

## Research Article

# Spectroscopic Study of $\text{Al}^{3+}$ -Substituted Strontium Hexaferrite

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The substituted Y type hexaferrites  $\text{Sr}_2\text{Zn}_2\text{Al}_x\text{Fe}_{12-x}\text{O}_{22}$  (where  $x = 2, 4, 6, 10$ ) are prepared by standard ceramic technique. The infrared absorption spectra of the prepared compounds are studied in the range  $400\text{ cm}^{-1}$  to  $4600\text{ cm}^{-1}$ . These spectra are used to locate the vibrational ranges due to substituted cations with the nearest oxygen layers and also to understand the band positions attributed to the lattice sites. The absorption regions found around  $460\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$  are the common features of all spinel ferrites. Both X-ray and IR spectroscopic studies in these ferrites do not detect the presence of  $\text{Fe}^{2+}$ . Also with increase in aluminium substitution, the higher frequency bands start disappearing. This may be due to reduced vibrations of trivalent cations Fe–O bonds at both octahedral and tetrahedral sites which in turn affect  $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$  superexchange interactions present in the structure.

## 1. Introduction

Infrared spectroscopy is the most powerful technique for the chemical identification of crystal structure. It provides useful information about the structure of molecules without tiresome evaluation methods, which are applied in other usual methods of structural analysis such as X-ray diffraction and neutron diffraction. With the absorption of infrared radiations, the molecules of the chemical substance vibrate at many rates of vibration, giving rise to close packed absorption bands. Thus such infrared spectra give the vibrational behavior of the crystal structure. It is interesting to note here that till date much less effort has been taken in studying the vibrational spectrum of the ferrites. In that, most of the work is concentrated on spinel ferrites [1–3]. Infrared spectral analysis has been carried out for several ferrites by Waldron in 1955, who reported two absorption bands within the wave numbers  $200\text{--}800\text{ cm}^{-1}$ , which are attributed to the tetrahedral and octahedral complexes of the spinel structure. Cr substituted Ni spinel ferrite is also studied [4] and authors attributed the existence of fine structure to the Jahn-Teller effect.  $\text{Gd}^{3+}$  substituted Cd-Ca spinel ferrite [5] and  $\text{Nd}^{3+}$  substituted Zn-Mg spinel ferrite [6] are also studied by using infrared absorption spectroscopy. Thus it is clear that as far as

the hexaferrite is concerned, no previous infrared studies of these materials were found in the literature with the exception of the reflection spectrum of  $\text{Ba}_2\text{-Y}$  type [7],  $\text{Sr}_2\text{-Y}$  with divalent substitution [8], and absorption spectra of Ba-M type ferrite [9].

In the present paper, the results regarding the infrared absorption spectral analysis of four hexagonal ferrites with general chemical formula  $\text{Sr}_2\text{Zn}_2\text{Al}_x\text{Fe}_{12-x}\text{O}_{22}$  ( $x = 2$  to 10) are discussed. The efforts are taken to find out the effect of less massive, nonmagnetic aluminum substitution in the Sr-Y type hexagonal ferrite using spectroscopic studies.

## 2. Experimental

The system of polycrystalline samples  $\text{Sr}_2\text{Zn}_2\text{Al}_x\text{Fe}_{12-x}\text{O}_{22}$  ( $x = 2$  to 10) was prepared by standard ceramic technique. The analar grade reactants  $\text{SrCO}_3$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  are mixed in the proper molar ratio and ground in the agate mortar for about 7 hours using acetone to achieve uniform grain size and homogeneity. With polyvinyl acetate as a binder and by applying a pressure of 10 tones psi for 5 to 7 minutes, pellets were prepared. These pellets are slowly heated in the furnace at  $600^\circ\text{C}$  for about 6 hours to remove

TABLE I: Lattice sites present in the Y type hexaferrite structure.

Position	Block	Coordinates	No. of ions per unit cell
6c <sub>iv</sub>	S	Tetrahedral	6
3b <sub>vi</sub>	S	Octahedral	3
18h <sub>vi</sub>	S-T	Octahedral	18
6c <sub>vi</sub>	T	Octahedral	6
6c <sub>iv*</sub>	T	Tetrahedral	6
3a <sub>vi</sub>	T	Octahedral	3

the binder [10] and fired at 1200°C, sintering temperature for 120 hours. The samples then cooled at a rate of 20°C per hour up to 1100°C and then at a rate of 60°C per hour up to 500°C. Later on, the furnace is cooled at room temperature in natural way. The pellets are then finely powdered and sieved through fine sieve. To confirm the completion of the solid state reaction, the compositions were subjected to characterization by X-ray diffraction.

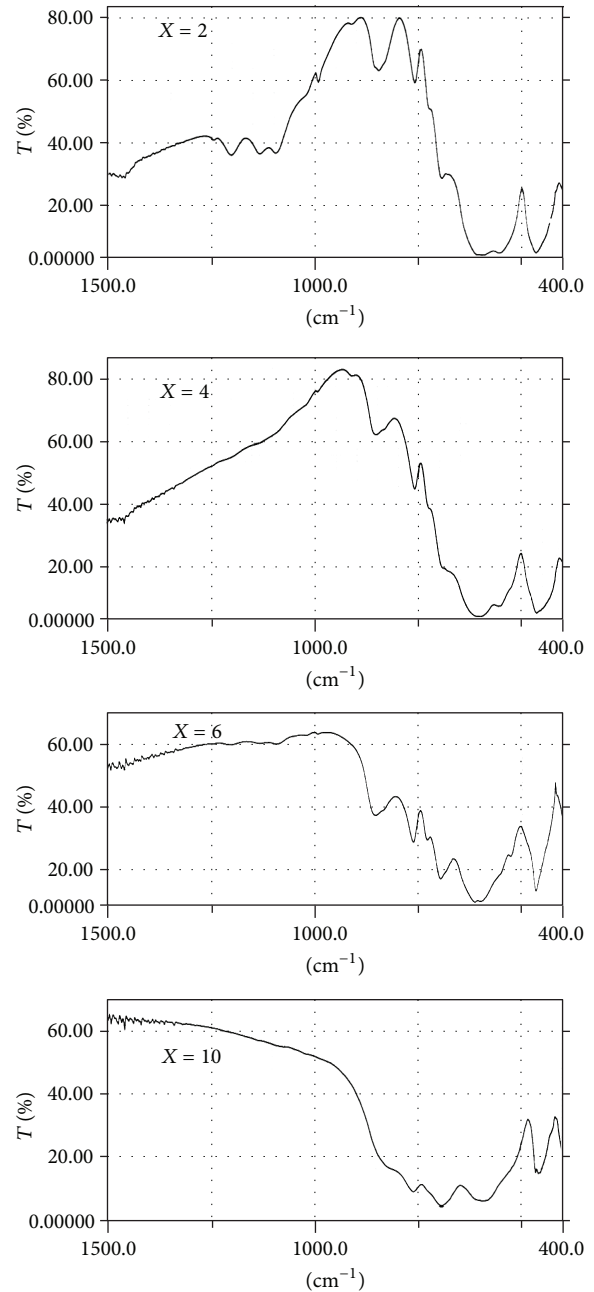
For infrared studies, the technique used by Mazen et al. [11] is applied to the sample preparation. Nearly 2 mg of ferrite powdered is mixed with powdered KBr in the ratio 1:100 by weighing to ensure uniform dispersion. The mixed powder is then pressed in a die of 12 mm diameter and thickness about 1 mm by applying a pressure of 10 tones per square inch for about 5 minutes. The spectra were recorded on Infrared Spectrophotometer model FTIR-8001 with resolution 4.0 cm<sup>-1</sup> in the region of 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

### 3. Results and Discussion

X-ray diffractograms of powdered compounds under investigation reveal the formation of single phase hexagonal Y type phase, showing well-defined reflections of allowed planes. The results regarding X-ray analysis are reported elsewhere [12].

The infrared spectra of the prepared Al<sup>3+</sup> substituted Sr-Y ferrite compounds are recorded in the range 400 cm<sup>-1</sup> to 4600 cm<sup>-1</sup>. The spectra are shown in Figure 1. In the spectra, no absorption bands were present above 1250 cm<sup>-1</sup> except the band at 3460 cm<sup>-1</sup> from the OH group of the moisture present (always) in the sample, which is the major disadvantage of the pressed pellet technique used in the infrared spectroscopy [13]. The spectra of all the aluminium substituted Sr-Y type ferrite are used to locate the band positions, which are shown in Table 2.

The Y type hexagonal ferrite, namely, Ba<sub>2</sub>Zn<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>, has alternate stacking of the spinel S and hexagonal T block along hexagonal *c* axis as (TS)'|(TS)(TS)'(TS)''|(TS) where the prime means that the corresponding block is rotated 120° around the *c* axis. The space group is R $\bar{3}m$  [14]. Here the cations occupy six different tetrahedral and octahedral sites present in the structure in different blocks S and T, respectively, as shown in Table I. We tried to throw some light on the I. R. spectra of such compounds and showed that the vibration frequencies are below 1250 cm<sup>-1</sup> [8]. In the substituted Y type ferrite, the divalent Zn<sup>2+</sup> cations and two

FIGURE 1: Infrared absorption spectra of Sr<sub>2</sub>Zn<sub>2</sub>Al<sub>x</sub>Fe<sub>12-x</sub>O<sub>22</sub> series.

Fe<sup>3+</sup> ions are statistically distributed among the tetrahedral 6c positions of the spinel and hexagonal blocks and the remaining 10 Fe<sup>3+</sup> ions occupy 3a and 6c positions on the T block, 3b site in the S blocks while 18h on the T-S block boundaries [15]. Now with the replacement of Fe<sup>3+</sup> ions by Al<sup>3+</sup> ions, aluminium is distributed among the 3b, 18h, and 6c octahedral positions in the whole complex structure [16].

As mentioned in Introduction, very few efforts are taken for spectroscopic measurements of hexaferrites, so we tried to interpret the infrared spectra of our prepared hexaferrite samples in the shade of spinel ferrites. This is owing to the following.

TABLE 2: Infrared absorption bands in the  $\text{Sr}_2\text{Zn}_2\text{Al}_x\text{Fe}_{12-x}\text{O}_{22}$  system.

Compound	Infrared absorption bands (in $\text{cm}^{-1}$ )							
$\text{Sr}_2\text{Zn}_2\text{Al}_2\text{Fe}_{10}\text{O}_{22}$	1202.8	1089	994.3	848.7	759.2	694.9	601.8	464.3
$\text{Sr}_2\text{Zn}_2\text{Al}_4\text{Fe}_8\text{O}_{22}$	—	—	994.3	852.4	759.2	694.9	604.0	464.3
$\text{Sr}_2\text{Zn}_2\text{Al}_6\text{Fe}_6\text{O}_{22}$	—	—	—	852.4	759.2	964.9	612.9	464.3
$\text{Sr}_2\text{Zn}_2\text{Al}_{10}\text{Fe}_2\text{O}_{22}$	—	—	—	—	759.2	690.5	590.7	459.4

- (1) Lot of work has been done on spectroscopic study of spinel ferrites.
- (2) Spinel infrared study has been started with rhombohedral primitive cell by Waldron in 1955 where Y type hexaferrite is rhombohedral itself.
- (3) Y type hexagonal ferrite already consists of spinel block alternately stacked with T block along  $c$  axis.
- (4) In both the ferrites, only tetrahedral and octahedral sites are present.

From Figure 1, in Y type hexagonal ferrite compounds, the absorption frequency bands are in the region as follows: the low frequency bands are at  $(462 \pm 3) \text{ cm}^{-1}$ , and the medium frequency bands are at  $(600 \pm 12) \text{ cm}^{-1}$ ,  $(692 \pm 2) \text{ cm}^{-1}$  and  $759.2 \text{ cm}^{-1}$ , respectively, while the higher frequency absorption bands are observed at  $(850 \pm 2) \text{ cm}^{-1}$ ,  $1089 \text{ cm}^{-1}$  and  $1202.8 \text{ cm}^{-1}$ , respectively.

As far as the interpretation of the low frequency bands and the first element in the medium frequency is concerned, from the literature reported data, Waldron [1] and Hafner [17] attributed the low frequency band around  $400 \text{ cm}^{-1}$  to the stretching vibrations of octahedral complexes while the band around  $600 \text{ cm}^{-1}$  to the intrinsic vibrations of tetrahedral complexes in the spinel structure as these absorption ranges are the common features of all spinel ferrites. For these bands, Tarte and coworkers [3, 18] observed that this attribution is true only when tetrahedral cation is of higher valence than octahedral cation. In the present work, Tarte's assumption feels true, so here the absorption at  $(462 \pm 3) \text{ cm}^{-1}$  is assigned to the stretching vibrations of the tetrahedral complexes in spinel blocks. The intensity of this band decreases slowly with decrease in  $\text{Fe}^{3+}$  concentration, which indicates the decrease in the occupancy of the iron cations at tetrahedral sites in S blocks. Also the absorption band at  $(600 \pm 12) \text{ cm}^{-1}$  is attributed to the stretching vibrations of the octahedral group in spinel blocks. The broadness of this band decreases with decrease in magnetic substitutions, so this may be the effect of magnetic substitutions in the vibrations. Splitting is observed at higher frequency side near to  $(692 \pm 2) \text{ cm}^{-1}$ . The increase in significance of this absorption band may be attributed to the presence of aluminium vibration at octahedral sites in T-S block boundaries.

In a crystal, the cation-oxygen vibration frequencies depend on the mass of the cations, the cation oxygen bonding force, distance related to cation electronic structure, ionic radius and chemical nature of the neighboring cations, and also on the unit cell parameters [19]. Thus as the aluminium has less atomic mass (atomic weight 26.982) compared to

iron (atomic weight 55.847) and also less ionic radius of the  $\text{Al}^{3+}$  cation, the cell volume as well as bond strength Al–O decreases with  $\text{Al}^{3+}$  substitution. This weakening of the bond strength increases the vibrations of the octahedral aluminium cations at  $759.2 \text{ cm}^{-1}$  in both S and T blocks. This band is sharp and more significant. The increase in the intensity may be due to occupancy of  $\text{Al}^{3+}$  cation on the octahedral sites in both S and T blocks of the whole complex Y structure.

Towards higher frequency side in the absorption spectra of Sr-Y type hexaferrite, it is observed that with the dilution of  $\text{Fe}^{3+}$  by  $\text{Al}^{3+}$ , the absorption bands gradually start disappearing. These higher frequency absorption bands are assigned to the vibrations of octahedral and tetrahedral substitutions of the metallic cation  $\text{Fe}^{3+}$  with oxygen layer. By replacing trivalent Fe cation by less massive trivalent Al cation, the contribution of Fe–O vibrations decreases. Thus the disappearance of the higher frequency bands is attributed to the decrease of Fe cations with decrease in Fe–O vibrations in the whole complex structure.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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