The structural, electrical and magnetic properties of perovskite (1-x)Ba(Fe$_{1/2}$Nb$_{1/2}$)O$_3$–xBaTiO$_3$ ceramics

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ABSTRACT

Lead-free pseudo-binary compounds (1-x)Ba(Fe$_{1/2}$Nb$_{1/2}$)O$_3$–xBaTiO$_3$; ($0 \leq x \leq 1$) have been synthesized at 1200°C using conventional ceramic technique and characterized by X-ray diffraction, scanning electron microscopy, dielectric and vibration sample magnetometer studies. The crystal structure of the compounds is found to be monoclinic with the space group *P*2/*m* except for BaTiO$_3$ for which it is tetragonal (*P*4/*mmm*). The incorporation of BaTiO$_3$ significantly reduces the dielectric loss and improve the frequency and temperature stability of the dielectric properties of Ba(Fe$_{1/2}$Nb$_{1/2}$)O$_3$. Compound 0.25Ba(Fe$_{1/2}$Nb$_{1/2}$)O$_3$-0.75BaTiO$_3$ exhibited a low value of temperature coefficient of capacitance ($< \pm 3\%$) in the working temperature range (up to +85°C), room temperature dielectric constant equal to 282 and low loss tangent (~10^{-2}) which meets the specifications for "Z5D" of Class II dielectrics of *Electronic Industries Association*. Hence, this composition might be a suitable candidate for capacitor applications. Besides, magnetic studies indicated the possibility of magneto-electric coupling in the system. Copyright © 2014 VBRI press.

Keywords: Lead-free; perovskite; permittivity; ceramic; capacitor; magnetic behavior.

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Introduction

In recent years, development of perovskite ABO_3-type environment-friendly materials exhibiting high dielectric constant, are of considerable interest as they play important role in microelectronics and various other technological applications. Among them much attention has been paid nowadays on $Ba(Fe_{1/2}Nb_{1/2})O_3$ (abbreviated as BFN) which show giant dielectric constant $\sim 10^4$ [1]. Besides, $BaTiO_3$ (abbreviated as BT) is a well-known perovskite ferroelectric, which shows high dielectric constant and low dielectric loss. BT finds widespread applications as a capacitor material. Furthermore, it is observed that BFN is having high dielectric loss, which limits its uses for practical purposes. Therefore, efforts are being made to lower down the dielectric loss without affecting its dielectric constant. Recently, solid solutions of BFN with $BaTiO_3$ [2-8], $SrTiO_3$ [8-10], $Ba(Zr,Ti)O_3$ [11], $PbZr_{0.52}Ti_{0.48}O_3$ [12] have been reported to modify its performance characteristics. It is observed that addition of BT into BFN lower down the dielectric loss of BFN [2]. Also, both the compounds are lead-free and ensure environment-friendly applications. However, the information about the phase structure as well as electrical properties of BFN and BT solid-solution are still not complete and consistent. Besides, magnetoelectric materials are promising to possess better adjustability for regulating electromagnetic parameters of EM wave absorption materials, due to the coexistence of dielectric polarization and magnetic polarization processes, arousing great interest in researchers [13]. Also, such materials find widespread applications in information storage, sensors, spintronic devices, multistage memory elements, etc. [14]. Therefore, it is expected the solid solutions of $Ba(Fe_{1/2}Nb_{1/2})O_3$ and $BaTiO_3$ may show magnetic property as it contains iron as one of the constituent element. Furthermore, magnetic property of this system is not yet carried out and hence deserved further investigation.

Keeping in view the growing interest in BFN and BFN-based solid solutions, present work reports the structural (X-ray and their Rietveld analyses), microstructural, dielectric and magnetic properties of pseudo-binary perovskite $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3–xBaTiO_3$ (abbreviated hereafter BFN-BT) solid-solutions with different compositions ($x = 0, 0.25, 0.50, 0.75$ and 1.0).

Experimental

Materials and method

Polycrystalline samples of $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3–xBaTiO_3$; $x = 0, 0.25, 0.50, 0.75$ and 1.0 were prepared using AR grade (99.9%+ pure) chemicals: $BaCO_3$ (Merck, Germany) Fe_2O_3 (Strem Chemicals, USA), Nb_2O_5 (Aldrich, USA) and TiO_2 (Aldrich, USA) by solid-state synthesis route. The optimized calcination and sintering conditions used were 1200°C for 5 h and 1250°C for 4h, respectively, under air atmosphere. Completion of the reaction and formation of the desired compound were checked by X-ray diffraction (XRD) technique. The detailed procedure adopted for the preparation of the BFN-BT ceramics is described elsewhere [1].

The XRD data were taken on sintered pellets of BFN-BT with an X-ray diffractometer (XPERT-PRO, Pan Analytical) at room temperature, using CuK_α radiation ($\lambda = 1.5405$ Å), over a wide range of Bragg angles ($20° \leq 2\theta \leq 80°$) with a scanning speed of $5.08°$ min^{-1}. The crystal structure, space group, dimensions of the unit cell and *hkl* values were obtained from Rietveld refinement using the software FullProf 2012. A sintered pellet of each composition was polished and electroded with air-drying silver paste (SPI supplier, USA) to measure the electrical properties. Real and imaginary parts of the electrical impedance were measured as a function of frequency (1 Hz - 1 MHz) and temperature (20°C - 450°C) using a computer-controlled Solartron SI1260 impedance/gain-phase analyser. The real and imaginary parts of permittivity were obtained from the impedance data using the relations:

$$\varepsilon'(\omega) = Z'' / \omega C_o |Z|^2 \quad \text{and} \quad \varepsilon''(\omega) = Z' / \omega C_o |Z|^2, \quad \text{where}$$

$|Z| = [(Z')^2 + (Z'')^2]^{1/2}$. Further, the temperature coefficient of capacitance (T_{CC}) which is an important parameter for the low-temperature dependence of capacitance is defined as: $T_{CC}(\%) = [(C_T - C_{RT})/C_{RT}] \times 100$; where C_T and C_{RT} represent the values of capacitance at the elevated and at room temperature, respectively. The magnetization behavior was studied using a vibrating sample magnetometer (model PAR-155).
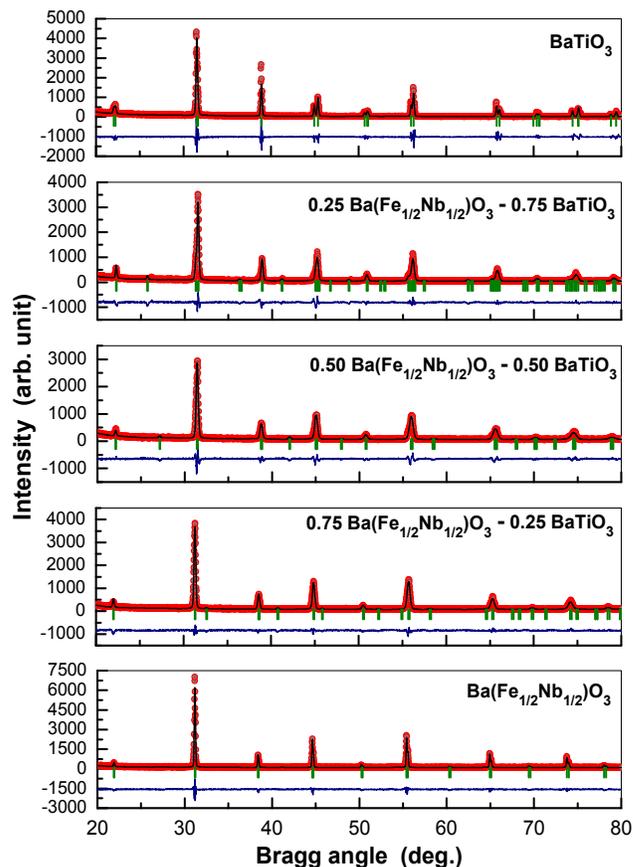

Fig. 1. Rietveld refined pattern of $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3–xBaTiO_3$; $x = 0$, 0.25, 0.50, 0.75 and 1.0 ceramics. Symbols represent the observed data points and the solid lines their Rietveld fit.
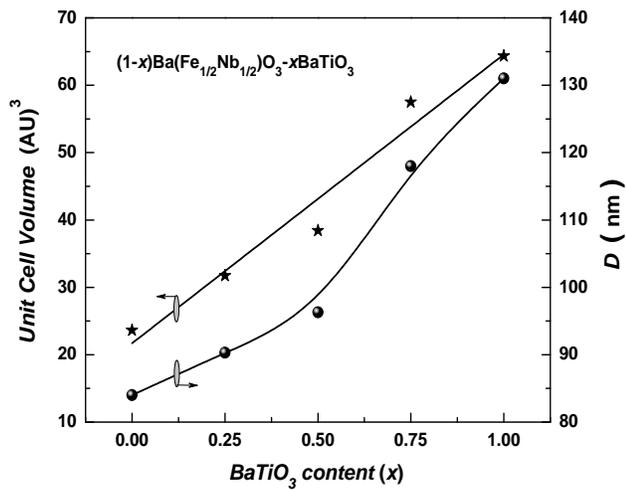
Fig. 2. Variation of apparent particle size and unit cell volume with composition of $(1-x)\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 - x\text{BaTiO}_3$; x = 0, 0.25, 0.50, 0.75 and 1.0 ceramics.

Table 1. The crystal data and refinement factors of $(1-x)\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 - x\text{BaTiO}_3$; x = 0, 0.25, 0.50, 0.75 and 1.0 ceramics obtained from X-ray powder diffraction data.

Parameters	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1.0$
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P2/m$	$P2/m$	$P2/m$	$P2/m$	$P4/mmm$
a (Å)	4.0584	4.0476	4.1108	5.8513	3.9956
b (Å)	2.8698	2.8579	2.8453	2.8379	3.9956
c (Å)	2.0290	2.7486	3.3579	4.0883	4.0310
α (°)	90.000	90.000	90.000	90.000	90.000
β (°)	90.004	93.182	101.866	122.139	90.000
γ (°)	90.000	90.000	90.000	90.000	90.000
V (Å³)	23.6317	31.7459	38.4377	57.4850	64.3535
R_p	39.8	31.2	34.0	33.2	40.7
R_{wp}	31.1	26.8	31.8	33.7	41.1
R_{exp}	17.2	17.1	17.1	16.3	16.6
R_B	1.87	1.18	1.10	1.91	5.59
R_F	1.49	1.72	1.19	2.17	4.08
χ^2	8.15	3.12	4.08	4.88	6.113
d	1.1051	0.9155	0.7872	0.5448	0.657
Q_D	1.8582	1.9055	1.9022	1.9022	1.8716
S	1.81	1.57	1.86	2.07	2.48

Description of parameters
R_p (profile factor) = $100[\Sigma|y_i\text{-}y_{ic}|/\Sigma|y_i|]$, where y_i is the observed intensity and y_{ic} is the calculated intensity at the ith step. R_{wp} (weighted profile factor) = $100[\Sigma\omega_i|y_i\text{-}y_{ic}|^2/\Sigma\omega_i(y_i)^2]^{1/2}$, where $\omega_i = 1/\sigma_i^2$ and σ_i^2 is variance of the observation. R_{exp} (expected weighted profile factor) = $100[(n\text{-}p)/\Sigma\omega_i(y_i)^2]^{1/2}$, where n and p are the number of profile points and refined parameters, respectively. R_B (Bragg factor) = $100[\Sigma|I_{obs}\text{-}I_{calc}|/\Sigma|I_{obs}|]$, where I_{obs} is the observed integrated intensity and I_{calc} is the calculated integrated intensity. R_F (crystallographic R_F factor) = $100[\Sigma|F_{obs}\text{-}F_{calc}|/\Sigma|F_{obs}|]$, where F is the structure factor, $F = \sqrt{(I/L)}$, where L is Lorentz polarization factor. $\chi^2 = \Sigma\omega_i(y_i\text{-}y_{ic})^2$. d (Durbin–Watson statistics) = $\Sigma\{[\omega_i(y_i\text{-}y_{ic})\text{-}\omega_{i\text{-}1}(y_{i\text{-}1}\text{-}y_{ic\text{-}1})]^2\}/\Sigma[\omega_i(y_i\text{-}y_{ic})]^2$. Q_D = expected d. S (goodness of fit) = (R_{wp}/R_{exp}).

Results and discussion

Fig. 1 depicts the observed, calculated and difference XRD profiles for BFN-BT after the final cycles of Rietveld refinements. It can be seen that the profiles for observed and calculated one are perfectly matching. The XRD profile fitting procedure adopted was minimizing the χ^2 function. The crystal data and refinement factors of BFN-BT obtained from XRD data are depicted in **Table 1**. XRD analyses indicated that BaTiO3 added BFN system do not change their basic (monoclinic with space group $P2/m$) structure rather some shifting in the peak positions and

changes in intensities of the peaks could be observed. It is observed that the value of unit cell volume increases with the increasing BaTiO3 content (**Fig. 2**), which could be due to the partial replacement of pseudo-cation $(\text{Fe}_{1/2}^{3+}\text{Nb}_{1/2}^{5+})^{4+}$ with Ti^{4+}. A linear least square fitting to concentration dependence of unit cell volume data yielded the relation: $V = 21.6942 - 42.8731x$ with r^2 = 0.9557. The apparent particle sizes (D) of BFN-BT were estimated using the Debye-Scherrer formula: $D = 0.89\lambda/B\cos\theta$, where B = full width at half maximum. An increase in the apparent particle size is observed with the increasing BaTiO3 content (**Fig. 2**).
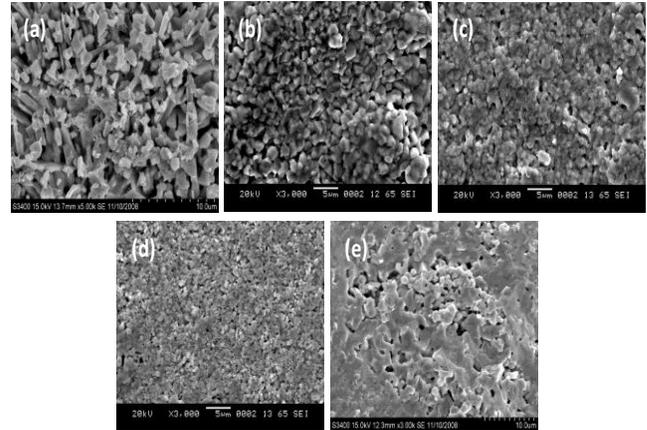

Fig. 3. Scanning electron micrographs of $(1-x)\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 - x\text{BaTiO}_3$ ceramics (a) x = 0, (b) x = 0.25, (c) x = 0.50, (d) x = 0.75 and (e) x = 1.0.

Fig. 3 shows the scanning electron micrographs of the fractured surface of BFN-BT ceramics. The photographs contain a very few voids suggesting the high density of the materials. The grains of unequal sizes (1-3 μm) appear to be distributed throughout the samples. It is also observed that a few number of grains are agglomerated, grow rapidly to a larger size relative to the average size which is termed as an abnormal grain growth or secondary crystallization. The ratio of the average particle size to the grain size for all the compositions is found to be of the order of 10^{-2}.

Fig. 4(a-e) illustrates the temperature dependence of real and imaginary parts of dielectric constant of BFN-BT ceramics at different frequencies. It is seen that the values of ε' and ε'', in general, increases for all the compounds except BaTiO3 in which the plot shows a broad maximum, T_m (*i.e.* diffuse phase transition, DPT) at 120°C. **Fig. 5** shows the compositional dependence of ε' and ε'' for BFN-BT ceramics at room temperature. It can be seen that the values of ε'' decreases with the increment in BT content (x) while ε' finds a minimum for x = 0.75. Furthermore, it is well known that BaTiO3 is an established material for capacitor applications. The value of T_{CC} is observed to be minimum for x = 0.75 (**Fig. 6**). Also, inset **Fig. 6** clearly illustrates that the values of T_{CC} varies within ± 3% for $0.25\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$ while for BaTiO3 it is less than ± 9% in the working temperature range (upto +85°C). Therefore, the lowest value of T_{CC} (< ±3%), ε' (= 282) and low tanδ (~10^{-2}) were found in case of $0.25\text{Ba}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-}0.75\text{BaTiO}_3$, which meets the

specifications for "Z5D" of Class II dielectrics of *Electronic Industries Association*. Therefore, adding 75% $BaTiO_3$ to $Ba(Fe_{1/2}Nb_{1/2})O_3$ led to the mark improvement in T_{CC}. Hence, this compound may be considered as a potential candidate for capacitor applications.
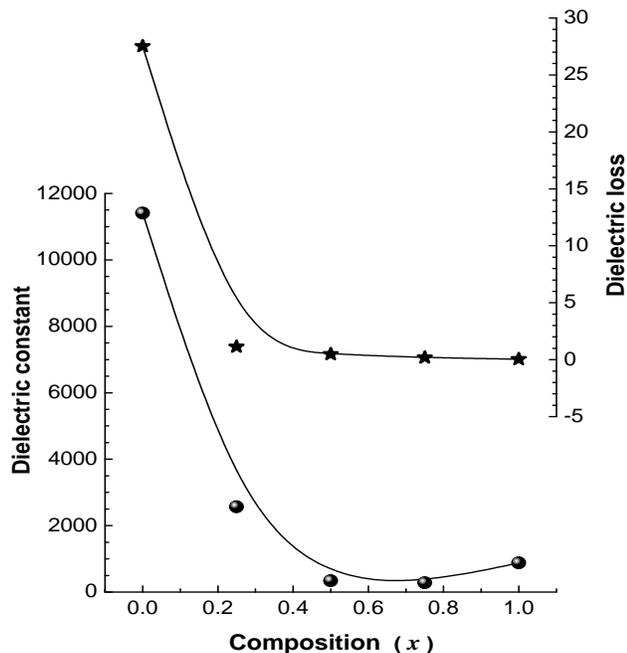

Fig. 4. Compositional variation of dielectric constant and dielectric loss of $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3$-$xBaTiO_3$ ceramics.
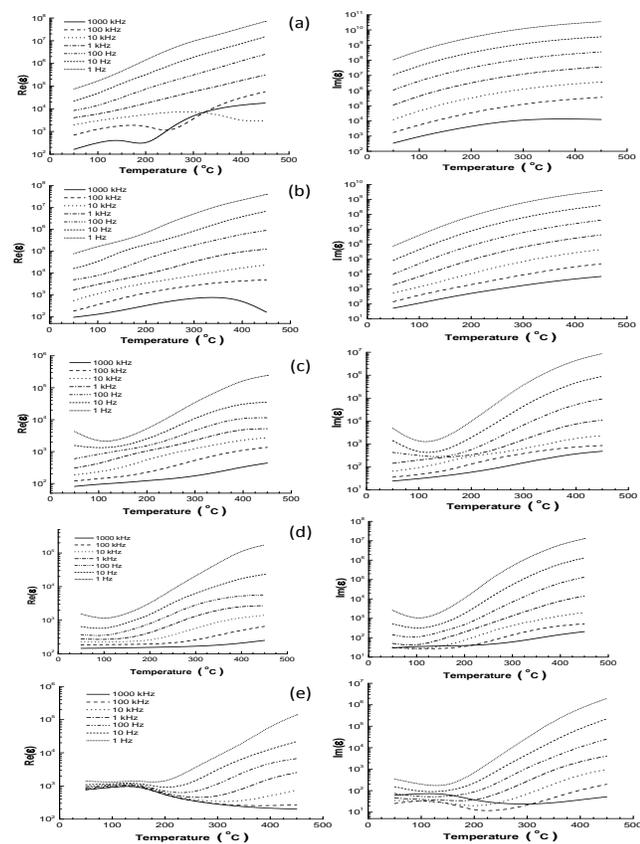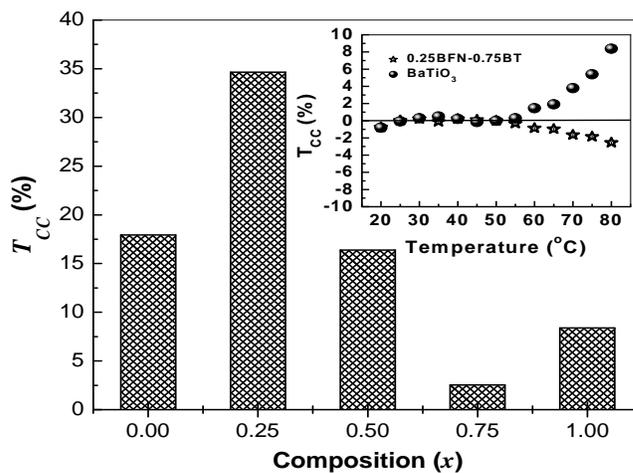

Fig. 5. Variation of real and imaginary parts of dielectric constant with temperature at different frequencies for $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3$–$xBaTiO_3$ ceramics (a) $x = 0$, (b) $x = 0.25$, (c) $x = 0.50$, (d) $x = 0.75$ and (e) $x = 1$.

Fig. 6. Compositional variation of $T_{CC}(\%)$ of $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3$-$xBaTiO_3$ ceramic. Inset: Variation of $T_{CC}(\%)$ with temperature for $x = 0.75$ and 1.0.
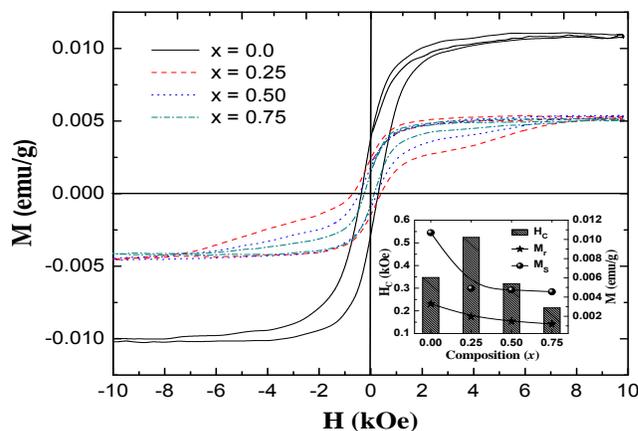

Fig. 7. Magnetization curves for $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3$–$xBaTiO_3$; $x = 0$, 0.25, 0.50 and 0.75 ceramics at room temperature. Inset: Compositional variation of H_C, M_r and M_S.

Fig. 7 shows the magnetization versus an applied field (M-H) for BFN-BT at room temperature. M-H data showed a well-saturated weak ferromagnetic hysteresis for all the compounds. Inset of **Fig. 7** shows variation of coercive field (H_C), remanent magnetization (M_r) and saturation magnetization (M_S) with increasing BT-content. Low values of H_C are found in all the compounds, which is suitable for the recording applications. Also, the values of M_r and M_S decrease with increasing BT-content. This study clearly indicates that there is a possibility of magneto-electric coupling, suggesting electric ordering controlling magnetic properties at the microscopic scale.

Conclusion

Polycrystalline $(1-x)Ba(Fe_{1/2}Nb_{1/2})O_3$–$xBaTiO_3$; $(0 \leq x \leq 1)$ prepared using a high-temperature solid-state reaction technique, were found to have a perovskite-type monoclinic structure with the space group $P2/m$ except $BaTiO_3$ (tetragonal, $P4mm$). Dielectric study revealed that the compound $0.25Ba(Fe_{1/2}Nb_{1/2})O_3$-$0.75BaTiO_3$ is having low ε' and ε'' and a low T_{CC} (< ±3%) in the working

temperature range (upto +85°C) which makes this composition suitable for capacitor application and may be designated as 'Z5D' *Class* II material as per the specifications of the *Electronic Industries Association*. Magnetic study indicated the possibility of magneto-electric coupling.

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