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Low temperature processing of Li-Mn-Ti ferrite ceramics with V_2O_5 addition and effects on microstructural and B-H loop properties.

Mamata Maisnam[a,]*, Jangkhohao Touthang[a] and Sumitra Phanjoubam[b]

[a]*Department of Physics, National Institute of Technology Manipur, Langol-795004, India.*

[b]*Department of Physics, Manipur University, Canchipur-795003, India*

Lithium manganese titanium ferrites were prepared by adding different amount of V_2O_5 by the ceramic technique. The compounds have the compositional formula $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$ +(x) V_2O_5 where x= 0.0, 0.1, 0.2 and 0.3 wt. % is the amount of V_2O_5 added. The samples were pre-sintered at 650 °C for 2 h and then finally sintered at 950 °C for 1 h. XRD studies confirmed all the samples with single phase spinel structures. Various structural parameters were obtained from the XRD data. SEM micrographs revealed the microstructures of the prepared samples. Curie temperature decreased with increase of V_2O_5 addition. B-H loops were traced from the sintered torroidal samples. Various hysteresis parameters like remanance, coercivity, remanance ratio etc for varied V_2O_5 additions were determined from the loop. These properties were compared with those measured from sample of same composition but prepared with 0.5 wt% of Bi_2O_3 addition and sintered at 1050 °C for 4 h.The results of the measurements are discussed in the paper.

Key words: Lithium ferrites, Ceramic technique, V_2O_5, Microstructures, B-H loops.

Introduction

Ferrites are ceramic materials composed of iron oxides and other metal oxides. They are polycrystalline complex systems comprising of crystallites, grains, grain boundaries and pores. Their interesting magnetic properties combined with being very good dielectrics make them an important material for electronic devices. For use in electronic systems a thorough understanding of their electrical and magnetic properties are required. Besides chemical composition, the role of microstructures like grain size, porosity, grain structure etc. on the magnetic properties is very significant and these parameters are controlled by the processing techniques and the sintering processes [1]. The role of microstructures especially the grain size and their distribution in controlling various magnetic properties of ferrites like spin wave linewidth, magnetic loss, hysteresis properties has been the subject of continuing study. Focus on controlled processing and then understanding mechanisms to improve microstructures like achieving uniform and finer grains, free from lattice defects and pores is important [2]. For the last few decades efforts to enhance the performance potential of spinel Li-ferrite families have been continuing by optimizing various processing parameters. Li-ferrites inherently possess useful properties like good temperature stability because of their high Curie temperature, high squareness of hysteresis loop, high saturation magnetization, low dielectric and magnetic loss. These make them find widespread applications in microwave devices [3, 4]. But it is very difficult to prepare stoichiometric compositions technologically and therefore has been restricted from broad utilization. So, these compounds are often prepared and processed by using a variety of additives and proper control of processing parameters. Various additives like Bi_2O_3, $CaCO_3$, SiO_2, V_2O_5, Nb_2O_5, Ta_2O_5 etc. may be used for processing of Li-ferrites to improve the microstructures and the properties of interest [5-7]. V_2O_5 is an interesting additive and adding a small amount acts as sintering aid in the preparation of ferrites influencing the growth of microstructures and densification in ferrites and hence the magnetic properties [8, 9]. The present paper reports on the influence of V_2O_5 additions on the microstructural and magnetic properties of lithium titanium manganese ferrites.

Experimental

V_2O_5 added Li-Mn-Ti ferrites with representative formula $Li_{0.6}Mn_{0.1}Ti_{0.1}Fe_{2.20}O_4$ + x (where x= 0.0, 0.1, 0.2 and 0.3) wt. % is the amount of V_2O_5 added, were prepared by ceramic technique. The raw materials used were high purity Li_2CO_3, Fe_2O_3, MnO_2, TiO_2 and V_2O_5. The powders in stoicheometric ratios were milled with distilled water for 10h, dried and pre-sintered at 650 °C for 2 h. The mixture was milled again for another 10 h, dried, ground into smooth powders and pressed into pellets and torroids using

*Corresponding author:
Tel : +91-358-2413031
Fax: +91-358-2413031
E-mail: mmaisnam.nitm@gmail.com

PVA (3 wt %) as binder. And finally these were sintered at 950 °C for 1 h. The samples were named as samples LMTV0, LMTV1, LMTV2 and LMTV3 for x = 0.0, 0.1, 0.2 and 0.3 wt. % of V_2O_5 respectively. One sample with representative formula $Li_{0.6}Mn_{0.1}Ti_{0.1}Fe_{2.20}O_4$ + 0.5 wt% of Bi_2O_3 was also prepared with the same method. As generally practiced for Li-ferrites, this sample (LMT) was pre-sintered at 850 °C for 4 h and finally sintered at 1050 °C for 4 h [3, 4] which is the normally adopted procedure for preparation of Li-ferrites. All studies of the properties were done in comparison with this sample. XRD patterns using Cu K_α radiation (λ= 1.5406 Å) were taken by Phillips X'PERT PRO to confirm the formation of phase structures. Structural parameters such as lattice constant, X-ray density and crystallite size were evaluated from the XRD data. Experimental density was obtained by the Archimedes principle. SEM Photomicrographs (by SEM Quanta 250) were taken on the fractured surface of each sample and the micrographs showed the microstructures like grain size, pores, and grain size variation of the samples. Curie temperature was measured by the method given by Soohoo [10]. B-H loops were traced on the sintered torroidal samples. Initially the dimensions of the torroids such as thickness, inner and outer diameter were recorded. Then the torroids were wound with primary and secondary windings of about 70 turns with enameled copper wire. The B-H loops were then traced on them using a computer controlled B-H Loop tracer. All the measurements were carried out at room temperature.

Results and Discussions

XRD patterns for all the samples are shown in Fig. 1. The specific planes corresponding to each peak are indexed in the figure. The intense lines corresponding to specific planes obtained in the XRD patterns confirmed the formation of single phase with spinel structures. It can be noted that the first set of four samples viz. LMTV0, LMTV1, LMTV2 and LMTV3 were sintered at lower temperature and shorter time compared to sample LMT. A comparative studies of the structural properties obtained from the XRD data were done and tabulated in Table 1. It is found that except for sample LMTV3, lattice constant for sample LMT is bigger than those of the other samples. Ridgley et al in their report [11] correlated the increase in the value of lattice constant value of Li-ferrites deviating from the stoicheometric value with loss of lithia and oxygen during sintering. They also reported that lithium ferrites losses lithia and oxygen at temperature above 1000 °C. Sample LMT which was sintered at 1050 °C for longer period compared to the other four; it is possible that the probability of material loss is higher in this sample. Hence, the rise in lattice constant is expected. In order to minimize material losses and preserve the stoichiometry and the important properties of Li-ferrites, it might seemed beneficial if these compounds be sintered at a lower temperature. And adding small amount of V_2O_5 seemed effective in lowering the sintering temperature with producing better structural properties. The lattice constant of sample LMTV1 with 0.1 wt% of V_2O_5 is found to be

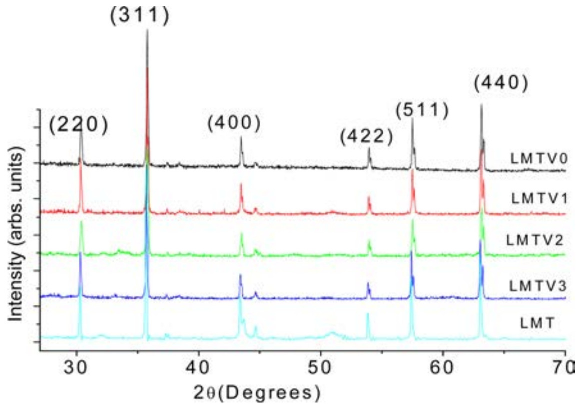

Fig. 1. XRD patterns of $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$ +(x) ferrites; LMTV0 (x= 0.0 wt% of V_2O_5), LMTV1 (x= 0.1 wt% of V_2O_5), LMTV2 (x= 0.2 wt% of V_2O_5), LMTV3 (x= 0.3 wt% of V_2O_5) and LMT (x= 0.5 wt% of Bi_2O_3).

Table 1. Structural properties of $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$ +(x) ferrites; LMTV0 (x= 0.0 wt% of V_2O_5), LMTV1 (x= 0.1 wt% of V_2O_5), LMTV2 (x= 0.2 wt% of V_2O_5), LMTV3 (x= 0.3 wt% of V_2O_5) and LMT (x= 0.5 wt% of Bi_2O_3).

Samples	Lattice constant (Å)	X-Ray density, d_x (g/cc)	Experimental density, d (g/cc)	Porosity (%)	Crystallite size (nm)
LMTV0 950 °C / 1 h	8.325	4.938	4.385	11.21	76.3
LMTV1 950 °C / 1 h	8.326	4.937	4.492	9.01	57.3
LMTV2 950 °C / 1 h	8.323	4.944	4.451	9.97	66.7
LMTV3 950 °C / 1 h	8.335	4.922	4.429	10.01	74.3
LMT 1050 °C /4 h	8.334	4.925	4.389	10.98	83.95

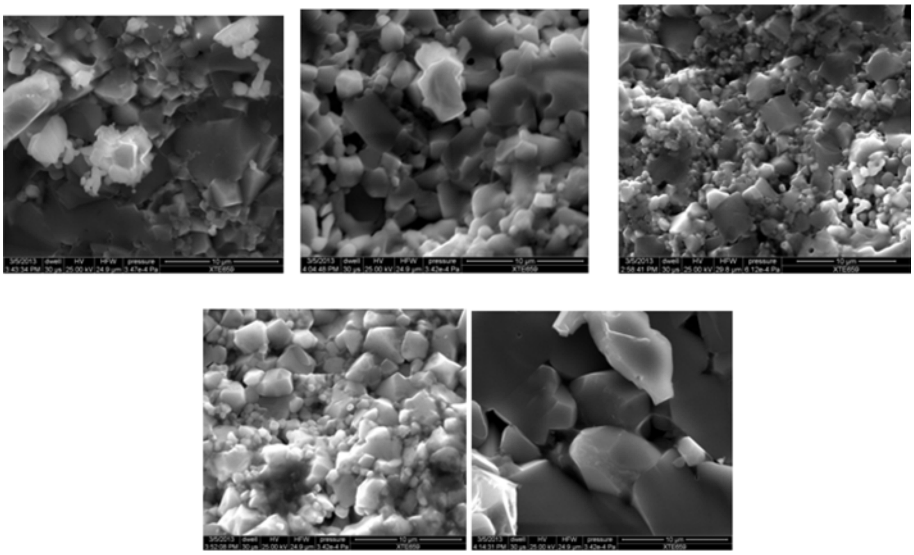

Fig. 2. SEM micrographs of $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$+(x) ferrites; LMTV0 (x= 0.0 wt% of V2O5), LMTV1 (x= 0.1 wt% of V2O5), LMTV2 (x= 0.2 wt% of V_2O_5), LMTV3 (x= 0.3 wt% of V_2O_5) and LMT (x= 0.5 wt% of Bi_2O_3).

8.326 Å and it is closest to the stoichiometric value (8.3296 Å) for Li-ferrites [7, 11].

Studying the value of the densities for the different samples (Table 1) it is found that densification is higher in V_2O_5 added samples compared to sample LMT sintered with Bi_2O_3. Sample LMTV0 which was sintered without any additives has been found to have least densification with the highest porosity level of 11.21%. At the sintering conditions applied and without any additives, proper densification might not have been attained in this sample.

The crystallite size evaluated from the XRD data using the Debye Scherer is depicted in Table 1 and it is found that Bi_2O_3 added sample (LMT) showed the largest crystallite size of all the samples. The microstructural study was further done by taking SEM photomicrographs of the samples. The photomicrographs were taken on the fractured surface of the samples and the microstructural features are shown in Fig. 2. The grain size shown by the SEM micrograph is bigger than the crystallite size evaluated from the XRD data. It is seen that the samples that contain V_2O_5, that is, LMTV1, LMTV2 and LMTV3 showed smaller microstructures compared to sample without V_2O_5 (LMTV0) which comprises of big abnormal grains along with smaller grains. This sample LMTV0 showed large grain size variation indicating grain growth is not uniform. It was prepared without any additives and in such condition crystal growth occurred with no flux to prevent grain migration for intergranullar collective recrystallization which results in bigger microstructure with large grain size variation [9]. However in the other three samples, the presence of V_2O_5 resulted in microstructure with comparatively uniform and very finer grains. Reports have shown that V_2O_5 during the sintering process melts at the grain boundaries and thin films of this molten flux envelop the grains and acts as grain growth inhibitor [12]. Letyuk in his study of preparation of ceramic ferrites with low melting point additives divided the process of grain growth into two stages- one of comparatively slow and the latter of intense grain growth. Starting from temperature ~ 1100 ºC, the grain growth enters the second phase and grains at once grow rapidly [9]. The presence of V_2O_5 has sintered the present ferrites with slower grain growth to the observed density (Table 1) in shorter time and at the lower temperature before the onset of intense grain growth. Such finer microstructure obtained with better densification is beneficial in enhancing the magnetic and electrical properties.

However as the amount of V_2O_5 addition is increased the grain size is observed to increased (Fig. 2) similar to the variation of crystallite size (Table 1). The SEM photomicrograph of the sample sintered with Bi_2O_3 (LMT) as seen in Fig. 2 is found to contain very large grains with large pores compared to the other four. Rodrique [2] in his paper mentioned that Bi_2O_3 as an additive in preparation of Li-ferrites promote explosive grain growth within a very narrow range of temperature. With the sintering temperature > 1000 ºC and the very large size of grains seen in sample LMT it is obvious that intense grain growth have occurred in this sample [2, 9]. But with V_2O_5 additions, it is found that the present lithium based ferrites have been sintered at lower temperature with better densification and minimal growth.

The variation of Curie temperature (T_c) for the different V_2O_5 additions is depicted in Fig. 3. Sample LMT showed the highest value. Bi_2O_3 when used as a sintering flux remained as secondary phase along the grain boundaries and do not disturb the lattice vis the active iron linkages that determines the Curie temperature

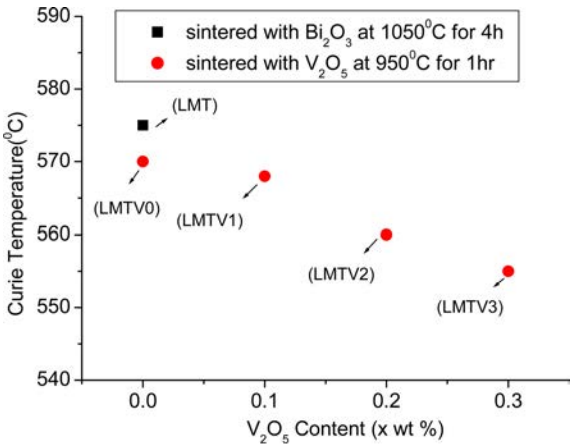

Fig. 3. Curie temperature of $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$ +(x) ferrites; LMTV0 (x= 0.0 wt% of V_2O_5), LMTV1 (x= 0.1wt% of V_2O_5), LMTV2 (x= 0.2 wt% of V_2O_5), LMTV3 (x= 0.3 wt% of V_2O_5) and LMT (x= 0.5 wt% of Bi_2O_3).

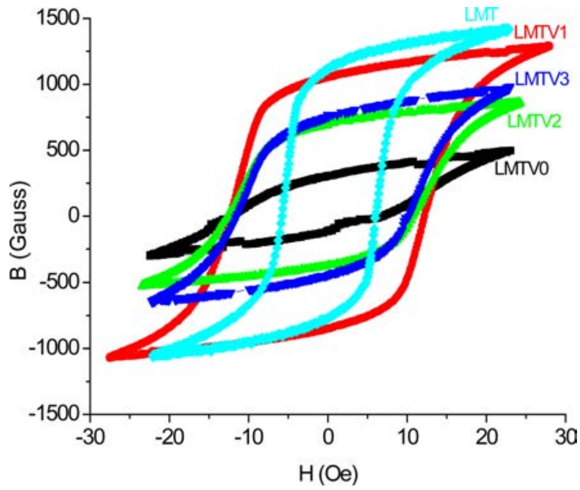

Fig. 4. B-H loops of $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$ +(x) ferrites; LMTV0 (x= 0.0 wt% of V_2O_5), LMTV1 (x= 0.1 wt% of V_2O_5), LMTV2 (x= 0.2 wt% of V_2O_5), LMTV3 (x= 0.3 wt% of V_2O_5) and LMT (x= 0.5 wt% of Bi_2O_3).

of ferrites [13]. Comparing with it, the value for LMTV0 is slightly lowered. Since densification in this sample is comparatively lower, it implies the iron linkages per unit packing volume is expected to be less resulting in slightly lesser value of T_c. Still further, for the other samples the T_c value drops gradually as V_2O_5 addition is increased. Others [4] have reported that when V_2O_5 is used as additives it may partly enter the lattice and substitute the Fe ions at both A and B sites. It is therefore possible that with addition of V_2O_5 flux, some Fe^{3+} ions may have been replaced. Therefore the active linkages i. e. Fe_A^{3+}-O^{2-}-Fe_B^{3+} is decreased as flux content is increased. Hence a fall in T_c may be expected.

B-H hysteresis loops taken on the toroidal samples are depicted in Fig. 4. The shape and size of hysteresis loop and hence the hysteresis parameters depend not only on chemical composition, formation of secondary phase and defect structure but also on several microstructural properties like grain size, grain homogeneity, porosity, size and shape of pores etc [1, 14]. Hysteresis parameters of ferrites are important properties and the various hysteresis parameters vis remanence, coercivity and rectangularity of the hysteresis loop determine their applicability in microwave devices. Lithium based ferrites are known for their rectangular hysteresis loop. If tailored carefully so that their electrical properties are improved, they become good candidates for memory or microwave devices. The values of the hysteresis parameters obtained from the B-H loops for the different samples are tabulated in Table 2. A sudden increase in the coercivity, H_c is observed in sample LMTV1 with 0.1 wt% V_2O_5 addition from that of pure ferrite (LMTV0) followed by slight decrease as the addition amount is increased. But sample LMT sintered with Bi_2O_3 showed the lowest value of H_c amongst all the samples. Addition of V_2O_5 sensitively influence the microstructure of the synthesized ferrites as observed in the SEM micrographs. Microstructural studies from SEM micrographs revealed that grain size of samples LMT showed the highest followed by LMTV0 and

Table 2. B-H loop parameters of $Li^{+}_{0.6}Mn^{4+}_{0.1}Ti^{4+}_{0.1}Fe^{3+}_{2.20}O^{2-}_{4}$ +(x) ferrites; LMTV0 (x= 0.0wt% of V_2O_5), LMTV1 (x= 0.1 wt% of V_2O_5), LMTV2 (x= 0.2 wt% of V_2O_5), LMTV3 (x= 0.3 wt% of V_2O_5) and LMT (x= 0.5 wt% of Bi_2O_3).

Samples	H_c (Oe)	B_r (Gauss)	B_m (Gauss)	H_m (Oe)	B_r/B_m	$(B_m-B_r)/H_m$ (Gauss/Oe)
LMTV0 950 °C / 1 h	9.52	207	396	22.79	0.52	8.29
LMTV1 950 °C / 1 h	12.24	952	1182	27.75	0.81	8.28
LMTV2 950 °C / 1 h	11.66	534	695	23.89	0.77	6.73
LMTV3 950 °C / 1 h	10.88	597	814	22.61	0.73	9.59
LMT 1050 °C /4 h	5.91	944	1241	22.47	0.76	13.21

much reduced grain size in the other V_2O_5 added samples. The observed hysteresis behaviour obtained for the different samples can well be interpreted from the microstructural features such as grain size, porosity for the different ferrite samples.

Magnetic hysteresis is related to intergranular domain wall motion [15] and when the magnetization is not easily reversed, the coercivity, H_c is high. A thorough study revealed that microstructural effect significantly influenced the hysteresis behavior. Igarashi et al. [14] and Van der Zaag et al. [16] reported that H_c is inversely proportional to grain size. As the grain size decreases, they tend to contain lesser number of domain walls and the hindrances to intergranular domain wall movement increases. Therefore, samples with smaller grains are expected to have higher coercivity as depicted in Table 2. The values of remanence (B_r) obtained for the different samples are shown in table 2. This can be understood from the various porosity levels as seen in Table 1. Remanence is reported to be inversely proportional to the porosity [14, 16]. As porosity decreased, density or packing of magnetic material in a specific volume increased leading to a rise in B_r. Porosity dropped from 0 to 0.1 wt % of V_2O_5 addition and then increased on further increase of V_2O_5 addition. Remanence with minimum porosity in sample LMTV1 showed highest value and exceeded that of sample LMT. Sample with maximum porosity, LMTV0, showed the least value of remanence. However increasing the V_2O_5 content above 0.1wt% the B_r value decreased below that of sample LMT indicating that besides porosity level, flux content have caused a change in the remanence value. The values of B_m (maximum flux density) and H_m (maximum applied field) obtained from the loops are tabulated in Table 2 and V_2O_5 added samples were found to require comparatively higher fields for obtaining the maximum flux density than samples LMT or LMTV0. This is understood from the finer grains obtained in the finer grained samples [17]. The value of ratio of B_r/B_m gives the squareness ratio of the hysteresis loop (Table 2) and sample LMTV1 with 0.1 wt% of V_2O_5 addition showed the highest value. Observing the values of $(B_m-B_r)/H_m$ ratio (table 2), it is found that samples with V_2O_5 have lower values than that with Bi_2O_3. Improvements in squareness ratio and $(B_m-B_r)/H_m$ ratio has been observed with V_2O_5 addition and further investigation and understanding of other properties that follows with refined microstructures like power loss, energy dissipation is essential in these V_2O_5 added ferrites to find better potential applications in memory and microwave applications.

Conclusions

Li-Mn-Ti ferrites were prepared by ceramic technique by adding varying amount of V_2O_5. The samples get sintered at lower sintering temperature and time with V_2O_5 addition. Fine microstructures were obtained with V_2O_5 addition. B-H loop measurements showed increased coercivity with V_2O_5 addition.

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