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The Devonshire thermodynamic theory cannot be used to describe systems with broad phase transitions, such as SBN, and no other quantitative interpretation of the dielectric and pyroelectric behavior was attempted.

The nature of the electrodes and specimen thickness had a pronounced effect on the dielectric properties of SBN, presumably due to low permittivity layers at the electrode-ferroelectric interface.

Analysis of the theory of pyroelectric detection showed that the merit of a detector material is determined by the ratio $\lambda/\sigma^{1/2}$ for the frequency range where Nyquist noise is dominant, and either by λ/κ' , or λ (depending on whether the load capacitance is smaller or greater than the detector capacitance) at high frequencies when amplifier noise is dominant. Because of dielectric relaxation σ and κ' decrease with increasing frequency thus tending to improve these figures of merit. From the data presented, and the theoretical analysis it is possible to choose the detector material composition, or bias field, best suited for individual experimental situations. For general use, when linearity of response with input power is not the primary requirement, it seems that SBN with $x=0.33$ is the most useful, using the edge electrode configuration (light incident normal

to the crystal polar axis). This detector has a detectivity D^* of 1.4×10^8 cm(cps) $^{1/2}$ W $^{-1}$ and a responsivity of 53 V/W at 1 kHz, and no observable oscillatory piezoelectric signals due to mechanical resonances up to 50 MHz. The responsivity and detectivity decrease with increasing frequency.

At present SBN has a faster response than any other room temperature operating thermal detector. The response can be made flat over a wide spectral range, and detectors can be used without any window materials. Thus in situations where detector sensitivity is less important than high frequency response, room temperature operation, or broad spectral response, SBN is a very useful detector.

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Mössbauer Effect in the Ferroelectric $PbTiO_3$ - $BiFeO_3$ Solid Solutions*

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The Mössbauer spectra of the system $(PbTiO_3)_{0.95}(BiFeO_3)_{0.05}$ have been studied from room temperature to 585°C. From the isomer-shift of 0.491 ± 0.02 mmsec $^{-1}$ at room temperature, the ionicity is found to be 60% \pm 20%. A discontinuity in the plot of isomer-shift versus temperature at T_c is observed. The quadrupole splitting at room temperature is 0.295 ± 0.02 mm/sec $^{-1}$. A dip in the Mössbauer fraction is observed at the Curie temperature.

INTRODUCTION

The Mössbauer effect has been employed to study phase transitions in some perovskite-type ferroelectrics such as $BaTiO_3$,¹ $SrTiO_3$,² and $PbFe_{1/2}Nb_{1/2}O_3$.^{3,4} We present here the results of such an investigation of the solid solution, $(PbTiO_3)_{0.95}(BiFeO_3)_{0.05}$.

$PbTiO_3$ is reported to be a tetragonally distorted

perovskite at room temperature with $c/a=1.063$.^{5,6} It is ferroelectric with a Curie temperature of about 490°C.⁷ It is cubic above 490°C. The x-ray and the electric properties of the $PbTiO_3$ - $BiFeO_3$ systems have been reported in great detail.^{8,9,10} In the system $PbTiO_3$ - $BiFeO_3$ there is a continuous series of solid solutions.⁸

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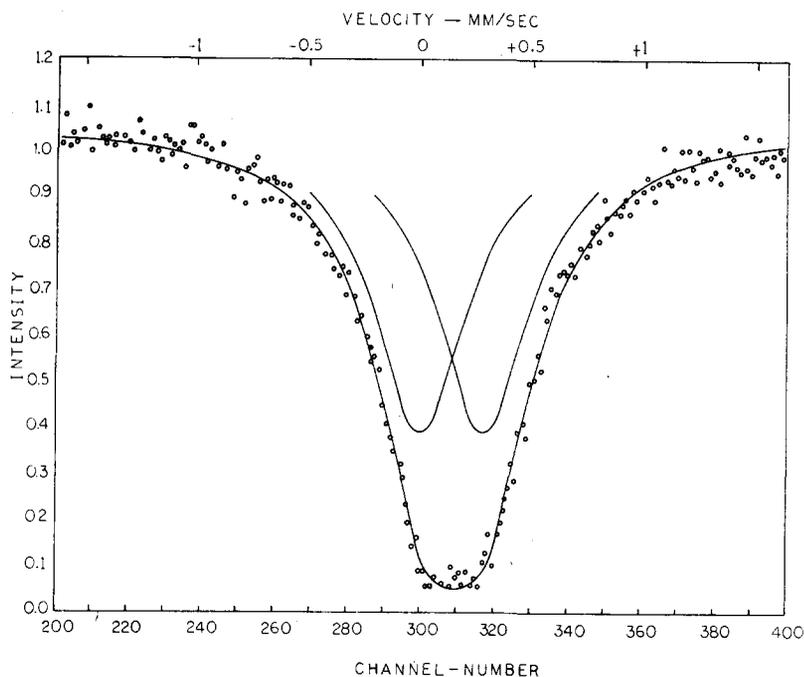


FIG. 1. Mössbauer absorption spectrum of $(\text{PbTiO}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$ at room temperature.

The structure is tetragonal to approximately 70 wt% of BiFeO_3 and then becomes rhombohedral. The tetragonal distortion (c/a) increases continuously from 1.063 to 1.169 up to 70 wt% of BiFeO_3 .

EXPERIMENTAL

The solid solution $(\text{PbTiO}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$ was prepared by reacting the constituent oxides (PbO , Bi_2O_3 , TiO_2 , and Fe_2O_3 enriched with ^{57}Fe to 90.3%) at 800°C for 1 h and then heated one more hour at 960°C . The formation of the solid solution was checked by x-ray diffraction.

The Mössbauer spectra were taken with a ^{57}Co source

in a copper matrix. The source was moved with respect to a stationary absorber. The apparatus was mounted vertically to enable the use of a powder sample with a minimum absorption loss due to the sample holder. The powder was deposited on a pure beryllium foil, 0.003-in. thick, using acetone as a suspension medium. The absorber temperature was monitored with a Chromel-Alumel thermocouple. Good uniformity of temperature was obtained and the fluctuations never exceeded more than $\pm 2^\circ\text{C}$ for days. The description of the apparatus used for the present work has been discussed elsewhere.¹¹ The source was at room temperature during the course of all temperature measurements.

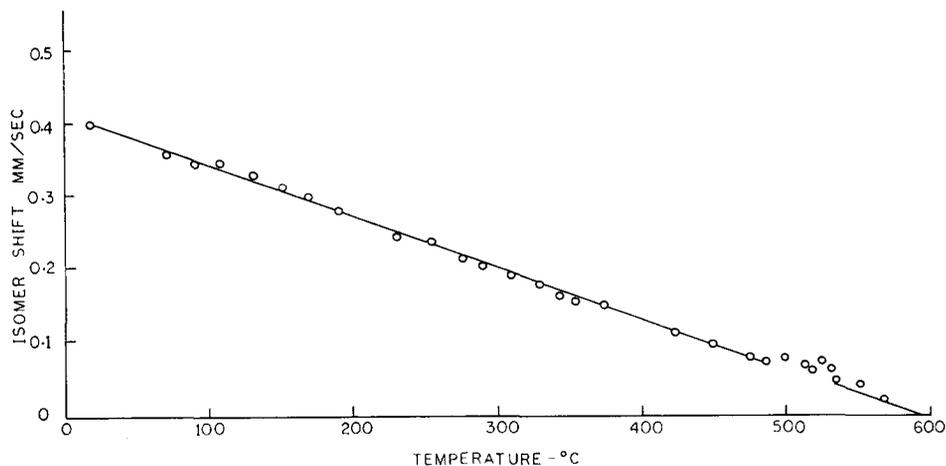


FIG. 2. Isomer shift with respect to iron as a function of temperature.

¹¹ J. P. Canner, Doctoral dissertation, University of Missouri-Rolla, 1969.

RESULTS AND DISCUSSION

The Mössbauer spectrum of $(\text{PbTiO}_3)_{0.95}(\text{BiFeO}_3)_{0.05}$ at room temperature is shown in Fig. 1. The resonance absorption spectrum in the ferroelectric region exhibits a weakly resolved doublet. In order to extract the Mössbauer parameters a least-square fit was made to the data. The isomer shift was found to be 0.49 ± 0.02 mm sec^{-1} at room temperature. This value of isomer shift is typical for a high spin Fe^{3+} ion. The observation of a high spin ferric state further confirms the EPR studies by Gainon.¹² The isomer-shift of 0.49 ± 0.02 mm sec^{-1} indicates that the sample is partially ionic. From the systematics of Bhide *et al.*¹³ the ionicity is found to be $60\% \pm 20\%$. The temperature dependence of the isomer shift $(1/E)(\partial E/\partial T)$ is -2.25×10^{-15} deg^{-1} , in good agreement with the theoretical value of the second-order Doppler shift arising from the lattice vibrations.¹⁴ A discontinuity in the plot of isomer shift and temperature (Fig. 2) at the phase transition may be explained as due to the change in the s -electron density at the iron nuclei.

The quadrupole splitting is 0.295 ± 0.02 mm sec^{-1} at room temperature. This value is smaller than that found by Nicholson and Burns¹⁵ for Fe-doped BaTiO_3

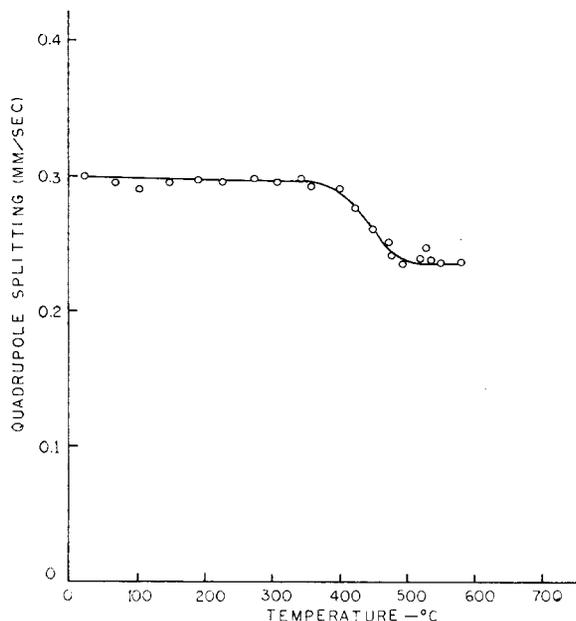


FIG. 3. Quadrupole splitting as a function of temperature.

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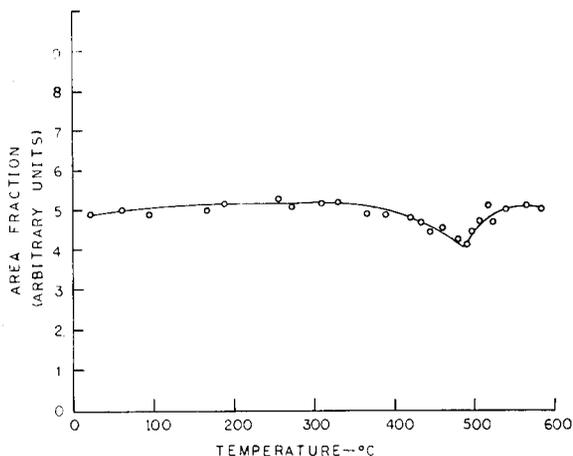


FIG. 4. Area under the absorption peak as a function of temperature.

and by Bhide *et al.*¹ for $^{57}\text{Co-BaTiO}_3$ even though PbTiO_3 is reported to be a more distorted perovskite compared to BaTiO_3 . This suggests that the displacement of the oxygen and lead ions in PbTiO_3 leaves the Ti ion in a more symmetric environment than that of Ti in BaTiO_3 . The variation of the quadrupole splitting with temperature is shown in Fig. 3. It is observed that the quadrupole splitting remains practically constant above the Curie temperature. The presence of quadrupole splitting above T_c has been reported by Bhide *et al.*¹⁶ for Fe- BaTiO_3 samples. The presence of quadrupole splitting even above the Curie temperature may be attributed to the random distribution of Fe and Ti ions on the B sites.

Figure 4 shows the temperature dependence of the area under the resonance curve. It is seen that the area under the curve decreases on approaching the Curie point from the paraelectric region, passes through a minimum, and then begins to increase with decrease of temperature. The minimum at the phase transition can be attributed to the temperature dependence of the frequency of the anomalous optical branch important in the theory of ferroelectrics.^{17,18} The Curie temperature is found to be $490^\circ \pm 10^\circ\text{C}$ from the minimum of this curve. This value is close to that estimated from electrical data¹⁰ within experimental error limits.

The Mössbauer spectra of the solid solutions containing $(\text{PbTiO}_3)_{0.80}(\text{BiFeO}_3)_{0.20}$ and $(\text{PbTiO}_3)_{0.60}(\text{BiFeO}_3)_{0.40}$ showed a well-resolved quadrupole splitting of 0.44 ± 0.02 and 0.50 ± 0.02 mm sec^{-1} respectively. These systems will be discussed in more detail in a later paper.¹⁹

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¹⁹ C. M. Yagnik *et al.* (unpublished).