounds are very promising materials for electroceramic applications due to their attractive properties. The important characteristics required for DR are high ε_r and low tan δ (Sebastian et al., 2008). BZT compound with excellent dielectric properties has been selected because of the potential applications in satellite broadcasting at frequencies higher than 10 GHz. Zirconia tin titanate, $(Zr_{1-x}Sn_x)TiO_4$, BZN and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT), having high ε_r are also widely used as a DR but these materials are not suitable in high frequency applications due to high tan δ at high frequency range (Sebastian et al., 2008). Therefore, BZT is the best materials due to the stability of it properties in high frequency range.

The formation of BZT materials into dense ceramic resonators with excellent dielectric properties required very careful and demanding processing procedures because BZT is difficult to optimize on a commercial scale. This is a significant problem related to the BZT production cost. The atomic scale structure of BZT depends on the processing conditions since they control the extent to which the octahedral B-sites of the parent simple perovksite are occupied in an order manner by the Zn and Ta cations (Bieringer et al., 2003). The most common method that always uses to produce complex perovskites is solid state method. Even though this method is the easiest and the

cheapest method compare to the sol-gel, hydrothermal and etc., this method is still dealing with the high sintering temperature and long soaking time to produce very excellent dielectric properties. BZT has to be sintered at high temperature (1550°C) and long soaking time (120 hours). However, this procedure will also leads to volatilization of ZnO and increase the manufacturing cost. The escape of ZnO led to poor densification and decreases the dielectric properties of BZT (Cava et al., 2001). To overcome these problems, many researchers tried to dope BZT with many elements, respectively. It has been reported by Kim et al. (2004) that addition of small amount of 1 mol% TiO_2 and 0.75 mol% Al_2O_3 can improve the Q and ε_r values of BZT. Another study found that extra addition of 0.3 mol% Ta_2O_5 can also increase dielectric properties (Jeong et al., 2005). For example, a small amount of Ta_2O_5 can improved the Q values and the 1:2 order structure still maintain without changing to 1:1 ordering. Lee et al. (1997, 1998) found that lanthanum (La) substitution at the A site in BZT decreased the 1:2 ordering and at higher concentrations transformed to 1:1 ordered phase. Most of the researchers are successfully produce good dielectric properties compare to the pure BZT but the problem that involved with high sintering temperature is still cannot be solved. If they can sintered in short soaking time (6 to 10 hours) they still required high sintering temperature (>1550°C) in order to produce excellent dielectric properties (Sebastian et al., 2008).

The reason of using CaO, CuO and V_2O_5 is that these dopant have never been reported in previous literature. However, these dopants have been used in many materials such as $BaTiO_3$ (Moura et al., 2007), bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) and barium zirconate titanate ($Ba(Zr_{0.07}Ti_{0.93})O_3$, BZT), Bi_2O_3–ZnO–Ta_2O_5

(Shen et al., 2004), bismuth based pyrochlores (Iqbal et al., 2010) and produce excellent dielectric properties at low sintering temperature. CaO is introduced as a doping compound because the Ca substitution form a new structured and avoid deteriorated microwave dielectric properties in high frequency range. CaO also exhibits high radiation resistance and also produce high ε_r. While, adding CuO can avoid Zn evaporation problem which lower the dielectric properties. The selection of V_2O_5 as a doping compound is to improve BZT dielectric since V_2O_5 has a relatively low melting point and can produce excellent dielectric properties. Therefore, with appropriate compositional design and selection of sintering temperature and duration, there is a possibility to decrease the sintering temperature and soaking time without Zn vaporization and produced BZT with excellent dielectric properties.

1.3 Research Objective

This study is focusing on dielectric properties of doped BZT and characterization of the BZT doped by various elements using solid state method. Therefore, the main objectives are:

i. To investigate the lowest calcination temperature for producing single phase of BZT using solid state method.

ii. To study the effect of reducing sintering temperature of BZT by doping with CaO, CuO and V_2O_5 respectively

iii. To study the dielectric properties of BZT doped with CaO, CuO and V_2O_5, respectively.

1.4 Scope of Work

Basically, this study can be divided into 3 phases which are:

i. Finding the lowest calcination temperature to produce single phase of BZT using solid state method.
ii. Reducing the sintering temperature of BZT by doped-BZT.with CaO, CuO and V_2O_5 respectively.
iii. Studying the dielectric properties of doped-BZT.

In the first phase, the solid state method used by other researchers such as Kawashima at al. (1983), Kim et al. (2001), Roulland et al. (2003) and Zaou et al. (2005) to produce BZT was employed. However, survey of the literature has not revealed any researcher using exactly the same chemicals in synthesizing a BZT doped CuO, CaO and V_2O_5 powder. Hence, these doped elements is seemed to be a newly elements developed during this thesis work. For the calcination process, the pure BZT powders obtained from the solid state method were calcined in a furnace at various temperatures ranging from 750 to 1250°C. The powders, calcined at different temperatures were then examined for their phase(s) content.

For the second phase, the BZT produced from the first phase was pressed and sintered at 1250°C, 1300°C and 1350°C in 4 hours soaking time, respectively. This is to determine the reference sintering temperature for pure BZT. Meanwhile, the BZT that produced from the first phase doped with 0.1 to 2.5 mol % of CuO, CaO and V_2O_5. The mixture were then calcined at 1150°C in 1 hour soaking time before being pressed into

pellets and sintered in three different sintering temperatures at 1200°C, 1250°C and 1300°C in 4 hours soaking time, respectively.

While, for the third phase, the final product of the doped-BZT were analyzed using network analyzer to investigate the doped-BZT microwave dielectric properties.

Characterization work was carried out after finding the optimum sintering temperature. Different properties of the sintered doped BZT such as grain size and microstructure, density, phase formation, resistivity, shrinkage and dielectric properties were examined with various analytical equipments such as Field Emission Scanning Electron Microscopy (FESEM), network analyzer and etc.

CHAPTER 2

LITERATURE REVIEW

2.1 Microwave Communications

Electromagnetic waves travel in a straight line at approximately the speed of light and are made up of magnetic and electric fields that are the right angles to each other and at right angles to the direction of propagation (Tomasi et al., 2004). Modern microwave and radio frequency (RF) engineering were widely used due to the explosion in demand for voice, data and video communication capacity (Golio et al., 2001). Microwave technology almost controlling the communication industry because increase in demand for communications systems such as mobile telephony, broadcast video and GPS to environmental monitoring via satellites (Golio et al., 2001). Most of the microwave based device systems are located from the range 300 MHz to 300 GHz as shown in Figure 2.1 (Golio et al., 2001). The microwave region can be divided into three sections, ultra high frequency (UHF) region from 300 MHz to 3 GHz, super high frequency (SHF) region from 3 GHz to 30 GHz and extremely high frequency (EHF) region from 30 GHz to 300 GHz (The Spectrum Plan, 2006). Compare with the radio waves, microwave can carried much more information because they have higher frequency and shorter wavelength (λ). Higher frequency can produce large BW that can achieve higher data transmission rates while the short λ allows the energy to be concentrated into a small area.

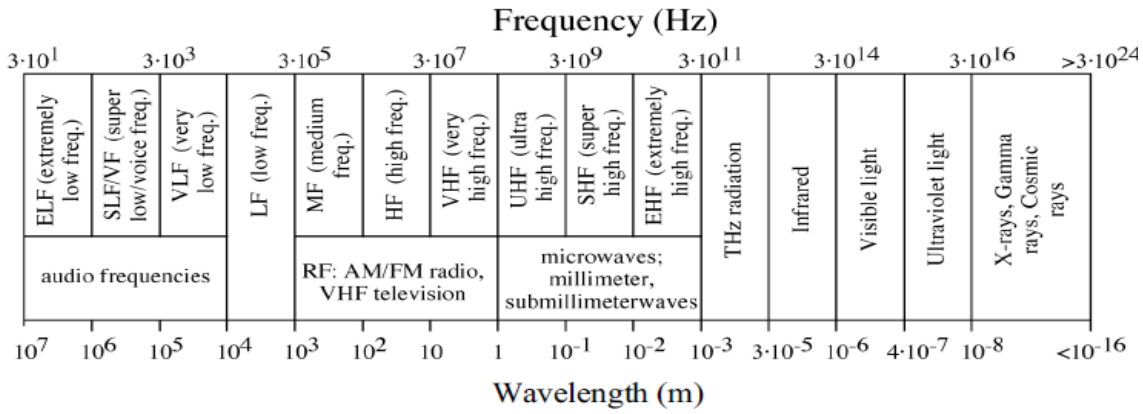


Figure 2.1: Microwave spectrum and applications (Golio et al., 2001).

2.1.1 Dielectric Resonators (DR)

A DR is an electromagnetic component that exhibits resonance with useful properties for narrow range of frequencies (Sebastian et al., 2008). DR is always used as a filters and oscillators. Richinger et al. (1939) showed that microwaves resonators in the form of unmetallized dielectric objects can function similarly to bulk metallic cavities and in late 1960s, the DR started to be used due to the development of low tan δ ceramics materials. A DR tends to resonate at the frequency of the carrier signal to allow the signal to be efficiently separated from other signals in the microwave band; this frequency is called the *f*. The *f* depends on the dielectric material and the size of the resonator.

Around 1960s, many researchers investigated the behavior of dielectrics at microwave frequencies including Okaya et al. (1962), Barash et al. (1962), Coleman et al. (1960), Hakki et al. (1960) and Cohn et al. (1968). Many problems occurred at that time due to the limited number of the suitable materials. The first DR was in the form of TiO_2 single crystal (Khisk et al., 2007). Rutile (TiO_2) has high ε_r and low tan δ but its

large *f* of the temperature coefficient made it impractical for many applications. By the 1970s, the commercialization of DR for real applications had begun introduced to the worldwide.

2.1.2 Dielectric Resonator Antenna (DRA)

Several DR can fabricate to form DRA. DRA can produce high degree of flexibility and versatility over a wide frequency range that suit many requirements. DRA offer many advantages. First, the DRA size is proportional to the $\lambda_o / \sqrt{\varepsilon_r}$ where ε_r the dielectric constant of the DRA and λ_o is the wavelength of the *f*. The different values of ε_r (range from 4 to 100) can be used. Therefore, it gives the flexibility to control the size and BW (Khisk et al., 2007). Second, DRA has much wider impedance BW compare with microstrip antenna. Compared with microstrip antenna, DRA can radiate through the whole antenna surface except the grounded part while microstrip antenna can radiates only through narrow radiation slot (Khisk et al., 2007). The DRA operating BW can be varies by choosing suitably ε_r of resonator material and its dimensions. Third, DRA consists high dielectric strength and high power handling capacity. This antenna can operate in wide temperature range due to the temperature stable ceramics.

There are three major of important properties that need to be considered to choose the materials for DRA. The ε_r controls the resonator dimensions and should be as high as possible. A low tan δ is very important for high performance devices because the lower tan δ, the higher the efficiency and lower the noise (Pern et al., 1999). To increase the efficiency of DR in telecommunication applications, low return loss and high BW are required.

2.1.2.1 Effect of DRA Height and Shape

The mode of operation and performance of a DRA can be varied by selecting a DR with desired structure. The systematic research already been conducted in 1983 and 1984 towards the different shape of DRA such as cylindrical, hemisphere, and rectangular shape (Long et al., 1983). Each of these shape were characterized with the value of ε_r , radius (*a*), height (*h),* and thickness (*d*). Mridula et al. (2004) state that the different between *h* and width (*w*) for rectangular DRA give an effect to the *f* and return loss.

Figure 2.2 shows those two units of DRA that have different *h* which is DR_1 and DR_2. The *f* for DR_1 exist at 1.795 GHz with 6.12% BW and suitable to operate at GSM 1800 (1710-1880 MHz) frequency. While, the *f* for DR_2 occurred at 2.445 GHz and it is suitable to operate in wireless local area network (WLAN) frequency (2.4-2.484 GHz). In Figure 2.3, two units of DRA that have different BW which is DR_3 and DR_4. For DR_3, it is suitable for GPS band (1.565-1.585 GHz) and for DR_4 for PCS 1900 band (1.85-1.99 GHz). These results show that different dimension of DR can produce different *f* for different applications.

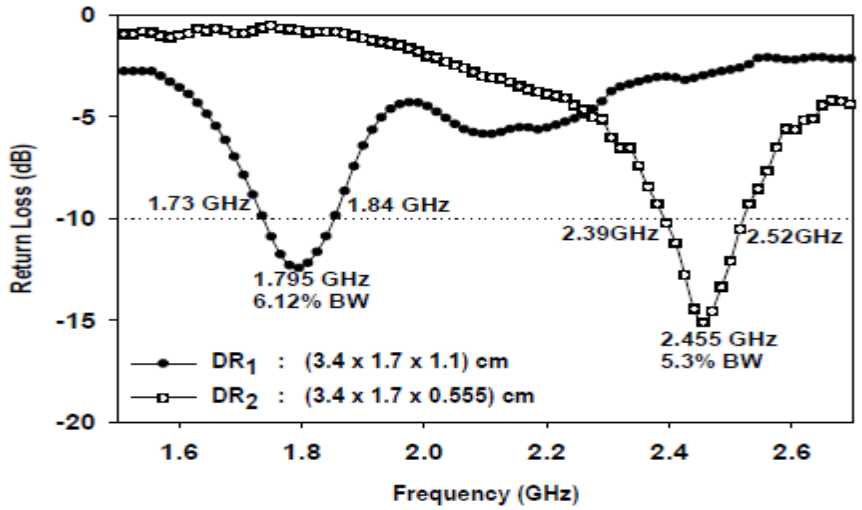


Figure 2.2: Return loss for antenna with two samples different *h* (Mrindula et al., 2004)

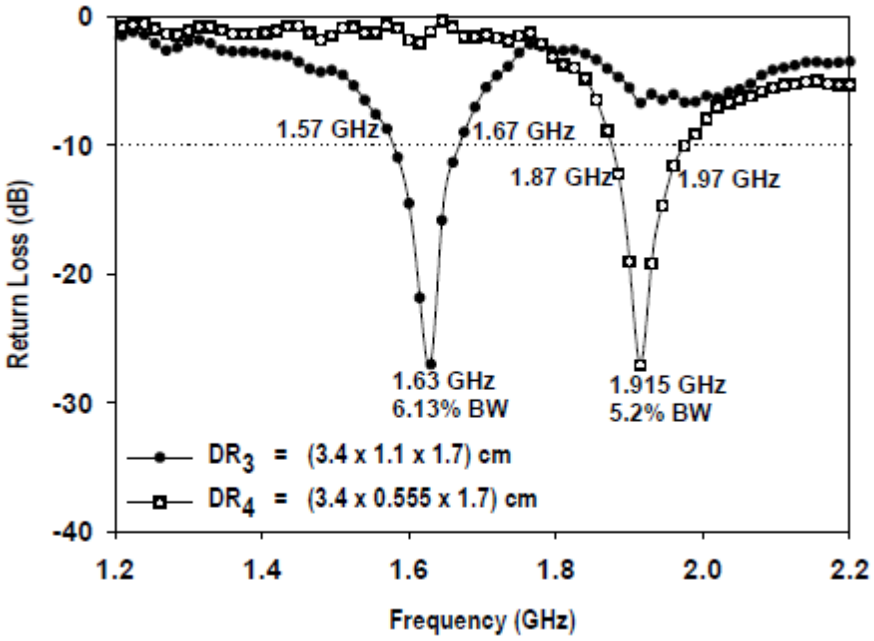


Figure 2.3: Return loss for antenna with two samples different BW (Mrindula et al., 2004)

2.1.2.2 The Hemispherical DRA

The geometry of the hemispherical DRA is shown in Figure 2.4. The hemispherical DRA is of limited practical value. It is because due to the difficulty involved in fabrication and lack of any degree freedom in choosing the design parameters. For the materials that have certain ε_r, the radius of sphere will determine both the *f* and the radiation that will produce. Therefore, the designer cannot control the size of the antenna and its BW. The designer has difficulty to control the size of antenna or BW due to the limited characterization.

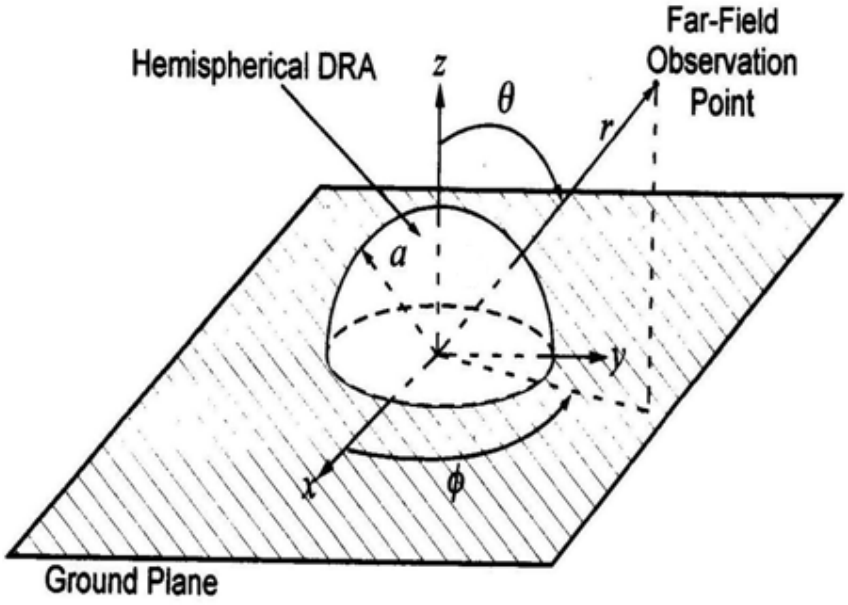


Figure 2.4: Hemispherical DRA (Petosa et al., 2007)

2.1.2.3 The Rectangular DRA

The DRA with a rectangular cross section is characterized by *h*, *w*, *d*, and ε_r as shown in Figure 2.5. The rectangular shape offers a second degree of freedom which is *h*/*w* and *d*/*w* making it most versatile of the basic shape. There is greater amount of flexibility in designing the rectangular DRA to achieve desired profile and BW characteristics for a given f and ε_r since the ratio of (*d*/*w*) and (*h*/*w*) can be chosen independently. The choice of aspect ratio will also have an impact in the radiation. Thus, it allowed the designer to make many choices to design the DRA for certain application.

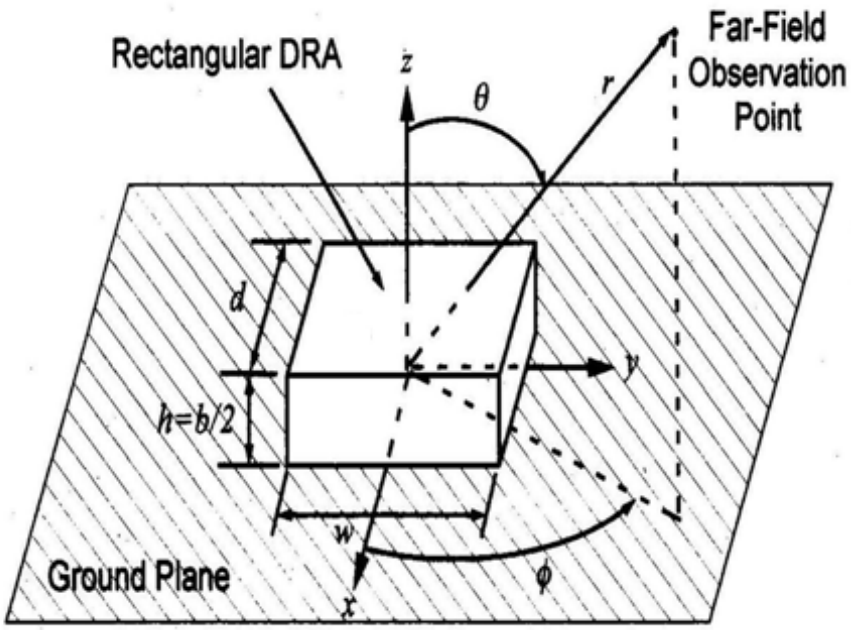


Figure 2.5: Rectangular DRA (Petosa et al., 2007)

2.1.2.4 The Cylindrical DRA

The cylindrical DRA offers greater design flexibility, where the ratio of *a/h* controls the *f* and dielectric properties. So, for a given ε_r and *f*, different tan δ can be obtained by varying the DRA dimensions. Fabrication is also simpler than the hemispherical DRA. The cylindrical DRA is characterized by *h*, *a*, and ε_r as shown in Figure 2.6. The cylindrical shape offers one degree of freedom more than hemispherical shape which is the aspect ratio *a/h*. Thus, the cylindrical DRA can be made to resonate at the same frequency as a wide and thin cylindrical DRA. However, the tan δ for both resonators is different. DRA that use for electronic circuit usually been produce in cylindrical shape or pellet that have high ε_r(>35) (Long et al., 1983).

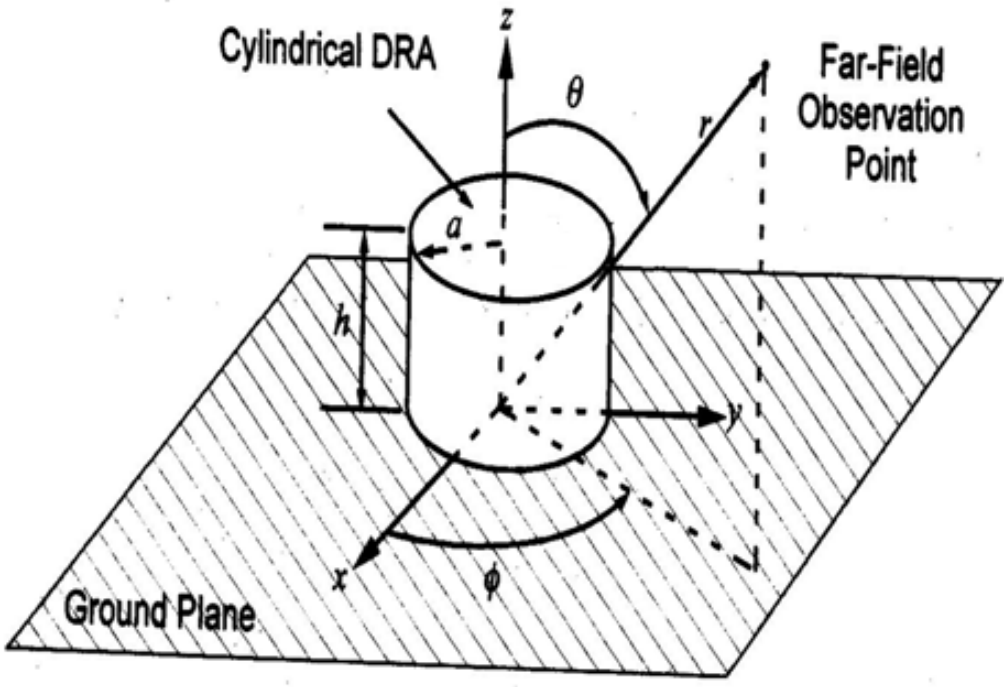


Figure 2.6: Cylindrical DRA (Petosa et al., 2007)

2.1.3 Dielectric Microwave Properties

2.1.3.1 Dielectric Resonance Frequency (*f*)

The *f* is the frequency which capacitance and inductance are cancelling to each others. The *f* of a DR in the $HE_{11\delta}$ mode can be estimated by Equation 2.1 formulated by Long et al. (1988).

$$f = \frac{6.324c}{2\pi a\sqrt{\varepsilon_r} + 2}\left[0.27 + 0.36\left(\frac{a}{2d}\right) + 0.02\left(\frac{a}{2d}\right)^2\right] \quad (2.1)$$

where;

f = Resonance frequency

ε_r = Dielectric constant

a = Radius of resonator (m)

d = Thickness of resonator (m)

The *f* can be changed by altering the dimensions of DR. *f* increase when the size of DR decreases and ε_r values are low.

2.1.3.2 Dielectric Constant (ε_r)

The ε_r is the degree of polarizability or energy storing capacity when the potential is applied across it. High ε_r values were needed for circuit miniaturization. This is because the λ inside the DR is inversely proportional to the square root of its ε_r as given by the Equation 2.2.

$$\lambda_d = \lambda_o / \sqrt{\varepsilon_r} \qquad (2.2)$$

Where;

λ_d = Wavelength in dielectric

λ_o = Wavelength in air

ε_r = Dielectric constant

High ε_r values can reduce the size of the antenna. A relatively small antenna can efficiently radiate high frequency electromagnetic wave. When $\sqrt{\varepsilon_r}$ increase, the λ_d will decrease and when the microwave frequency enter the dielectric material, the length of λ will decrease and produce short λ that performed better frequency as shown in Figure 2.7. Materials with low ε_r values are used for electrical insulator applications. Materials with high ε_r values are used as a DR or capacitors for charge storage and other function.

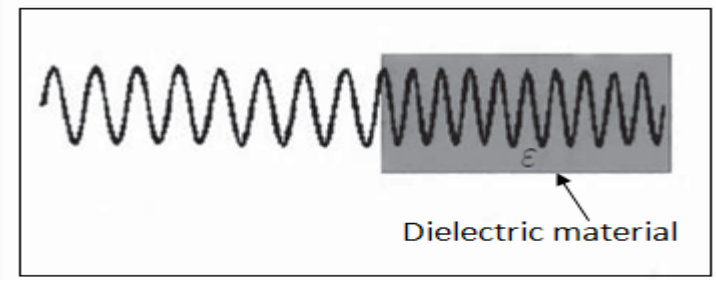


Figure 2.7: The λ is reduced by factor of $\sqrt{\varepsilon_r}$ when the waves enter the dielectric material (Sebastian et al., 2008)

Polarization happen when electric field is applied to a dielectric material, there are no long range of transport of charge of material but the charge of material are displaced in response to the applied field. The orientation of the charge reduce the effective of electric field between the plates because the charged tied up charges on the plate of the condenser but it increase the ability of the plates to store charge. Relaxation time was needed to achieve the equilibrium orientation and relaxation frequency as a reciprocal for relaxation time.

Figure 2.8 shows various types of polarization. At the highest frequencies (10^{13} to 10^{15} Hz), the electron is the polarizing species in a material. Electronic polarization occurs when an applied electric field causes the shift of the electron cloud. Ionic polarization occurs at frequencies below 10^{13} Hz and this is due to the displacement of positive and negative ions with respect to each other (Nair et al., 2002). Below 10^{10} Hz, orientation polarization occur because molecules that contain permanent dipole rotating between the two equivalent equilibrium positions and space charge polarization that produced at frequencies below 10^{5} Hz form due to the mobile charge carriers that are impeded by physical barrier (Nair et al., 2002).

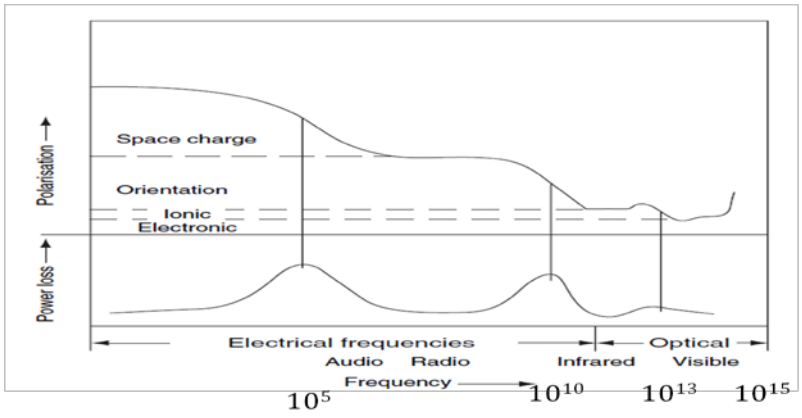


Figure 2.8: Frequency dependence of polarization process and peak power losses (Sebastian et al., 2008)

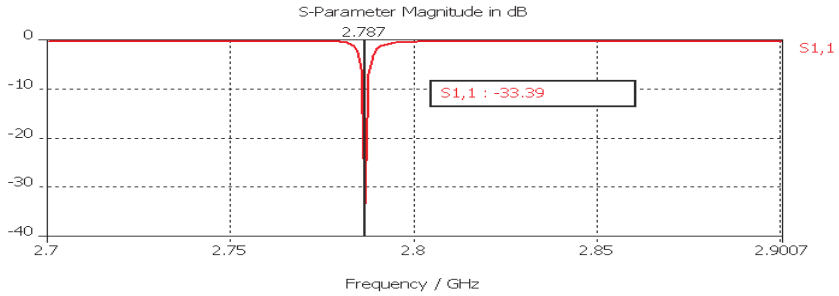
2.1.3.3 Dielectric Loss (tan δ)

Due to the different physical processes such as dielectric resonance, electrical conduction and dielectric relaxation, the tan δ of a material denotes quantitatively dissipation of the electrical energy (Bartfoot et al., 1967). The total tan δ is the sum of the intrinsic and extrinsic losses. The intrinsic losses are dependant on the composition of the material while the extrinsic losses are the additional losses due to the imperfections in crystal structure. The losses are determined by the phonon interactions in ideal crystals, impurities, vacancies, porosity, grain boundaries and dopants in real materials.

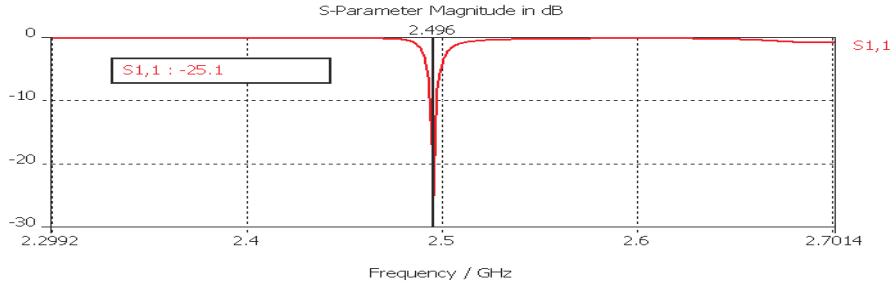
The intrinsic losses happen due to the anharmonic lattice forces that control the interaction of phonon system. This is because the microwave frequency is lower than phonon frequency so the microwaves cannot directly interact with the individual phonons. From theory, lowest tan δ can be achieved from a single crystal since defects and impurities can increase the phonon scattering. Extrinsic losses can be divided into two groups; 1) losses in real homogeneous single crystals causes by dopant, impurity and vacancies and 2) losses in inhomogeneous ceramics due to extended grain boundaries, vacancies and second phase. The losses from point 1 can be seen as energy transfer from the excited microwave to transverse optical phonons. Through scattering and interaction with other phonon, thermal phonons can be generating from these optical phonons.

2.1.3.4 Minimum Return Loss

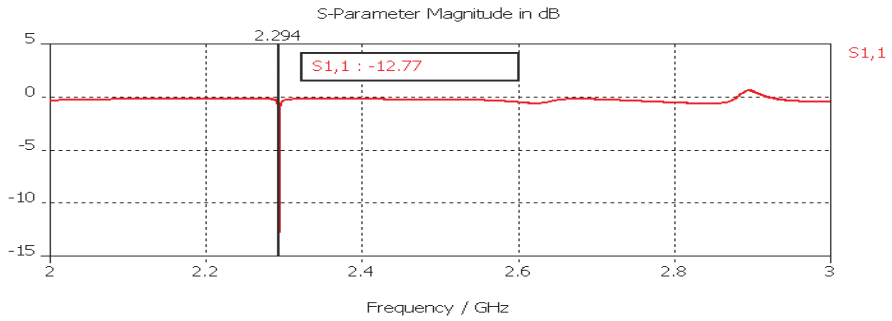
Minimum return loss is a portion of a signal that cannot be absorbed by the end of line termination, or cannot cross an impedance change at some point in the transmission system. Minimum return loss value must less than -10 dB. The minimum return loss is influence by the thickness of the DRA. It proves by Ain et al. (2007) that use different thickness of resonator were produced different operation of *f*. Based on Figure 2.9, the minimum return loss decreased when the thickness of DR decrease. Therefore, the minimum return loss values indicated that by reduce the thickness of DR can minimize the return loss during the operation. This suggests that with low value of minimum return loss, this DR has very good efficiency in a telecommunication system. This result also proven that the *f* can be achieved by modified the resonator from many aspect such as thickness, sintering time and dopants.



(a)



(b)



(c)

Figure 2.9: Thickness effect for the DR towards return loss. (a) 2 mm, (b) 2.5 mm (c) 3 mm (Ain et al., 2007)

2.1.3.5 Bandwidth (BW)

BW is a total distance or range between the highest and lowest frequency of acceptable operation and multiplied by 100 and represented by % BW as in Equation 2.3.

$$\% BW = \frac{f_2 - f_1}{f_c} \times 100 \qquad (2.3)$$

Where;

f_1 = lower frequency limit where the magnitude of the spectrum is 10 dB weaker than the strongest frequency component in the whole occupied spectrum.

f_2 = higher frequency limit where the magnitude of the spectrum is 10 dB weaker than the strongest frequency component in the whole occupied spectrum.

f_c = center frequency defined as the averaged between the higher frequency limit and the lower frequency limit divided by 2.

For both higher and lower frequency limits are taken at -10 dB levels. It is because the BW can be accepted when the specific range of the frequencies over which antenna is capable of transmitting and receiving signals above -19 dB relative to the strongest frequency component in the entire spectrum

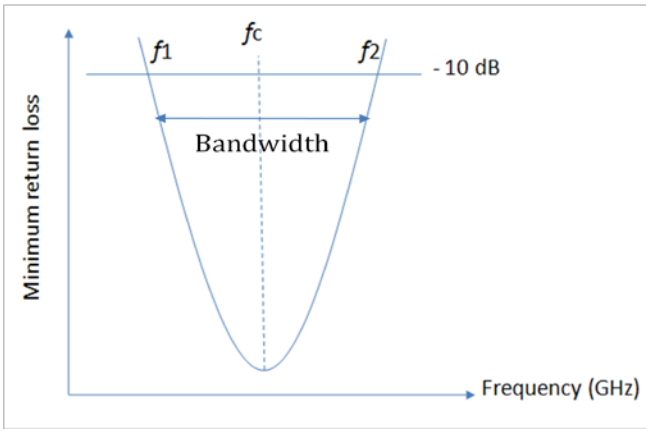


Figure 2.10: Measurement of BW based from the *f*

The resonator BW is depends on the *f*, ε_r, tan δ and the thickness (*d*) of the pellets. But in this research the scope are more in *f* and the ε_r. The BW and ε_r are interrelated; therefore there is always a trade off between them in arriving at optimum dielectric properties for telecommunication applications.

2.2 Perovskite Structure

The structural chemistry of ABO_3 perovskites can be described in terms of close packing of AO_3 layers, where at the B-sites cations occupy 100% of resultant BO_6 oxygen octahedra. The BO_6 octahedra is connected exclusively through corner sharing when the AO_3 layers are arranged in cubic close packing and then, the structure form in a cubic perovskite. In an ideal cubic perovskite, the A and B cations have an equilibrium bond distances to oxygen without any distortion of the unit cell. So, it was classified in the space group Pm3m and the tolerance factor, t = 1 (Long et al., 1983).

As shown in Figure 2.11, the B atoms are at the center of 6 oxygen that are arranged at the corner of a regular octahedron. The octahedra are linked at their corner into a three dimensional simple cubic network, enclosing large holes that are occupied