Structural and dielectric properties of LaBi$_2$Fe$_5$O$_{12}$

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The polycrystalline sample of LaBi$_2$Fe$_5$O$_{12}$ (LBIG) distorted perovskite compound is prepared using a high-temperature solid-state reaction technique. Room temperature preliminary X-ray diffraction (XRD) studies of the compound show the tetragonal splitting. It confirms the formation of single-phase compound with $\approx$2% of pyrochlore phase. The elemental content of the compound has been verified by energy dispersive spectroscopy (EDS) microanalysis. Microstructural analysis by scanning electron microscopy (SEM) shows that the grains are homogeneously as well as uniformly distributed throughout the surface of the sample. Dielectric studies as a function of temperature (30-360°C) at four different frequencies (1, 10, 100, 1000 kHz) yielded a dielectric anomaly at 325°C. It is interesting to note that the loss tangent (tanδ) seems to be reduced at higher frequencies after reaching the instrumental saturation. Also, dielectric measurement as a function of frequency (100 Hz-1 MHz) at room temperature reveals the presence of different types of polarization mechanisms involved in the material. Again the frequency dependent loss tangent (tanδ) shows the sinusoidal variation, which is unusual for this kind of measurement. This variation has been confirmed by repeating the measurement at various temperatures.

Since the discovery of magnetoelectric effect$^{1-4}$ and the importance of the material for magneto-optical devices$^{5,7}$, a lot of work has been carried in the past$^{8-13}$ by replacing yttrium by rare earths and other oxides. Recently, bismuth iron garnet (BIG) based material is emerging as a promising candidate to develop magnetoelectric, magneto-optical and multifunctional devices$^{14-17}$. It is clear that whatever work carried out in BIG gives much attention to magnetic and magneto-optical measurements$^{18,19}$. The advantage of La$^{3+}$ modification for structural stability$^{20}$ and higher magneto ferroelectric properties$^{21}$ in a BiFeO$_3$ opens a new way to fabricate a structurally stable BIG. The structural and dielectric measurements of La$_{3/2}$Bi$_{3/2}$Fe$_5$O$_{12}$ compound have been reported earlier$^{22}$. In the present work we have observed the influence of more bismuth content (LaBi$_2$Fe$_5$O$_{12}$) in structural stability and dielectric properties.

Experimental Procedure

Material preparation

The polycrystalline sample of LaBi$_2$Fe$_5$O$_{12}$ was prepared by a standard high-temperature solid-state reaction technique using high purity precursors: La$_2$O$_3$ (99.9%, M/s Indian Rare Earth Ltd., India), Bi$_2$O$_3$ (99.9%, M/s Loba Chemi Pvt. Ltd., India) and Fe$_2$O$_3$ (99.9%, M/s Loba Chemi Pvt. Ltd., India) in a desired stoichiometry. The powders of dried oxides were thoroughly mixed in an agate mortar for 6 h, then wet grinding in ethanol media for 1 h. The mixture was dried again and calcined at 880°C in an alumina crucible for 8 h. The process of grinding and calcinations were repeated until the single-phase compound was formed (verified by XRD). The calcined powder was grinded finely again and mixed with binder material, polyvinyl alcohol (PVA) and pressed into a cylindrical pellets of diameter 10 mm and thickness of 1-3 mm approximately, under an isostatic pressure of about $5 \times 10^7$ kg/m$^2$ using a hydraulic press. These pellets were then sintered at 900°C for 2 h in an air atmosphere. The sintered pellets were polished with zero grain emery paper and coated with high purity silver paste and then dried for 2 h at 150°C.

Material characterization

The formation of single phase compound was checked by an X-ray diffraction (XRD) technique using Rigaku X-ray powder diffractometer (model: Miniflex) in a wide range of the Bragg angles (20° ≤ 2θ ≤ 80°) with CuK$_\alpha$ ($\lambda=1.5405$ Å). The surface micrograph of gold sputtered sintered pellet was taken

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by Jeol (model: JSM-5800F) scanning electron microscope (SEM). The same instrument was also used for energy dispersive spectroscopy (EDS) microanalysis (i.e., quantitative estimation of individual elements present in the sample) of the sintered pellet. The dielectric constant ($\varepsilon$) and loss ($\tan\delta$) of the titled compound were obtained as a function of frequency (100 Hz-1 MHz) at different temperatures (30-450°C) using computer-controlled Hioki LCR Hitester (model: 3532) along with the laboratory made sample holder and heating arrangement. The same instrument was also used for dielectric measurement as a function of temperature (30-360°C) at four different frequencies (1, 10, 100, 1000 kHz).

Results and discussion

Structural analysis

The sharp and single peaks of the XRD pattern (Fig. 1), which are quite different in position and intensity from those of ingredient precursors, confirm the formation of single-phase compound. With the observed $d$ (interplanar spacing) values, all the peaks of diffraction pattern were indexed, and unit cell parameters were calculated in different crystal system and cell configuration using a standard computer program package POWD$^{23}$. A very good agreement between $d_{\text{obs}}$ and $d_{\text{cal}}$ was observed in a tetragonal crystal system and its cell parameters were selected for which $\sum \Delta d = \sum (d_{\text{obs}}-d_{\text{cal}})$ was found to be minimum. The refined lattice parameters are: $a = 3.9482(8)$ Å, $b = 3.9129(8)$ Å. The average crystallite/particle size (200 Å) was determined using Scherrer’s equation$^{24}$. The small peaks just adjacent to (101) peak may be due to unreacted Fe$_2$O$_3$ or unknown impurity phase. The removal of this secondary/pyrochlore phase (≈2%) is very difficult even in simple BiFeO$_3$ perovskite oxide$^{25,26}$. Our titled compound chemically belongs to garnet stoichiometry but the XRD proves the compound being perovskite structurally. This can be explained on the basis of thermodynamical based phase equilibrium$^{27}$. As per their studies, Fe-Fe$_2$O$_3$-La$_2$O$_3$ belongs to A-type, will form only a stable LaFeO$_3$ ternary compound instead of La$_3$Fe$_5$O$_{12}$. The structurally unstable nature of bulk Bi$_3$Fe$_5$O$_{12}$ and La$_3$Fe$_5$O$_{12}$ cause the formation of stable perovskite of BiFeO$_3$ and LaFeO$_3$ in garnet stoichiometry. This can also be verified by a computer simulation$^{28}$ based on perovskite structure prediction software (SPuDS). From this study, it can be inferred that our titled compound has four-fold ‘distorted perovskite of BiFeO$_3$ in which one A site of BiFeO$_3$ is occupied by Fe$^{3+}$ ion and forms FeFeO$_3$ and another A site of BiFeO$_3$ is occupied by La$^{3+}$ ion and form LaFeO$_3$. Since the unstable nature of FeFeO$_3$ leads to the formation of Fe$_2$O$_3$ again which causes the pyrochlore phase in the XRD pattern. It has been inferred that this unreacted spices will be responsible for the spontaneous magnetization in the material$^{29,30}$.

EDS X-ray microanalysis was carried out for the verification of the presence of individual elements in the prepared sample as per our tailored stoichiometry. This was done on the sintered pellet prior to gold sputtering. The normalization$^{31}$ has been done on the basis of fixed Fe concentration. The surface property and microstructure of the ceramic have been investigated using scanning electron microscopy. The sintered pellet previously used for EDS X-ray microanalysis was gold coated by a conventional sputtering technique. The SEM micrograph of the compound at ×1500 magnification is shown in Fig. 2.
It shows the polycrystalline texture of the material. Highly distinctive, more or less uniform and compact grain distributions were seen throughout the surface. The grains have typical dimension in the range of 1-2 µm approximately, and are mostly spherical in nature.

**Dielectric properties**

The temperature dependent relative dielectric constant ($\varepsilon$) and loss tangent (tan$\delta$) is shown in Fig. 3 at selected frequencies (1, 10, 100, 1000 kHz). We have observed a dielectric anomaly at 325°C. It was also observed from Fig. 3 that the loss tangent changes very slowly with temperature up to 300°C, after that it increases abruptly and reaches instrumental saturation. But at high frequency (1 MHz) the loss tangent seem to be decreased. This will gives an inference of the presence of loss peak at around 340°C. This low loss nature at high frequency will be suitable for high frequency application, such as microwave filters and infrared devices. In addition, the maximum dielectric constant ($\varepsilon_{\text{max}}$) of 50,000 falls down to 2000 as the frequency increases from 1 kHz to 1 MHz shows that the dielectric relaxation behaviour in the materials is complicated and new. The influence of interfacial polarization plays an important role on this diffuse like phase transition. The accumulation of charge at the grain boundaries is responsible for higher values of dielectric constant at low frequencies and vice versa.

Figure 4 shows the variation of dielectric constant and loss tangent as function of frequency. The dielectric constant decreases almost linearly with the increase of frequency, which is the normal behaviour of a dielectric material. At low frequencies all the different types of polarizations (electronic, ionic, dipolar and interfacial/surface polarization) contribute to the total dielectric constant. At high frequencies the contribution from interfacial, dipolar and atomic/ionic is zero, and hence the electronic contribution alone influences the dielectric constant. As a result we are having lower values of dielectric constant. But what is abnormal in our studies is the sinusoidal variation of loss tangent with frequency. That is, at low frequencies (100 Hz-10 kHz), the loss tangent drops down from higher value and once again rises to the maximum value at mid range of frequencies (10 kHz-500 kHz). Finally, it drops down at higher frequencies (above 500 kHz). Also the variation is in the form of sinusoidal. To confirm this trend we continue the measurement at different temperatures (Fig. 5). An attempt has to be made to explain the physical insight of this behaviour of the loss tangent with respect to frequency.
Conclusions

It is concluded that LaBi$_2$Fe$_5$O$_{12}$ has tetragonal structure at room temperature basically forming a distorted perovskite with the garnet stoichiometry. The microstructure of the material shows the formation of uniformly distributed grains throughout the surface. The compound shows diffuse-type of dielectric anomaly well above the room temperature (325°C). However, the loss tangent reaches its instrumental saturation at low frequencies. The decreasing trend in the loss tangent at high frequencies infers that the material can be used (at high frequency) as microwave SAW filters and infrared devices. However, the normal behaviour of dielectric constant as a function of frequency is observed.

References

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