Influence of Pentavalent Substitution on Dielectric Behavior of Karrooite

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Abstract

$MgTi_2O_5$ (MTO), $MgTi_{1.8}V_{0.16}O_5$ (MTV) and $MgTi_{1.8}Nb_{0.16}O_5$ (MTNb) are prepared using known high temperature solid state reaction technique. Single orthorhombic phase karrooite formation is confirmed by XRD patterns. The pentavalent substitution is observed to enhance the grain size as well as dielectric constant (K') at all frequencies. However, the contribution of interfacial polarization is more in MTNb. The dielectric constant (K') versus temperature curve displays a hysteresis corresponding to order – disorder transition. The MTO shows that the K' is fairly independent of temperature up to 550 K. The loop area is the least for MTNb and makes it more passive. The resistivities measured at 1 kHz and at room temperature are smaller in the pentavalent substituted karrooites. This enhances the PTCR in MTV and MTNb. The materials may be useful as thermistors.

Key words : MTO, MTV, MTNb, dielectric, thermal hysteresis, disorder

Introduction

Karrooite is an end member of the $MgTi_2O_5 – FeTi_2O_5$ (ferropseudobrookite) system and occurs in many volcanic and metamorphic rocks [1]. $MgTi_2O_5$ (karrooite) received much attention during the Apollo mission because of their implications for the cooling histories of lunar basalts . It is natural mineral . It is added in microwave ceramics to improve permittivity, Q factor and thermal stability . Its addition improves both impact resistance and thermal strain and makes the ceramic highly compact, thus avoiding dielectric loss [2]. Therefore it becomes an important constituent of refractory ceramics [3]. It exhibits an unusually large thermal anisotropy [4]. Karrooite ($MgTi_2O_5$) has the pseudobrookite structure with space group Bbmm [5]. A wide range of non-convergent cation distribution/disorder between M1 and M2 sites is responsible for its high temperature stabilization [6]. The cation disorder in addition to composition and structure can also affect the elasticity of the crystalline phase [7].

Niobium exhibits an insulating dielectric oxide with outstanding properties. Nb based oxides have been found to be good candidate for novel dielectric applications. Many of their oxides show excellent microwave dielectric properties. Nb_2O_5 exhibits higher values of relative permittivity. This makes Nb based capacitor promising candidates as new high capacitance devices [8].In ceramic oxides, the grain size and dielectric constant found to be increased with increase in Nb content [9]. It is known that small

addition of V_2O_5 reduces the sintering temperature of many ceramic oxides [10]. Addition of V_2O_5 effectively increases the dielectric properties of many ceramic oxides [11].

The above-mentioned effects of Nb_2O_5 and V_2O_5 prompted us to study the influence of pentavalent substitution on dielectric behavior of karrooite.

Experimental

All the samples are charge balanced and have been synthesized by high temperature solid state reaction technique and are sintered at 1200°C. Several presinterings are given to MTV below the melting point of V_2O_5.

$$MgO + 2TiO_2 \rightarrow MgTi_2O_5 \quad \text{(MTO)}$$
$$MgO + 1.8TiO_2 + 0.08V_2O_5 \rightarrow MgTi_{1.8}V_{0.16}O_5 \quad \text{(MTV)}$$
$$MgO + 1.8TiO_2 + 0.08Nb_2O_5 \rightarrow MgTi_{1.8}Nb_{0.16}O_5 \quad \text{(MTNb)}$$

A microprocessor based JEOL JDX – 8030 X-ray diffractometer was used to determine the XRD data of the samples. The FTIR spectrum was taken to determine the vibrational frequencies of the dipoles at M1 and M2 sites. 'PERKIN – ELMER 683' spectrophotometer was used to determine IR spectra. The dielectric parameters were determined at room temperature in the frequency range 10 kHz and 1000 kHz using an impedance analyzer 'HP-4192'. The dielectric parameters were also measured in the temperature range 300 K and 835 K using 'LCR-Q bridge, Model No. 6018, Scientific' at 1 kHz.

RESULT & DISCUSSION :

Structural properties :

XRD pattern of all samples confirm the single phase karrooite formation with orthorhombic structure. The unit cell volume of MTNb is largest [Table 1] which may be due to larger ionic size of Nb^{+5}. The larger density of MTNb indicates that Nb_2O_5 improves densification whereas V_2O_5 decreases the density which is reflected in MTV (Table 2). The Debye particle size is large enough for mixed metal oxides perhaps due to strain free growth of lattice (very low inhomogeneity) [12]. SEM photographs of all karrooites are reproduced in Figures 1. Very large grain size as well as average particle size of MTV (Table 2) implies the large reduction in the sintering temperature due to V_2O_5 .. Compared to MTO, the average grain size of MTNb is large which shows that Nb enhances the grain size.

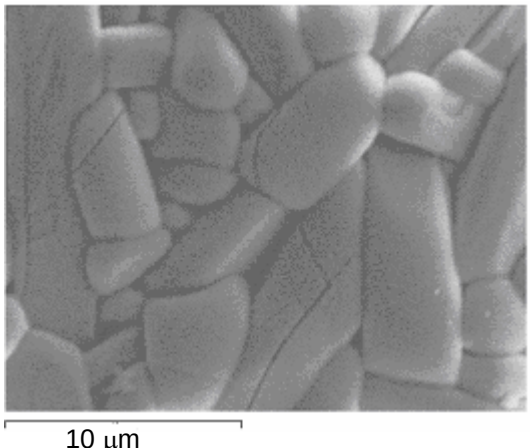

Fig.1 (c) : MTNb

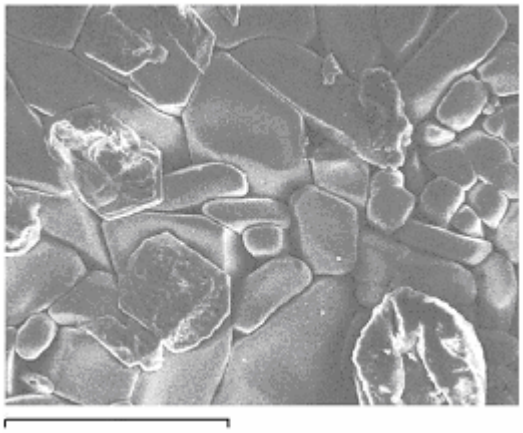

Fig. 1 (b) : MTV

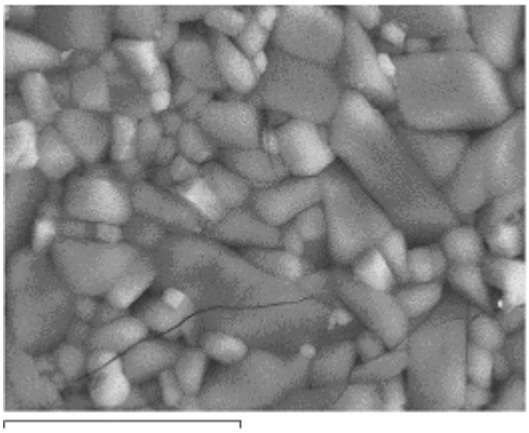

Fig.1 (a) : MTO

Table 1 : Lattice parameters, volume.

Sample	Lattice parameters			Volume (Å)^3
	a (Å)	b (Å)	c (Å)	
MTO	9.716	9.965	3.736	361.8
MTV	9.703	9.968	3.739	361.6
MTNb	9.748	10.043	3.741	366.3

Table 2 Density, porosity, inhomogeneity, average particle size and average grain size of the karrooites.

Sample	Density (g/cm^3)		Pore fraction X 10^{-3}	Inhomo-geneity X 10^{-3}	Average particle size (Å)	Average grain size (μm)
	Expt.	XRD				
MTO	3.49	3.67	49	-3.9	671	1.84
MTV	3.15	3.65	137	-0.8	1310	17.0
MTNb	3.39	3.72	89	-3.5	654	3.78

IR Spectra

The frequencies of FTIR absorption bands are given in Table 3. The bands at around 650 cm^{-1} and 500 cm^{-1} are assigned to octahedral stretching modes [13, 14] corresponding to M1 and M2 sites respectively. It is observed that the IR band separation (ν_1 - ν_2) is large in MTV as shown in Table 3, which indicate more random distribution of cations among M1 and M2 sites resulted from weak correlation between M1 and M2 sites, whereas strong correlation exist in MTNb.

Table 3 IR band frequencies

IR bands	MTO	MTV	MTNb	Possible bond assignment	Site
ν_1 (cm^{-1})	648	714	648	Mg – Ti / Mg – V / Mg – Nb stretching	M1
ν_2 (cm^{-1})	505	510	511	Mg – Ti / Mg – V / Mg – Nb stretching	M2
ν_1 - ν_2	143	204	137		

Dielectric properties

In order to determine exact nature of polarization in the karrooites, the measurement of capacitance as a function of temperature are carried out in the temperature range from 300 K to 838 K using two probe method. The optimum pressure is applied to the ceramics as they are found to be pressure sensitive. It is observed that the dielectric constant is observed to be fairly constant with temperature up to 550 K, at 1 kHz in MTO than the other samples as shown in Fig. 2.

The plots of heating and cooling cycles of dielectric constant (K') versus absolute temperature above 550 K are reproduced in Figures 3 (a), (b) and (c). The dielectric constant (K') increases rapidly for all samples but the rise is large in MTO and least in MTNb. It is measured in terms of temperature coefficient of dielectric constant (K_T'). It is interesting to note that each sample show a distinct loop, which is attributed to change in cation distribution among M1 and M2 octahedra which is temperature dependent . The transition temperature (see Table 4) at which K' starts rising rapidly, which is attributed to commencement of order disorder transition is the highest in MTV (Table 4) which may be due to the weak correlation between M1 and M2 sites. The low temperature coefficient of dielectric constant (K'_T) and loop area of MTNb (refer Table 4) shows more passive nature, which is due to strong correlation between M1 and M2 octahedral.

Table 4 Loop area, Temperature coefficient of dielectric constant and Transition temperature

Sample	Loop area (Energy dissipation)	$K'_T \times 10^{-2}$ near transition temp. (/°K)	Transition Temp. (K)
MTO	37964	4.12	713
MTV	17856	5.88	743
MTNb	5348	1.12	605

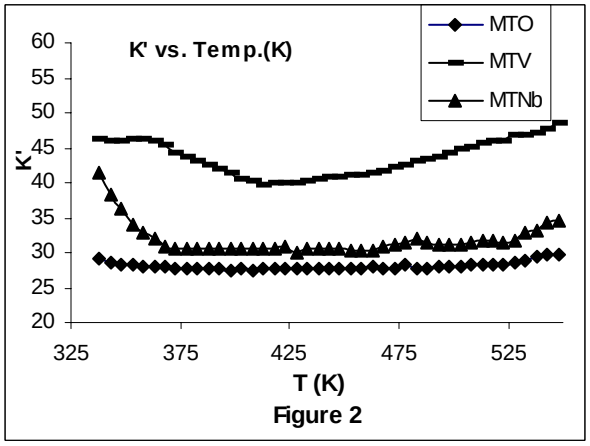

Figure 2

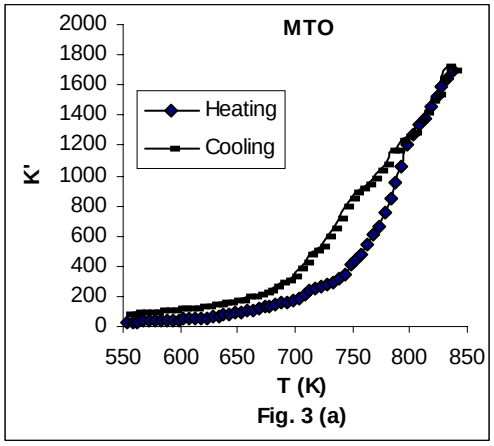

Fig. 3 (a)

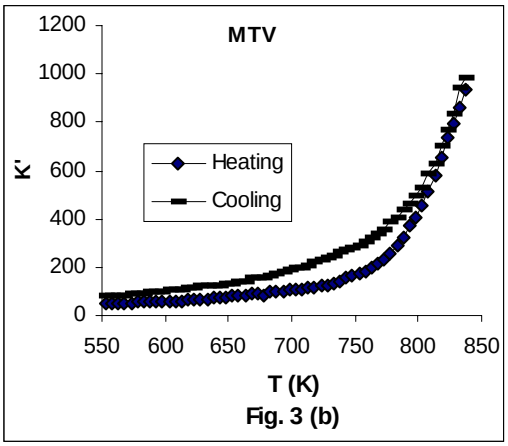

Fig. 3 (b)

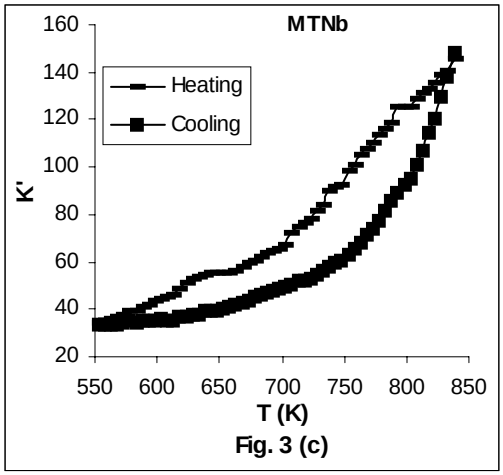

Fig. 3 (c)

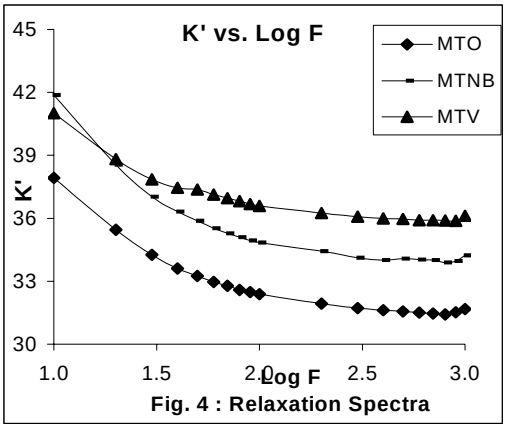

Fig. 4 : Relaxation Spectra

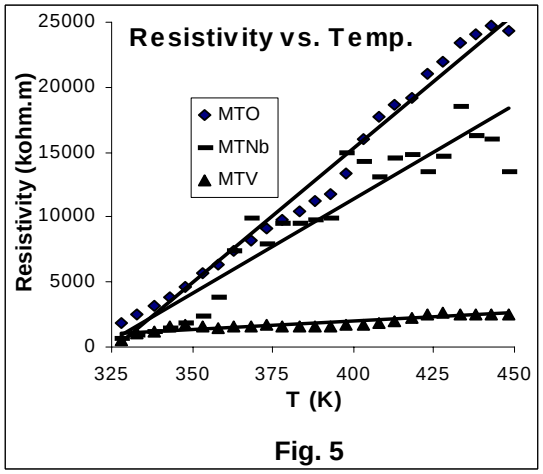

Fig. 5

The presence of space charge in the family of pseudobrookite prompted us to study their relaxation spectra. The relaxation spectra of these samples at room temperature are investigated between frequency range 10 kHz and 1000 kHz. The plots of dielectric constant (K') versus Log f is shown in Fig 4. The dielectric constant (K') of pentavalent substituted samples is observed to be higher than MTO in

the frequency range from 10 kHz to 1000 kHz. In comparison, MTNb appears to be good relaxor like material as interfacial / space charge polarization is larger. The concentration of Nb at the surface of TiO_2 particles is reported to be higher than that of bulk [15]. This is likely also in MTNb. This will increase the number of interfaces between dielectric layers in MTNb, resulting in larger interfacial polarization. The interfacial polarization is less in MTV than MTNb.

Electrical properties

The ac and dc resistivities (ρ_{ac} and ρ_{dc}) of all samples at room temperatures are listed in Table 5. The MTV and MTNb shows higher d.c. resisitivities which may be due to larger grain size.

The increase of resistivity with temperature shows PTCR effect in all karrooites as shown in Fig. 5. The smaller a.c. resistivities enhance the magnitude of PTCR ($PTCR_c$) in MTV and MTNb [Table 5]. It is attributed to recombination of electron - holes and impurity (disorder) scattering of M1 and M2 sites. Due to prominent PTCR effect, MTV and MTNb may be developed into thermistors.

Table 5 Resistivity, band gap, temperature coefficient of resisitivity and pressure coefficient of dielectric constant.

Sample	ρ_{ac} (kΩ.m) at room temp.	ρ_{dc} (kΩ.m) at room temp	$PTCR_c$ (/°K)	ac/b	K'_p (/Mpa) at room temp	K'_{gas} (/atm.) at room temp
MTO	2958	4280	0.0536	3.643	1.79	0.385
MTV	117	6908	0.1524	3.639	1.27	1.513
MTNb	422	5262	0.358	3.631	0.76	0.175

Conclusion

Pentavalent substitution enhances the grain size as well as dielectric constant (K') at all frequencies. The dielectric constant (K') versus temperature curve displays a hysteresis corresponding to order – disorder transition. The resistivities measured at 1 kHz and at room temperature are smaller in the pentavalent substituted karrooites. This enhances the PTCR in MTV and MTNb. The materials may be useful as thermistors..

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