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SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED CALCIUM HEXAFERRITES BY AUTOCOMBUSTION METHOD

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Abstract
The series of aluminium ions substituted calcium hexaferrite with composition $Ca_2Zn_2Fe_{12-x}Al_xO_{22}$ ($0 \le x \le 1$) were synthesized by sol-gel auto-combustion method. The X-ray diffraction pattern at room temperature showed the prepared samples have a single Y-type hexagonal ferrite phase and the effect of aluminium ions substitution on the unit cell parameters, density and porosity has been studied. The acoustic properties of the substituted calcium hexaferrite have been investigated by ultrasonic pulse technique. The acoustic studies indicate that the increase in elastic modulii with Al^{3+} ions concentration weaken the inter-atomic bonding between various atoms in the substituted calcium hexaferrite.

Key words: Y-type hexagonal ferrite, Acoustic properties, Sol-gel auto-combustion method.

1. Introduction

In order to improve the mechanical properties of ceramic materials it is essential to understand the relationship between porosity and its elastic behavior. The measured elastic moduli do not have much significance unless they are corrected to zero porosity. In engineering practice, the elastic constants often used are the Young's modulus, rigidity modulus and Poisson's ratio. The elastic constants are related to inter-atomic forces, co-ordination changes, etc. and also the impact shock, fracture and crack growth [1]. For porous materials like ceramics and most composites, the relation between elastic moduli and velocity are complex. Elastic moduli in these materials are function of pore size, shape and orientation. The other microstructural factors such as grain shape, grain boundaries, texture and precipitates have pronounced effect on the relation between elastic moduli and velocity [2-3].

In current research, the samples of Y-type aluminium substituted calcium hexaferrite have been synthesized by sol-gel auto-combustion method. The effect of substitution of Al^{3+} ion for Fe^{3+} ion on acoustic properties of substituted calcium hexaferrite has been investigated.

2. Experimental

2.1. Sample preparations

The Y-type substituted calcium hexaferrites having the following formula $Ca_2Zn_2Fe_{12-x}Al_xO_{22}$ with x = 0, 0.5 and 1 were prepared by sol-gel auto-combustion method. The starting materials to synthesized hexaferrite samples are AR grade $Ca(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2.4H_2O$, $CO(NH_2)_2$ and $Al(NO_3)_3.9H_2O$. Stoichiometric amount of metal nitrate was dissolved completely in deionized water. The fuel urea was also dissolved in deionized water. Two solutions as prepared were mixed together to form homogeneous transparent aqueous solution. The solution was then heated to about 50 ^oC with constant stirring. The aqueous solution of ammonium hydroxide was added to mixed solution and pH of the solution was adjusted to 7. After that, the solution was kept in the digitally controlled microwave oven of 2.45 GHz to evaporate the water and wet gel of high viscosity was obtained. After heating it was then converted into dry gel which in turn burnt completely by evaporating large volume of gases. The ash obtained was grind in agate mortar for about 15 minute.

2.2 Characterization

The phase analysis of the synthesized sample in powder form was performed by a Phillips X'pert Diffractometer and using Cu-Kα radiation source and λ=1.5406 Å with 40 mA 45 KV. Lattice constants a and c, cell volume (V), X ray density ($\rho_{x\text{-}ray}$), bulk density (ρ_m) and porosity (P) of samples were determined.

The ultrasonic pulse transmission technique [4] was used for the measurement of longitudinal wave velocity (V_l) and shear wave velocity (V_s) at 1MHz. The RF pulse generated by a pulse oscillator was applied to quartz transducer. The acoustic pulse were converted into electrical signals by receiving transducer. The out-put signal was displayed on a digital taxtronic 2230 oscilloscope. The difference in time (ΔT) between two overlapping received pulse train was noted with the help of timer. The sound velocity was measured using the equation $V=L/\Delta T$ where V is the sound velocity, L is the length of

superconducting specimen and T is the time. A number of research reports is available in the literature describing various aspects of elastic behavior of different superconducting systems [5-8].

The elastic constants of a material can be determined by measuring the velocity of the longitudinal (V_l) and shear wave (Vs) [9]. The ultrasonic velocities and elastic constants are related as given by the following equations.

Longitudinal modulus $L = \rho(V_l)^2$

Rigidity modulus $G = \rho(V_s)^2$

Bulk modulus $B = L - \frac{4}{3}G$

Poisson's ratio $\sigma = \frac{3B-2G}{6B+2G}$

Young's modulus $E = (1+\sigma)2G$

The acoustic Debye temperature of materials used to explain the well known solid state problem like lattice vibrations is determined using ultrasonic velocity. The relation is given as

$$\theta = \frac{h}{k_B}\left[\frac{3N_A P}{4\pi V}\right]^{\frac{1}{3}} V_m$$

Where h is the Planck's constant, k_B Boltzmann constant, N_A Avogadro number, V volume calculated from the effective molecular weight and the density (i.e. M/ρ), P the number of atoms in the molecular formula and V_m the mean sound velocity defined by the relation

$$v_m = \left[\frac{\frac{2}{v_s^3}+\frac{1}{v_l^3}}{3}\right]^{-\frac{1}{3}}$$

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the samples are shown in Fig 1. The crystallographic data are tabulated in Table 1. The data is analyzed by using computer software PCPDF Win, Powder-X and Full proof Suite. By comparing the patterns with JCPDS, the phases in the different samples are determined. The XRD pattern confirms the formation of single phase Y-type hexagonal ferrites. The space group of the sample is found to be ($R\bar{3}m$). Kuhikar [10] reported the values of 'a' and 'c' as 5.884 Å and 43.938 Å for $Ca_2Co_2Fe_{11}LaO_{22}$ sample. Moharkar [11] also reported the values 'a' and 'c' as 5.0418 (Å) and 44.1876 (Å) for $Ca_2Zn_2Fe_{12-x}Co_xO_{22}$ sample.

Other parameters such as lattice constants (a & c), cell volume (V), X-ray density ($\rho_{x\text{-}ray}$) and bulk density (ρ_m) are enumerated in Table 1. The lattice parameter 'a' and 'c' and 'V' slightly changes with substitution of Al^{3+} ion in calcium hexaferrite sample. This is due to relatively large ionic radius of Al^{3+} ion (0.53 Å) comparing to that of Fe^{3+} ion (0.64 Å) for six fold coordination. As a result, the cell volume of the samples of hexaferrite decreases after being doped with Al^{3+} ions. The decrease in X-ray density and bulk densities on substitution of Al^{3+} ion in hexaferrite samples is due to the smaller molar masses of the substituted ion. The X-ray density is higher than the bulk density (ρ_m) which indicates the presence of pores in the synthesized samples. The porosity increases with increase in the Al^{3+} ions content in calcium hexaferrites. These results agree well to that reported by M. B Solunke [12].

3.2 Acoustic studies

The values of ultrasonic wave velocity and Debye characteristic temperature of the synthesized samples are summarized in Tables 2. Table 3 depicts the values of longitudinal modulus, bulk modulus, Young's modulus, rigidity modulus and Poisson's Ratio with Al content (x). It can be seen from the Table 3 that, the longitudinal modulus, bulk modulus, Young's modulus and rigidity modulus increases with increase in Al^{3+} ions concentration (x) following Wooster's work [13]. The variation of elastic constant increase with in Al^{3+} ions concentration for Ca in $Ca_2Zn_2Fe_{12-x}Al_xO_{22}$ Superconducting system may be interpreted in term of interatomic bonding. Thus, it can be inferred from the increase in elastic modulii with concentration (x) that the inter-atomic bonding between various atoms is being weakened continuously. The strength of inter-atomic bonding and type of cations are involved in bond formation. Earlier it has been observed that, substitution of small amount of Pb for Bi in Bi-2212 and Bi-2223 systems enhanced superconducting properties but deteriorate the elastic properties. On the other hand when Fe^{3+} ion is replaced by Al^{3+} ions in $Ca_2Zn_2Fe_{12-x}Al_xO_{22}$ system, it improves the elastic behavior of the system. This finding can be explained on the basis of change in length of inter-atomic bonding. When Fe^{3+} ions with ionic radius (0.64 Å) are replaced by Al^{3+} ion with smaller ionic radius (0.53 Å), it decrease the bond length and as a result strength of inter-atomic bonding is expected to increase and in turn elastic moduli values.

The observed increase in Debye temperature (θ) (Table 2) with Al^{3+} ions concentration suggested that the lattice vibrations are decrease due to aluminium ions substitutions. The magnitude of elastic constants and Debye temperature are constant with other Bi2212 based superconducting systems. The values of Poission's ratio are found in the range 0.01-0.10 for all the concentrations. These values lie in the range from -1 to 0.5 which is in conformity with the theory of isotropic elasticity.

Table 1: Lattice constants (a) and (c), cell volume (V), X-ray density ($\rho_{x\text{-}ray}$), bulk density (ρ_m) and porosity (P) of samples

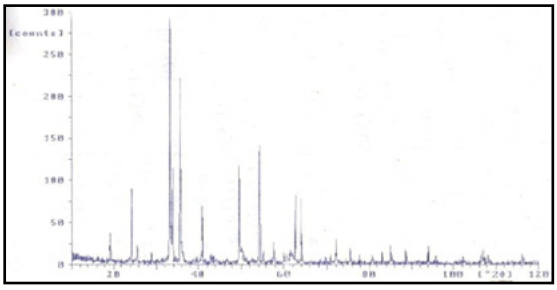
Sample	a (Å)	c (Å)	V $(Å)^3$	$\rho_{x\text{-}ray}$ (gm/cm^3)	ρ_m (gm/cm^3)	P(%)
$(Ca_2Zn_2Fe_{12}O_{22})$	5.0390	44.1072	1249.27	4.2239	3.0982	26.67
$(Ca_2Zn_2Fe_{11.5}Al_{0.5}O_{22})$	5.0452	44.2512	1245.11	4.1507	2.7761	33.11
$(Ca_2Zn_2Fe_{11}AlO_{22})$	5.0446	44.2056	1244.89	4.1067	3.1255	33.90

Table 2: Longitudinal Velocity (V_l), Transverse Velocity (V_s), Mean Sound Velocity (V_m), Mass Density (d), V_l/d $(Kg^{-1}m^4s^{-1})$, Vs/d $(Kg^{-1}m^4s^{-1})$ and Debye Temperature (θ) of the aluminium substituted calcium hexaferrite samples.

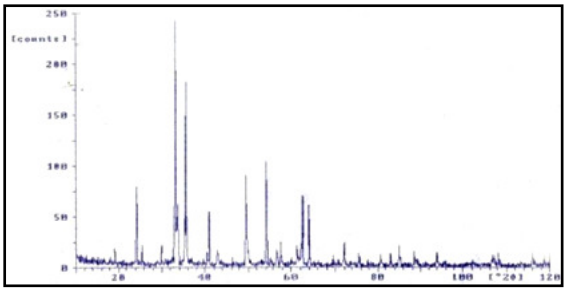
Sample	**x**	**v_l (m/s)**	**v_s (m/s)**	**v_m (m/s)**	**v_l/d $(Kg^{-1}m^4s^{-1})$**	**v_s/d $(Kg^{-1}m^4s^{-1})$**	**θ (K)**
$Ca_2Zn_2Fe_{12}O_{22}$	0	2333	1700	1600	0.75	0.50	2141.25
$Ca_2Zn_2Fe_{11.5}Al_{0.5}O_{22}$	0.5	2636	1503	1833	0.94	0.65	1695.14
$Ca_2Zn_2Fe_{11}AlO_{22}$	1	2894	2210	1600	0.92	0.65	2703.78

Table 3: Longitudinal Modulus (L), Bulk Modulus (B), Rigidity Modulus (G), Young's Modulus (E) and Poisson's Ratio (σ) of the aluminium substituted calcium hexaferrite

Sample	**X**	**L (GPa)**	**B (GPa)**	**G (GPa)**	**E (GPa)**	**σ**
$Ca_2Zn_2Fe_{12}O_{22}$	0	16.86	6.87	7.49	16.47	0.10
$Ca_2Zn_2Fe_{11.5}Al_{0.5}O_{22}$	0.5	19.14	6.99	9.11	19.05	0.04
$Ca_2Zn_2Fe_{11}AlO_{22}$	1	26.17	8.89	12.96	26.16	0.01



(a)



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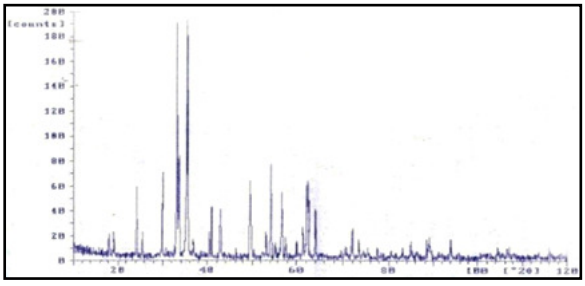

(c)

Figure 1.(a) Sample $Ca_2Zn_2Fe_{12}O_{22}$, (b) sample $Ca_2Zn_2Fe_{11.5}Al_{0.5}O_{22}$ and (c) $Ca_2Zn_2Fe_{11}AlO_{22}$: X-ray diffraction spectra.

4. Conclusion

The aluminium substituted calcium hexaferrite samples were synthesized by the sol-gel auto-combustion method. The XRD data have confirm the formation of Y-type hexaferrites and the values of a and c of the sample supports this confirmation. The increase in elastic moduli have confirmed the influence of Al^{3+} ions in calcium hexaferrite on acoustic parameter.

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