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Raman and Structural Characterization of Spinel Compound $Zn_{8/5}Al_{4/15}TiO_4$

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Microwave dielectric materials have been attracted enormous attention for their application in microwave communication. A new microwave dielectric material with composition $Zn_{8/5}Al_{4/15}TiO_4$ was synthesized by conventional solid-state reaction method. The structure of $Zn_{8/5}Al_{4/15}TiO_4$ was refined with the cubic $P4_332$ space group (number of formula unit per unit cell, Z = 4). The Rietveld refinement study revealed the theoretical density $\rho = 4.80$ g/cm^3 and lattice parameter a = 8.405 Å. This compound was crystallized in cubic spinel structure and 1:3 ordering was observed on the octahedral sites. Raman spectrum of the compound was collected at room temperature. Theoretical Factor group analysis for this compound predicts 40 Raman modes and 22 IR modes. However, experimentally 13 vibrational modes have been observed in the Raman spectrum which can be separated into internal TiO_6 vibration and external rotation and translation TiO_6 modes. Raman modes in the range of 500-800 cm^{-1} are assigned to internal vibrational modes.

Keywords: X-ray Diffraction; Rietveld refinement; Spinel structure; Raman spectroscopy

1 Introduction

Rapid growing communication has led to development of low cost and powerful microwave devices[1-3]. Low temperature co-fired ceramic (LTCC) technology has emerged as the dominant technology for the production of such types of economic microwave devices. For LTCC technology, the material should possess high quality factor (low dielectric loss), low dielectric constant, temperature stability of dielectric properties, high thermal conductivity and low coefficient of thermal expansion. In addition, ceramic material should be chemically compatible with the electrode material such as silver and its sintering temperature must be less than the melting point of electrode material. Development of microwave devices remains under huge manufacturing difficulties due to unavailability of low-cost materials with appropriate properties. Titanates are always being the great interest due to their good microwave dielectric properties. There are many titanates dielectric materials have been developed for microwave communication application such as $BaTi_4O_9$, $Zr_{0.8}Sn_{0.2}TiO_4$[4,5]. Zinc containing compounds have been also focused due to their low sintering temperature and good microwave dielectric materials[6]. There are very less reports on ZnO-Al_2O_3-TiO_2 system[7]. Investigation on the perovskite compounds revealed that the cation ordering has great influence on the quality factor at microwave frequency[8,9]. But this is not clearly understood in the spinel compounds. Therefore, In order to study the effect of cation ordering on properties, we have synthesized the new compound of ZnO-Al_2O_3-TiO_2 system.

This paper describes a crystallographic study of $Zn_{8/5}Al_{4/15}TiO_4$ compound by Rietveld refinement using powder X-ray diffraction. Raman spectrum of this compound is also analyzed on the basis of crystal structure with the help of factor group analysis.

2 Experimental

The polycrystalline $Zn_{8/5}Al_{4/15}TiO_4$was synthesized by solid state reaction method using highly pure reagents ZnO (99.9%), Al_2O_3(99.9%) and TiO_2(99.9%) from Alfa Aesar. These reagents were mixed with a stoichiometric ratio and ground for proper mixing. These mixed powders were calcined at 1200 °C for 4h and again ground for making fine powder. X-ray diffraction pattern of this calcined powder was obtained for phase confirmation using Philips PANalytical X'pert Pro diffractometer (Almedo, Netherlands). The powder X-ray diffraction data was collected at room temperature by using CuKα (λ=1.5406 Å) source in the range of 10-120° with step size of 0.016° for Rietveld refinement. The XRD data of this compound was analyzed using GSAS suite with EXPGUI[10,11] to obtain crystal

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system, atomic positions and cation arrangements. Raman spectrum was recorded in 100-900 cm^{-1} range using HORIBA Jobin Yvon's LabRAM800HR spectrometer at room temperature. The instrument was equipped with the He-Ne laser (632.8 nm) and CCD cooled detector in back scattered geometry. The measurements were carried out using power 7.5mW for 2 second with 100× objective lens and 600 grooves/mm grating.

3 Results and Discussion

3.1 Crystal Structure

The compounds with spinel structure have been well studied. The ideal spinel compounds having general formula AB_2O_4 and cubic closed packed array of oxide anions[12]. There are 96 interstitials between anions in cubic unit cell whereas only 24 are occupied by cations, one fourth of 64 tetrahedral sites and half of 32 octahedral sites. On the basis of cation distribution, these spinels are two types- normal spinel and complex spinel. In normal spinel A is occupied at tetrahedral site whereas B in octahedral site. In complex spinel, the tetrahedral and octahedral sites are occupied by more than one type of cations[13]. The cation distributions were only partial understood on the basis of ionic bonding and were affected by individual preference site of cations. The crystal structure and lattice vibrations of ternary spinel compounds are not well understood. Therefore, we have synthesized a ternary compound of ZnO-TiO_2-Al_2O_3 system using solid state reaction method.

Figure 1 shows the Rietveld refinement plot of $Zn_{8/5}Al_{4/15}TiO_4$ compound and goodness of fit of the XRD pattern. This graph clearly indicates good quality fitting pattern and the Rietveld discrepancy parameters R_p, $_wR_p < 3\%$ and χ^2 ~2.7 also reflect the relatively good refinement. The XRD pattern was refined with cubic crystal system with $P4_332$ space group (number of formula unit per unit cell, Z = 4). Rietveld refinement was carried out for several cation distribution models, to examine the detailed occupancy of cation sites. The theoretical density and lattice parameter are $\rho = 4.80$ g/$cm^3$and a = 8.405 Å respectively. The refined atomic positions and thermal parameters of $Zn_{8/5}Al_{4/15}TiO_4$ are given in Table. 1. Refinement reveals that Al^{3+} is occupied at octahedral (4b) and Zn^{2+} at tetrahedral (8c) whereas Ti^{4+} is occupied at octahedral (12d). Oxygen anions are situated at 8c and 24e sites.

The bond lengths for $Zn_{8/5}Al_{4/15}TiO_4$ compound are given in the Table. 2. The symmetry indicated that all Al-O bonds were of equal length. Zinc ions at the tetrahedral sites (C_3) are bonded with the two oxygen O1 and three O2 ions in a distorted tetrahedron. The other Ti^{4+} at the octahedral site (D_3) is connected to two O1 ion and four O2 ions in a distorted octahedron. The octahedra were connected through the edge sharing with other octahedra whereas tetrahedral with corner sharing.

In the ideal spinel AB_2O_4 with Fd-3m space group, there are two atomic positions 8a and 16d for cations whereas only one site (32e) is for anion. Ordered

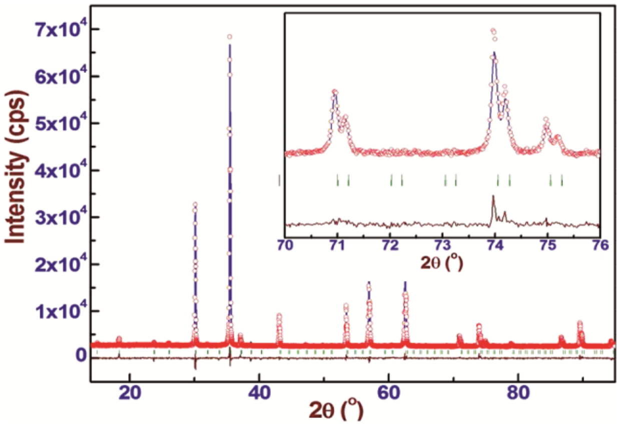

Fig. 1 — Rietveld refinement plot of the $Zn_{8/5}Al_{4/15}TiO_4$ compound.

Table 2 — Bond lengths (in Å) for $Zn_{8/5}Al_{4/15}TiO_4$ compound from XRD data.

Atom	Zn	Al	Ti
O1	2.0531×(1)	-	1.9830×(2)
O2	1.9258×(3)	1.9426×(6)	2.1570×(2) 2.0381×(2)

Table 1 — Refined atomic positions and thermal parameters of $Zn_{8/5}Al_{4/15}TiO_4$ compound.

	Site	x	y	z	Occupancy	U_{iso} (Å^3)
Zn	8c	0.9999(2)	0.9999(2)	0.9999(2)	1	0.0101
Al	4b	0.6250(0)	0.6250(0)	0.6250(0)	1	0.0100
Ti	12d	0.1250(0)	0.3738(2)	0.8760(2)	1	0.0009
O1	8c	0.3910(6)	0.3910(6)	0.3910(6)	1	0.0100
O2	24e	0.1318(5)	0.1058(4)	0.3832(6)	1	0.0100

cubic spinel with $P4_332$ space group, exists with 1:3 cation ordering on octahedral sites. This 1:3 ordering splits the 16d octahedral site into 4b and 12d octahedral sites and 32e oxygen site into 8c and 24e sites. Fig. 2 shows the arrangement of polyhedra of cations in this compound. The ZnO_4 tetrahedra around the 8c site are indicated in saddle brown, the AlO_6 octahedra (4b) in yellow and the TiO_6 octahedra (12d) in blue. This figure clearly indicates the 1:3 ordering of the octahedra of Al and Ti in the [110] direction.

Similarly, we saw 1:3 ordering in the [210] and [211] directions. Indexing of XRD pattern of $Zn_{8/5}Al_{4/15}TiO_4$ compound with $P4_332$ in black whereas Fd-3m in green (extra peaks), is shown in the Fig. 3. Since mixing of indices is forbidden for face centre crystal systems, the reflections (110), (210) and (211) are not possible in the normal spinel (Fd-3m). But these extra peaks are possible to index with new hkl indices ¼(440), ¼(840) and ¼(844) in Fd-3m space group. Therefore, it is clear that the extra peaks (110), (210) and (211) are arising due to 1: 3 ordering of the Al^{3+} and Ti^{4+}on octahedral sites.

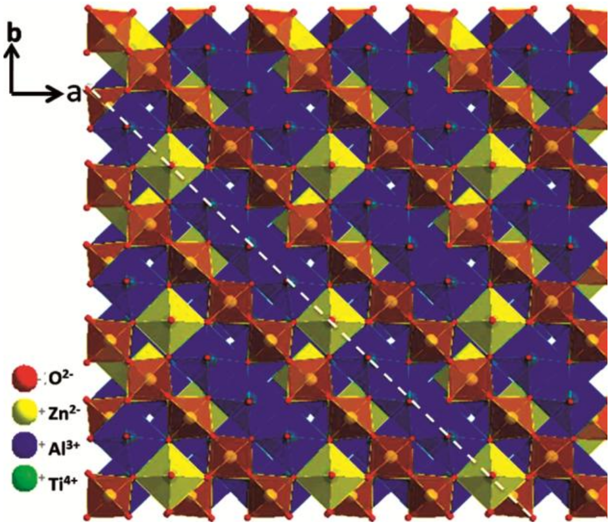

Fig. 2 — Representation of the spinel structure of $Zn_{8/5}Al_{4/15}TiO_4$ compound with 1:3 cation ordering, space group $P4_332$.

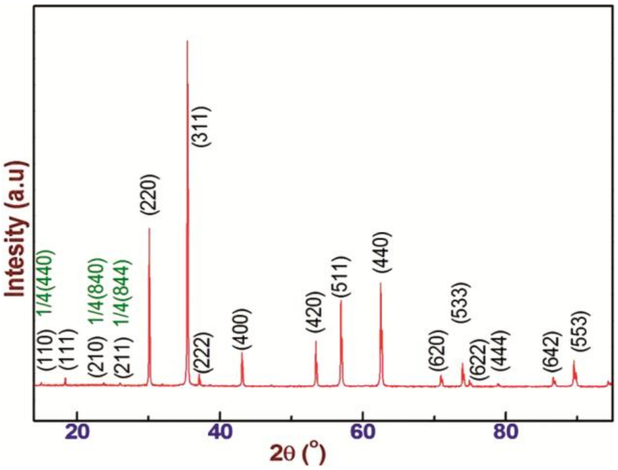

Fig. 3 — XRD pattern of the $Zn_{8/5}Al_{4/15}TiO_4$ compound and indexing of XRD reflections with $P4_332$ space group and Fd-3m.

3.2 Raman Spectroscopy

X-ray diffraction (XRD) has been developed into a standard method of determining structure of solids in inorganic systems. Compared to XRD, Raman is very sensitive tool for local structural analysis of the powder and thin films[14,15]. Raman spectrum of the $Zn_{8/5}Al_{4/15}TiO_4$ compound and it's fitting with lorentzian modes are shown in the Fig. 4. The experimental data are in solid dots and final fitting (blue line in Fig. 4) was obtained through a sum of 20 lorentzian lines (red line in the Fig. 4).

Theoretical group theory analysis of the $Zn_{8/5}Al_{4/15}TiO_4$ compound predicts 40 Raman modes and 22 IR modes which are given in the Table. 3.

Table 3 — Normal mode vibration of the $Zn_{8/5}Al_{4/15}TiO_4$ compound.

	Site	Normal modes
Zn	8c	A_1 (R)+ A_2 (I) + 2E(R) + $3T_1$(IR) + $3T_2$(R)
Al	4b	A_2 (I) + E(R) + $2T_1$(IR) + T_2(R)
Ti	12d	A_1 (R) + $2A_2$ (I) + 3E (R) + $5T_1$(IR) + $4T_2$(R)
O1	8c	A_1 (R) + A_2 (I) + 2E (R) + $3T_1$(IR) + $3T_2$(R)
O2	24e	$3A_1$ (R) + $3A_2$ (I) + 6E (R) + $9T_1$(IR) + $9T_2$(R)
Total Normal Modes	$6A_1$ (R) + $8A_2$ (I) + 14E (R) + $22T_1$(IR) + $20T_2$(R)	

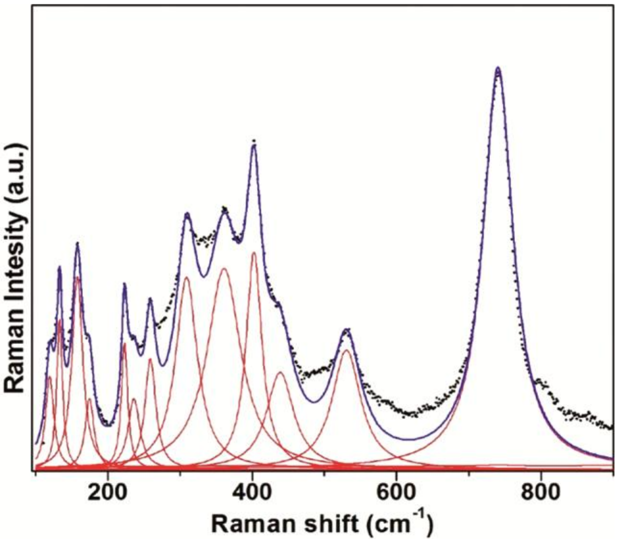

Fig. 4 — Raman spectra of the compound and its deconvolution.

Table 4 — Internal vibration of $(TiO_6)^{4-}$ Octahedra.

Free $(TiO_6)^{4-}$ (O_h)	Site symmetry (D_3)	Factor Group (O)
ν_1 (A_{1g})	A_1	A_1 (R)+ A_2 (I)+ E (R)
ν_2 (E_g)	E	E (R) + T_1 (IR) + T_2(R)
ν_3 (T_{1u})	A_2 + E	E (R) + $2T_1$ (IR)+ $2T_2$(R)
ν_4 (T_{1u})	A_2 + E	E (R) + $2T_1$ (IR)+ $2T_2$(R)
ν_5 (T_{2g})	A_1 + E	A_1 (R) + A_2 (I) +2E (R) + T_1 (IR)+ T_2(R)
Total internal vibrations	$2A_1$ (R) + $2A_2$ (I) + 6E (R) + $6T_1$ (IR)+ $6T_2$(R)	

Raman spectroscopy predicted 13 modes, which can be separated into internal TiO_6 vibration and external rotation and translation TiO_6 modes. All internal modes are found in the range of 500-800 cm^{-1}, where as the external modes arise at lower frequencies below 500 cm^{-1}.The compound having the $P4_332$ (O^6) space group, confirmed from XRD pattern, implies inversion center is the subgroup. As we know that if any compounds having the inversion center, all Raman active modes are IR inactive and vice versa, which can be clearly seen in Table. 3. To analyze the internal modes, site to factor group correlation analysis has been done for TiO_6. The free ion TiO_6 octahedral with O_h symmetry has six fundamental modes of vibration. These fundamental modes are symmetric stretching mode ν_1 (A_{1g}), asymmetric stretching modes ν_2 (E_g) and ν_3 (T_{1u}), asymmetric bending mode ν_4 (T_{1u}), symmetric bending ν_5 (T_{2g}) and the Raman and IR inactive mode ν_6 (T_{2u}). The ν_1, ν_2 and ν_5 modes are Raman active, whereas the ν_3 and ν_4 modes are IR active. The O_h is the highest symmetry space group and many subgroups originate by descent in symmetry. A loss of the symmetry could be arising due to lattice defects or ordering of the cations on their sites. In this compound, the loss of symmetry (space group changed from O_h to O^6) has happened due to 1:3 ordering of cation at octahedral sites. The $P4_332$ (O^6) space group having four subgroup $D_3(4)$, $C_3(8)$, $C_2(12)$ and $C_1(12)$. The $D_3(4)$ is site symmetry of the compound due to following two reasons (1) D_3 is the subgroup of both the space group O^6 of the crystal and molecular point group (O_h) of the isolated $(TiO_6)^{4-}$ octahedra, and (2) the number of the equivalent sites is 4 which is equal to the number of molecules in the unit cell (Z=4)[16]. Finally we carried out the group theoretical analysis with this site symmetry in factor group O and obtained irreducible representation are summarized in the Table. 4. This Table clearly indicates the 16 Raman modes ($2A_1$+ 8E + $6T_2$), 6 IR modes ($6T_1$) and 2 Inactive modes ($2A_2$) due to internal vibration of TiO_6.

In the Raman spectra only 2 of the 14 mode of internal vibration are identified whereas other modes are not able to identify due to its weak scattering intensity of mode. A_1 mode at 740.5 cm^{-1} is similar to the A_g mode in the normal spinel and is the uniform breathing of the ZnO_4 tetrahedra while the cation sublattice is at rest. The mode arising at 530.6 cm^{-1}, is due to T_2/E vibrations.

4 Conclusions

The $Zn_{8/5}Al_{4/15}TiO_4$ compound was prepared by conventional solid state reaction. The crystal structure was determined using Rietveld refinement and it possesses the cubic crystal system with $P4_332$ space group. The Al^{3+} and Ti^{4+} ions are occupied at octahedral sites (4b) and octahedral sites (12d), respectively and 1:3 ordering is observed at octahedral sites. Zn^{2+} ions are situated at tetrahedral sites and oxygen ions at 8c and 24e sites. The internal vibration of TiO_6 is analyzed using factor group analysis and Raman modes at 740.5 cm^{-1} and 530.6 cm^{-1} are due to A_1 and T_2/E vibrations respectively.

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