Magnetic and dielectric properties of Fe_3BO_6 nanoplates prepared through self-combustion method

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In the present investigation, a facile synthesis method is explored involving a self-combustion of a solid precursor mixture of iron oxide Fe_2O_3 and boric acid (H_3BO_3) using camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) as fuel in ambient air in order to form a single phase Fe_3BO_6 crystallites. X-ray diffraction (XRD), Field emission electron microscopy (FESEM), magnetic, and dielectric properties of as prepared sample are studied. From XRD pattern, a single phase compound is observed with an orthorhombic crystal structure (Pnma space group), with average crystallite size of 42 nm. A reasonably uniform size distribution of the plates and self-assemblies is retained in the sample. A magnetic transition is observed in dielectric permittivity (at ~ 445 K) and power loss (at ~ 435 K) when plotted against temperature. A weak peak occurs near 330 K due to the charge reordering in the sample. For temperatures above the transition temperature, a sharp increase of the dielectric loss is observed which occurs due to the presence of thermally activated charge carriers. A canted antiferromagnetic Fe^{3+} ordering in a Fe_3BO_6 lattice with a localized charge surface layer is an apparent source of exhibiting a ferroelectric feature in this unique example of a centrosymmetric compound. An induced spin current over the Fe sites thus could give rise to a polarization hysteresis loop. Due to the presence of both ferromagnetic as well as polarization ordering, Fe_3BO_6 behaves like a single phase multiferroic ceramics.

Keywords: Self-combustion; nanoplates; magnetic properties; dielectric properties; polarization; centrosymmetric.

1. Introduction

The iron oxyborates $\text{Fe}^{2+}\text{Fe}^{3+}\text{OBO}_3$, $\text{Fe}_2^{2+}\text{Fe}^{3+}\text{O}_2\text{BO}_3$, or $\text{Fe}_2^{3+}\text{Fe}^{3+}\text{O}_3\text{BO}_3$ divulge multifunctional magnetic, electrical and dielectric properties, which can be tuned usefully with a proper combination of iron valence of Fe^{2+} , Fe^{3+} , and relative O^{2-} density.^{1–8} This is required for applications of information storage, spintronics, magnets, and power sources for electric and hybrid vehicles.^{1,2,4–6} Biocompatible borates have bright future in terms of biological and medicinal compounds.^{9,10} Particularly, the compound Fe_3BO_6 , which consists of only one kind of Fe^{3+} ($3d^5$) spins, offers other emerging usages of color pigments, catalysts, barcodes, drugs, and biological tools.^{9,10} In bulk Fe_3BO_6 crystals, the $3d^5$ (Fe^{3+}) spins in a canted antiferromagnet displays an interesting magnetic orientational phase transition from one weak ferromagnet state Γ_2 to another ferromagnetic state Γ_4 .^{3,11} It results in a magnetoacoustic anomaly of a first-order phase transition near 448 K.¹¹ A transition $\Gamma_2 \rightarrow \Gamma_4$ occurs at 415 K in terms of the magnetization and coercivity (H_c) of an intermediate nature of the first and second order transitions.³ The low temperature state Γ_2 has the spins aligned in the [001] direction with the spontaneous moment lying in the [100] direction. On heating, the spins turn up

along the [100] axis in the state Γ_4 with the spontaneous moment rotated along the [001] axis. At the $\Gamma_2 \rightarrow \Gamma_4$ transition, the weak magnetic moment rotates by 90° in the (a, c) plane from c -axis to a -axis. A thermal variation of magnetic anisotropy (H_a), which passes through zero at the transition, evolves the transition.^{3,12} Ultrafast spin-dynamics observed in such systems has renewed interest in this kind of phase transitions.^{13,14}

An iron oxyborate with variable cationic valances adapts variable effective valence states, coordination number of cations with the O^{2-} ions in an oxygen polyhedron, and O^{2-} fraction with respect to the cations. Ultimately, it modifies single magnetic domains whose response in terms of magnetic properties highly depends on their average size, shape and surface topology. These local microscopic modifications affect functional properties such as structural, magnetic and dielectric properties. The electric, magnetic and structural order parameter can couple one another in a single system yield simultaneous effects on tailored properties^{15,16} useful for the applications. Most of the studies are limited to bulk oxyborates prepared by a conventional solid state reaction. A nanoscale borate is rarely prepared so far except Fe_3BO_5 nanorods are made recently using a hydrothermal method,¹⁷ or a solution phase reaction,⁸ and spherical Fe_3BO_6

nanoparticles made from a rheological phase reaction.⁶ Quite good numbers of studies are carried in authors' laboratory on the iron borate glasses with varieties of additives that yield small fibrils of ferrites and iron borates with tailored magnetic as well as dielectric properties.^{18–22}

In view to this, a new facile synthesis method is developed to obtain a single phase Fe_3BO_6 crystallites in the shape of nanoplates. Prepared sample have been characterized in terms of XRD pattern in correlation to the FESEM image to confirm the findings. Apart from this, dielectric properties and polarization characteristics have been studied in correlation to magnetic properties in this paper.

2. Experimental Procedure

A facile synthesis method is developed involving a self-combustion of a solid precursor mixture of $60\text{Fe}_2\text{O}_3-40\text{B}_2\text{O}_3$ using camphor as fuel in ambient air to obtain a stable phase Fe_3BO_6 crystallites. In this process, a prerequisite blend of Fe_2O_3 and H_3BO_3 were mixed with camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) by grinding in a mortar with a pestle and then mixture was transferred into a petridis and ignited in air for making a typical batch of a total 20 g sample. All chemicals were analytical grade iron oxide (Fe_2O_3) ($\geq 99.995\%$), boric acid (H_3BO_3) ($\geq 99.5\%$) and camphor ($\text{C}_{10}\text{H}_{16}\text{O}$) (96%) and were procured from the Merck chemicals (Germany). The fuel-to-oxidant ratio was derived from the total oxidizing and reducing valences of the oxidizer and fuel using the concepts of propellant chemistry.^{23–25} In a theoretical stoichiometric composition, oxidizing valence provided by the oxidizer is equal to reducing valence from the fuel. The chosen fuel with high reducing valences coupled with high enthalpy of combustion 9.27 kcal/g assisted to reach the ignition temperature and complete the combustion in short duration of the reaction time.²⁶ This process initially undergoes melting and later the mixture is decomposed into gaseous products building the ignition temperature well up to 740 K so as it gives a maximum yield of the product. The total time required to complete the combustion process was less than 60 s. Finally, the product was taken out of petridis and grinding was done to get fine powder of it. As it is analyzed with XRD pattern from the as-prepared powders at selective temperatures, a single phase compound Fe_3BO_6 gets formed even while the precursor burns in air. Evidently, this is a very simple, pretty fast and less expensive method, which can be scaled-up to produce a high quality powder Fe_3BO_6 at mass scale.

Crystalline structure and microstructure of the sample were analyzed with XRD and FESEM images under selective conditions. To measure a XRD pattern, a powder sample was loaded in a groove (sample holder) of a perspex plate and then mounted in an X-ray diffractometer of Regaku made model Ultima III. The powder was compressed gently in the groove by using a glass slide to have a specimen of a reasonably smoothened surface over which the X-ray beam is

focused. The diffraction data were recorded using a monochromatic radiation of CuK_α of wavelength $\lambda = 0.15406$ nm through an iron filter. The data were collected over a wide diffraction angle 2θ from 20° to 80° in most of the samples through a computer, interfaced with the diffractometer, at a scanning speed of $0.02^\circ/\text{s}$ or still lower in an applied voltage of 40 kV and 40 mA current. Field emission scanning electron microscope (FESEM) of Carl ZEISS-SUPRA 40 was used to study SEM images from the crystallized sample (plate) at an accelerated voltage 10–20 kV. The dielectric permittivity value and power loss measurements of the Fe_3BO_6 nanoplates were carried out by using computer controlled two probes (N4L PSM 1735) LCR impedance analyzer. Compact sample pellet of typically 10 mm diameter and 3 mm thicknesses, painted with a silver paste, and was used to measure the data at different frequencies in the range of 0.1 to 10^4 kHz at 300–525 K temperatures. To measure the $P-E$ hysteresis loops, the sintered pellet was poled at room temperature in a silicon oil bath (under an electric field ~ 2 kV/cm) for 24 h by using a DC power supply. Then, the data were recorded from the poled sample by varying applied voltage from 2 to 18 kV (at 100 Hz) by using an automatic $P-E$ loop tracer procured from MARINE India. Magnetic properties were studied by using a super conducting quantum interference device SQUID-VSM (Make: EverCool, Quantum Design), which can measure the data at varied temperatures from 4–600 K with an applied field up to ± 60 kOe. The thermomagnetic curve was obtained over 300–550 K of temperatures by applying an effectively high magnetic field such as 1 kOe.

3. Results and Discussion

3.1. Phase formation and microstructural analyses

Figure 1 describes the XRD pattern of a phase pure Fe_3BO_6 crystallites obtained from an as-burnt Fe_3BO_6 powder. The

Fig. 1. XRD pattern of Fe_3BO_6 crystallites obtained by a self-propagating combustion of a solid precursor with camphor in ambient air.

Table 1. The d_{hkl} and I_p -values in XRD peaks observed in Fe_3BO_6 nanocrystallites from a self-propagated combustion of a solid precursor of $60\text{Fe}_2\text{O}_3-40\text{B}_2\text{O}_3$ with camphor in open air.

As-prepared (nanocrystallites)		Bulk		h	k	l
d_{hkl} (nm)	I_p	d_{hkl} (nm)	I_p			
0.3675	30.7	0.3685	39.7	1	1	1
0.3183	43.4	0.3110	4.2	2	1	1
0.2695	100.0	0.2681	18.1	3	0	1
0.2513	81.9	0.2513	13.2	4	0	0
0.2290	13.3	0.2271	16.7	3	2	1
0.2205	25.7	0.2190	10.7	4	0	1
0.2078	9.4	0.2042	0.7	2	0	2
0.1839	39.1	0.1817	0.1	3	1	2
0.1694	43.5	0.1685	12.0	5	2	1
0.1598	9.4	0.1577	8.7	1	5	1
0.1485	24.7	0.1473	0.9	6	2	1
0.1454	28.8	0.1442	13.9	3	5	1
0.1349	4.3	0.1345	15.2	1	5	2
0.1311	9.9	0.1297	1.3	3	2	3
0.1258	9.1	0.1250	1.3	5	5	1
0.1226	5.7	0.1225	0.1	5	4	2

interplanar spacings d_{hkl} and peak intensity I_p -values observed in this sample are compared with the bulk values in Table 1. As shown in Table 1, the most intense (301) peak assumes $d_{hkl} = 0.2695$ nm which is very close to the bulk value 0.2681 nm but differs from it a reasonably enhanced peak intensity. Two reflections (400) and (521) from the lateral surfaces of the lattice in a crystallite share the second and third most intense peaks of the diffractogram at 0.2513 nm and 0.1694 nm of d_{hkl} -values, respectively. Hence, the formation of a single phase compound with an orthorhombic crystal structure (Pnma space group) is confirmed from the XRD pattern. An average crystallite size $D \sim 42$ nm of Fe_3BO_6 crystallites is determined by full width at half maximum (FWHM) values in the XRD peaks using Debye-Scherrer relation. The average lattice parameters $a = 1.0290$ nm, $b = 0.8125$ nm, and $c = 0.4535$ nm with density $\psi = 4.806$ g/cm³ determined from the d_{hkl} values in the characteristic diffraction peaks shown in Fig. 1 are fairly matching with the reported values $a = 1.0050$ nm, $b = 0.8550$ nm, and $c = 0.4470$ nm ($\psi = 4.744$ g/cm³) on the bulk Fe_3BO_6 .^{27,28}

The d_{hkl} values describe $a = 1.0290$ nm, $b = 0.8125$ nm, and $c = 0.4535$ nm for nanocrystallites, and $a = 1.0050$ nm, $b = 0.8555$ nm, $c = 0.4470$ nm for the bulk sample.²⁸

Figure 2 depicts FESEM image of Fe_3BO_6 crystallites in which mostly round shaped plates (diameter $d = 50$ – 140 nm) with a few rectangular plates (length $L = 50$ – 150 nm and width $W = 20$ – 60 nm) are observed. It appears that the Fe_3BO_6 image in Fig. 2 is formed by stacking the plate-like basic structures one over other. A reasonably uniform size distribution of the plates and self-assemblies is retained in the sample. Average size and morphology of the structures

Fig. 2. FESEM image of as prepared Fe_3BO_6 crystallites grown in shapes of thin plates and assemblies from a self-propagating combustion of a solid precursor with camphor in open air.

depend strongly on the way of the combustion (preparation technique).

3.2. Magnetic properties and polarization hysteresis

Figure 3 shows the M – H curves measured for a sample of Fe_3BO_6 nanoplates at different temperatures such as (a) 5 K, (b) 100 K, (c) 200 K, (d) 300 K, (e) 400 K, (f) 450 K, (g) 500 K, and (h) 550 K, (magnified parts in the insets) with magnetic field 50 kOe used here. Magnetic phase-1 and phase-2 are shown above the antiferromagnetic phase 0 in the model diagrams. The magnetization does not saturate with the field varied up to 50 kOe at any temperature chosen in this range. It implies that the Fe_3BO_6 behaves on average to be a canted antiferromagnet with a large fraction of uncompensated spins (which do not saturate easily at the fields chosen in this experiment) at the nanoplate surfaces. An S-shaped magnetization behavior incurs over two major regimes (i) 5–300 K and (ii) 400–550 K of temperatures, which characterize two canted ferromagnetic states (phases 1 and 2) of the sample against a bulk antiferromagnetic state (phase 0). As it is described in the model diagram in Fig. 3, the phase 1 is a high magnetic phase which bears a magnetization nearly twice compared to the value in the high temperature phase 2. Parts of the M – H curves magnified in the insets describe part of closed loops of a canted antiferromagnet (or a ferrimagnetic phase), wherein the coercivity (H_c) is raised gradually from 0.167 kOe at 550 K to as large as 0.361 kOe at 5 K.

A thermomagnetic curve measured over subsequently higher temperatures 300–550 K, as it is plotted in Fig. 4 with an applied 1 kOe field, clearly indicates a distinct T_{C1} transition near 427 K before a higher temperature magnetic phase 2 turns-up and extends over higher temperatures. Another T_{C2} point is marked at ~ 525 K in this magnetic phase 2. As it is well known in shape memory Heusler alloys,^{29–31} a reversible magnetic phase 2 $\leftrightarrow$ phase 1 transition shown in heating and cooling cycles in this sample Fe_3BO_6 under an applied magnetic field might be useful in developing magnetocaloric effect and its applications. The surface spins in small

Fig. 3. M - H curves measured for a sample of Fe_3BO_6 nanoplates at different temperatures such as (a) 5 K, (b) 100 K, (c) 200 K, (d) 300 K, (e) 400 K, (f) 450 K, (g) 500 K, and (h) 550 K, (magnified parts in the insets) with magnetic field 50 kOe. Magnetic phases 1 and 2 are shown above the antiferromagnetic phase 0 in the model diagrams.

Fig. 4. A thermomagnetic curve measured over 300–550 K at 1 kOe field for a sample of Fe_3BO_6 nanoplates.

crystallites, especially when prepared in a shape of nanoplates, which offer an effectively large surface and in turn a concomitantly large number of the surface spins, play a crucial role in tracing out a reversible phase 2 $\leftrightarrow$ phase 1 transition.

Polarization hysteresis loops have been studied for the Fe_3BO_6 sample at room temperature and they do not saturate over electric fields ≤ 26 kV/cm at 100 Hz frequency as shown in Fig. 5. The ferroelectric features arise in this compound from a canted antiferromagnetic Fe^{3+} ordering. Interestingly, some other orthoferrites (viz., SmFeO_3 , LuFeO_3 and YFeO_3 , etc.) occurrences of weak ferroelectric characteristics have been explained to be due to the canted antiferromagnetic ordering of Fe^{3+} cations.^{32–35} With increasing a bias electric-field, a P - E hysteresis loop thus grows larger and wider as per the magnetoelectric features. In general, three major kinds of the polarization processes involve (i) highly polarizable polarons, (ii) local displacements of the space charges and ionic vacancies, and

Fig. 5. P - E hysteresis loops for Fe_3BO_6 nanoplates at room temperature with various applied fields.

(iii) reorientation of switchable domains. In Fig. 5, an asymmetric shape of the P - E loop is shown which expands progressively over remnant polarization (P_r) and coercivity (E_c) upon an applied field increased from ± 3.2 to ± 25.9 kV/cm. With increasing field, the maximum polarization (P_s), P_r and E_c values increase progressively in the surface charge species, and uncompensated magnetic spins share the high field polarization. A discontinuous loop as it is seen over here possibly arises due to a field induced reorientation of switchable ferroelectric domains, while an asymmetric shape of it propagates on an electric field induced magnetic effect in the domains. At room temperature, a maximum polarization of $P_s = 0.08 \mu\text{C}/\text{cm}^2$ is observed along with $P_r = 0.04 \mu\text{C}/\text{cm}^2$ and $E_c = 13.8$ kV/cm at an applied field up to 25.9 kV/cm. This novel result demonstrates the importance of Fe_3BO_6 in devising newer ferroelectric material with superior functionalized properties of surface confined ideal single domains.

3.3. Dielectric characteristics

As described elsewhere,^{36,37} the frequency dependent complex dielectric permittivity of a material thus can be written in a simple form as

$$\varepsilon = \varepsilon' - j\varepsilon'', \quad (1)$$

where ε is the resultant value with ε' the real part and ε'' the imaginary part of it.

The $Z = Z' - jZ''$ value is related to the relative permittivity $\varepsilon = \varepsilon' - j\varepsilon'' = (j\omega C_0 Z)^{-1}$, where $\omega = 2\pi f$ is the angular frequency and $C_0 = \varepsilon_0 S \ell^{-1}$ is the geometrical capacitance with $\varepsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$ the permittivity of the free space and S the area of the electrode deposited on the sample of thickness ℓ .

The power-loss can be expressed as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}. \quad (2)$$

An antiferromagnetic spins reorientation transition at 415 K with Néel temperature $T_N = 508 \text{ K}$,^{3,11} of compound Fe_3BO_6 provides a model system for devising multifunctional properties for actuators, transducers, and storage devices. In this argument, ε_r -value and power loss have been studied at different temperatures 300–550 K and frequencies 0.1– 10^3 kHz of Fe_3BO_6 nanoplates. Figure 6 plots ε_r -values measured as a function of frequency at different temperatures such as (a) 375 K (b) 400 K, (c) 425 K, and (d) 450 K. The inset presents a modified profile in enhanced ε_r -value at room temperature. As it is portrayed in the inset, at room temperature, ε_r -value gets enhanced to be as large as ~ 350 at low frequency such as 100 Hz due to the presence of a bonded B_2O_3 surface layer on the Fe_3BO_6 nanoplates. The ε_r -value, which is decreasing regularly on increasing frequency from 0.1 to 10^3 kHz, rises-up progressively in a thermally activated dielectric polarization process of the charge carriers on

Fig. 6. Frequency dependence variation of ε_r -value for Fe_3BO_6 nanoplates at different temperatures such as (a) 375 K (b) 400 K, (c) 425 K, and (d) 450 K. The inset presents a modified profile in enhanced ε_r -value at room temperature.

Fig. 7. Temperature dependence variation of ε_r -value for Fe_3BO_6 nanoplates at different frequencies (a) 1 kHz, (b) 10 kHz, (c) 50 kHz, (d) 100 kHz, (e) 500 kHz, and (f) 1000 kHz.

increasing temperatures.³⁸ Two kinds of the charge carriers can be proposed on account of the frequency dependence ε_r -value. At low frequencies, the charges accumulate at the interface between the sample and electrodes, i.e., the space charge polarization, describing so high ε_r -value which falls down rapidly against the frequencies. When one considers free charge motion of the majority carriers, such species primarily include oxygen ion vacancies and/or interstitials which could pick-up a credibly fast temperature limited thermal diffusion. Figure 7 shows the temperature dependence variation of ε_r -value at different frequencies (a) 1 kHz, (b) 10 kHz, (c) 50 kHz, (d) 100 kHz, (e) 500 kHz, and (f) 1000 kHz. In Fig. 7, the ε_r -value, which decreases regularly on increasing the frequency, traces a prominent peak at 445 K (a magnetic transition $\Gamma_2 \rightarrow \Gamma_4$) after a weak peak at 330 K when plotted against temperature. Two kinds of the charge species from the surface and core in Fe_3BO_6 can emerge two distinct peaks in a magnetic or ferroelectric transition on thermal induced deviation in their dynamics. The main peak ascribes to the core with a satellite peak shown from the surface species. The weak peak of 330 K infers to a charge reordering in the surface species.

Figure 8 shows the frequency dependence variation of power-loss at different temperatures such as (a) 300 K, (b) 325 K, (c) 375 K, (d) 425 K, (e) 475 K, and (g) 525 K for Fe_3BO_6 nanoplates. The inset plots a peculiarly enhanced power-loss at onset of the T_N point. In Fig. 8, the power-loss decreases with increasing frequency while it increases on increasing the temperature. At low temperatures (at frequencies below 10 kHz), the power-loss is almost frequency independent. Strong low frequency dispersion up to 10 kHz in the power-loss plot is a consequence of the onset of DC conductivity probably due to the oxygen ion vacancies. Figure 9 shows the temperature dependence variation of power-loss for Fe_3BO_6 nanoplates at different frequencies (a) 10 kHz, (b) 50 kHz, (c) 100 kHz, (d) 500 kHz, and

Fig. 8. Frequency dependence variation of power-loss at different temperatures such as (a) 300 K, (b) 325 K, (c) 375 K, (d) 425 K, (e) 475 K, and (g) 525 K for Fe_3BO_6 nanoplates. The inset plots a peculiarly enhanced power-loss at onset of the T_N point.

Fig. 9. Temperature dependence variation of power-loss for Fe_3BO_6 nanoplates at different frequencies (a) 10 kHz, (b) 50 kHz, (c) 100 kHz, (d) 500 kHz, and (e) 1000 kHz.

(e) 1000 kHz. In Fig. 9, A magnetic transition $\Gamma_2 \rightarrow \Gamma_4$ is obtained at 435 K with a charge reordering near 325 K. This is possibly due to preponderant DC conductivity contribution as a consequence of large grain boundaries favoring inter-grain conductivity. For temperatures above the transition point, a sharp increase of the dielectric loss is representative of thermally activated charge carriers. It is strongly frequency dependent as it involves interaction of free charge carriers in the grain boundaries with an increased conductivity.^{39,40}

4. Conclusions

In summary, a new class of a magnetodielectric compound is developed by self-combustion method in a specific shape of Fe_3BO_6 nanoplates in correlation to the microstructure. The formation of a single phase Fe_3BO_6 compound was

confirmed through XRD pattern. Magnetic transition is observed in dielectric characteristic plot which can be correlated with magnetic properties. The ferroelectric features arise from a canted antiferromagnetic Fe^{3+} ordering in a self-confined Fe_3BO_6 . Due to the presence of both ferromagnetic as well as polarization ordering, Fe_3BO_6 behaves like a single phase multiferroic ceramics. Co-existence of magnetic and dielectric properties in such compounds is highly important for magnetoelectric devices, sensors, and other applications.

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References

- J. P. Attfield, A. M. T. Bell, L. M. R. Martinez, J. M. Greneche, R. Retoux, M. Leblanc, R. J. Cernik, J. F. Clarke and D. A. Perkins, Synthesis, structure and properties of a semivalent iron oxoborate, Fe_2OBO_3 , *J. Mater. Chem.* **9**, 205 (1999).
- J. L. C. Rowsell, J. Gaubicher and L. F. Nazar, A new class of materials for lithium-ion batteries: Iron (III) borates, *J. Power Sources* **97–98**, 254 (2001).
- L. T. Tsymbal, Y. B. Bazaliy, L. N. Bezmaternykh, A. S. Waniewska, S. V. Vasiliev, N. Nedelko, A. I. Linnik, A. N. Cherkasov, Y. I. Nepochatykh, V. Y. Dmitrenko, G. N. Kakazei and P. E. Wigen, Orientation phase transition in Fe_3BO_6 : Experimental determination of the order of the transition, *Phys. Rev. B* **74**, 134429 (2006).
- S. Shimomura, S. Nakamura, N. Ikeda, E. Kaneko, K. Kato and K. Kohn, Structural properties of a mixed valence compound Fe_2BO_4 , *J. Magn. Magn. Mater.* **310**, 793 (2007).
- M. S. Andújar, A. C. Couceiro and M. A. S. Rodríguez, Characterization of the charge ordering state by maximum entropy method, *Solid State Commun.* **141**, 615 (2007).
- X. Shi, C. Chang, J. Xiang, Y. Xiao, L. Yuan and J. Sun, Synthesis of nanospherical Fe_3BO_6 anode material for lithium-ion battery by the rheological phase reaction method, *J. Solid State Chem.* **181**, 2231 (2008).
- D. C. Freitas, M. A. Continentino, R. B. Guimarães, J. C. Fernandes, J. Ellena and L. Ghivelder, Structure and magnetism of homometallic ludwigites: $\text{Co}_3\text{O}_2\text{BO}_3$ versus $\text{Fe}_3\text{O}_2\text{BO}_3$, *Phys. Rev. B* **77**, 184422 (2008).
- Y. Liu, S. Peng, Y. Ding, C. Rong, J. Kim, J. P. Liu, Z. L. Wang and S. Sun, Synthesis and characterization of ferroferriboate (Fe_3BO_5) nanorods, *Adv. Func. Mater.* **19**, 3146 (2009).
- L. A. Bauer, N. S. Birenbaum and G. J. Meyer, Biological applications of high aspect ratio nanoparticles, *J. Mater. Chem.* **14**, 517 (2004).
- J. Dobson, Remote control of cellular behaviour with magnetic nanoparticles, *Nat. Nanotechnol.* **3**, 139 (2008).
- V. Buchelnikov, N. Danshin, D. Dolgushin, A. Isotov, V. Shavrov, L. T. Tsymbal, G. Kakazei, T. Takagi and P. Wigen, The magnetoacoustic anomaly in Fe_3BO_6 , *J. Magn. Magn. Mater.* **272–276**, 2113 (2004).

- ¹²R. Diehl and G. Brandt, Refinement of the crystal structure of Fe_3BO_6 , *Acta Cryst. B* **31**, 1662 (1975).
- ¹³A. V. Kimel, A. Kirilyuk, A. Tsvetkov, R. V. Pisarev and T. Rasing, Laser-induced ultrafast spin reorientation in the anti-ferromagnet TmFeO_3 , *Nature (London)* **429**, 850 (2004).
- ¹⁴N. P. Duong, T. Satoh and M. Fiebig, Ultrafast manipulation of antiferromagnetism of NiO , *Phys. Rev. Lett.* **93**, 117402 (2004).
- ¹⁵G. Catalan and J. F. Scott, Physics and applications of bismuth ferrite, *Adv. Mater.* **21**, 2463 (2009).
- ¹⁶E. K. H. Salje, *Phase Transformations in Ferroelectrics, Ferroelastic And Co-Elastic Crystals* (Cambridge University Press, Cambridge, 1990).
- ¹⁷H. Qi and Q. Chen, Preparation of plywood-like Fe_3BO_5 nanorods by a facile hydrothermal method at low temperature, *Chem. Lett.* **37**, 752 (2008).
- ¹⁸S. Ram, Crystallization of acicular platelet particles of W-type hexagonal strontium ferrite for magnetic recording applications, *J. Mater. Sci.* **25**, 2465 (1990).
- ¹⁹S. Ram, Infrared study of the dynamics of boroxol rings in the crystallization of $\text{BaFe}_{12}\text{O}_{19}$ microcrystals in borate glasses, *Phys. Rev. B* **51**, 6280 (1995).
- ²⁰S. Ram, Crystallisation of $\text{BaFe}_{12}\text{O}_{19}$ Hexagonal ferrite with an aid of B_2O_3 and the effects on microstructure and magnetic properties useful for permanent magnets and magnetic recording devices, *J. Magn. Magn. Mater.* **82**, 129 (1989).
- ²¹S. Ram, K. Kumari and R. K. Kotnala, Synthesis of norbergite Fe_3BO_6 of single crystallites from a borate glass, *Trans. Ind. Ceram. Soc.* **69**(3), 165 (2010).
- ²²K. Kumari, S. Ram and R. K. Kotnala, Frequency-temperature dependent dynamics of dielectrics in ferric oxoborate Fe_3BO_6 of cocktail structure of nanorods, *Philos. Mag. Lett.* **91**, 498 (2011).
- ²³J. Yang, X. Li, J. Zhou, Y. Tang, Y. Zhang and Y. Li, Factors controlling pure phase magnetic BiFeO_3 powders synthesized by solution combustion synthesis, *J. Alloys Compd.* **509**, 9271 (2011).
- ²⁴A. B. Salunkhe, V. M. Khot, M. R. Phadatare and S. H. Pawar, Combustion synthesis of cobalt ferrite nanoparticles-Influence of fuel to oxidizer ratio, *J. Alloys Compd.* **514**, 91 (2012).
- ²⁵R. Köferstein, Synthesis, phase evolution and properties of phase-pure nanocrystalline BiFeO_3 prepared by a starch-based combustion method, *J. Alloys Compd.* **590**, 324 (2014).
- ²⁶<https://www.chemed.com/cid/28-017-2/Camphor.pdf>.
- ²⁷J. G. White, A. Miller and R. E. Nielsen, Fe_3BO_6 , a borate isostructural with the mineral norbergite, *Acta Cryst. B* **19**, 1060 (1965).
- ²⁸W. F. McClume, JCPDS X-ray Powder Diffraction Files (a) 73-1385: Fe_3BO_6 , Joint committee on powder diffraction standards, International centre for diffraction data, Swarthmore, USA (1999).
- ²⁹A. Planes, L. Mañosa and M. Acet, Magnetocaloric effect and its relation to shape-memory properties in ferromagnetic heusler alloys, *J. Phys.: Condens. Matter* **197**, 233201 (2009).
- ³⁰L. Mañosa, D. G. Alonso, A. Planes, E. Bonnot, M. Barrio, J.-L. Tamarit, S. Aksoy and M. Acet, Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy, *Nat. Mater.* **9**, 478 (2010).
- ³¹E. S. Taulats, P. O. C. Villa, L. Mañosa, C. Frontera, S. Pramanick, S. Majumdar and A. Planes, magnetocaloric effect in the low hysteresis Ni-Mn-In metamagnetic shape-memory heusler alloy, *J. Appl. Phys.* **115**, 173907 (2014).
- ³²J.-H. Lee, Y. K. Jeong, J. H. Park, M.-A. Oak, H. M. Jang, J. Y. Son and J. F. Scott, Spin-canting-induced improper ferroelectricity and spontaneous magnetization reversal in SmFeO_3 , *Phys. Rev. Lett.* **107**, 117201 (2011).
- ³³Y. Qin, X. Q. Liu and X. M. Chen, Dielectric, ferroelectric and magnetic Properties of Mn-doped LuFeO_3 Ceramics, *J. Appl. Phys.* **113**, 044113 (2013).
- ³⁴M. Shang, C. Zhang, T. Zhang, L. Yuan, L. Ge, H. Yuan and S. Feng, The multiferroic perovskite YFeO_3 , *Appl. Phys. Lett.* **102**, 062903 (2013).
- ³⁵T. Wang, L. Jin, C. Li, Q. Hu and X. Wei, Relaxor ferroelectric $\text{BaTiO}_3\text{-Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ ceramics for energy storage application, *J. Am. Ceram. Soc.* **98**, 559 (2015).
- ³⁶J. R. Macdonald, *Impedance Spectroscopy* (John Wiley and Sons, New York, 1987).
- ³⁷R. V. Hippel, *Dielectric Materials and Applications* (Technology Press, New York, 1954).
- ³⁸A. Shukla, N. Shukla and R. N. P. Choudhary, Dielectric characteristics of La-modified PbTiO_3 nanoceramics, *Phase Transit.* **90**, 362 (2017).
- ³⁹O. Raymond, R. Font, N. S. Almodovar and J. M. Siqueiros, Frequency temperature response of ferroelectromagnetic $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramics obtained by different precursors. Part I. structural and thermo-electrical characterization, *J. Appl. Phys.* **97**, 084107 (2005).
- ⁴⁰T. Wang, J. Hu, H. Yang, L. Jin, X. Wei, C. Li, F. Yan and Y. Lin, Dielectric relaxation and Maxwell-Wagner interface polarization in Nb_2O_5 doped $0.65\text{BiFeO}_3\text{-}0.35\text{BaTiO}_3$ ceramics, *J. Appl. Phys.* **121**, 084103 (2017).