and also made use of the normalization of $\langle|(x)|^2\rangle_{\rm av}$ determined from the generalized Ginzburg-Landau equations,[10]

$$\langle|\Delta|^2\rangle_{\rm av}=(\tfrac{1}{2}\pi)^{1/2}\,\frac{0.59eT}{\sigma}\times\frac{H_{c3}-H}{2\kappa_2^2(t)-0.334}[\Psi^{(1)}(\tfrac{1}{2}+\rho)]^{-1}. \quad \text{(A13)}$$

Finally, the surface impedance is given by

$$Z\cong R_n\left\{1+i-(2\pi)^{1/2}\left(\frac{\delta_0}{\xi(t)}\right)A_3(t)\left(\frac{H_{c3}-H}{H_{c3}}\right)\times[2\kappa_2^2(t)-0.334]^{-1}\right\}, \quad \text{(A14)}$$

and from (A14) we can derive $s_3^1(t)$:

$$s_3^1(t)=\frac{H_{c3}}{R_n}\left(\frac{\partial R(H)}{\partial H}\right)\bigg|_{H=H_{c3}}=(2\pi)^{1/2}\left(\frac{\delta_0}{\xi(t)}\right)\frac{A_3(t)}{2\kappa_2^2(t)-0.334}. \quad \text{(A15)}$$

It is also very easy to repeat the calculation for the configuration when the polarization vector $\mathbf{E}_\omega$ of the microwaves spans an angle θ with the dc magnetic field $\mathbf{H}$. A calculation similar to the one just performed gives

$$s_3(t,\theta)=(2\pi)^{1/2}\left(\frac{\delta_0}{\xi(t)}\right)\frac{A_3(t,\theta)}{2\kappa_2^2(t)-0.334}, \quad \text{(A16)}$$

and

$$A_3(t,\theta)=1-\sin^2\theta\frac{2[\Psi(\frac{1}{2}+5.60\rho)-\Psi(\frac{1}{2}+\rho)]}{(4.60)^2\rho\Psi^{(1)}(\frac{1}{2}+\rho)}. \quad \text{(A17)}$$

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Gamma-Irradiation Effects in Single-Crystalline Barium Titanate

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This study presents the results of an experimental investigation of Co^{60} γ-irradiation effects in single-crystalline barium titanate. Two test groups of crystals were utilized in this study. Prior to being irradiated, one group was etched in phosphoric acid at 145°C to remove a surface layer having properties which differ from the bulk of the crystal. The second group of crystals was irradiated in the as-grown condition. Following irradiation at various γ doses, the ferroelectric hysteresis loop was determined, measurements were taken of the optical absorption spectrum in the wavelength range 0.43–0.70 μ, and photomicrographs of the domain structure were obtained. The temperature was maintained at 20°C during irradiation, and all post-irradiation measurements were made at 23°C. The etched crystals were irradiated in the poled condition to a maximum dose of 1.60×10^9 rad. The remanent polarization P_r was unaffected by a total γ dose of about 2×10^8 rad. Irradiation to higher dose levels caused a reduction in P_r. The coercive field E_c was reduced with initial irradiation. At a dose of about 5×10^8 rad, a minimum value was reached and E_c then increased with continued irradiation. The domain structure of the c-domain crystals was unaffected by a total γ dose of 1.60×10^9 rad. No absorption peaks were observed in the wavelength range studied as a result of Co^{60} γ irradiation. The radiation-induced changes observed in the ferroelectric hysteresis loop of etched crystals cannot be attributed to changes in the domain structure or to the presence of point defects consisting of an oxygen vacancy with a single trapped electron. The unetched crystals were irradiated to a maximum dose of 2.91×10^8 rad. With initial irradiation, the polarization reversal process was enhanced as the remanent polarization increased and the coercive field decreased. With increasing dose above 2×10^7 rad, the hysteresis loop gradually deteriorated. The unetched crystals were found to be much more sensitive to Co^{60} γ radiation than were the etched crystals.

I. INTRODUCTION

The details of radiation effects upon the electrical properties of single-crystalline barium titanate are not well understood. A few investigations have been reported; however, in most cases the results are not consistent or in good agreement. The disagreement of experimental results has limited the development of a satisfactory model for radiation damage in $BaTiO_3$.

Lefkowitz and Mitsui[1] studied the effect of Co^{60} γ-ray and reactor irradiation on the hysteresis loop of single-crystalline $BaTiO_3$. For a neutron ($E>0.4$ eV) dosage of $2.8\times10^{16} n/\text{cm}^2$, they observed a decrease in coercive field and an increase in spontaneous polarization. Similar

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[1] I. Lefkowitz and T. Mitsui, J. Appl. Phys. **30**, 269 (1959).

results were reported for room-temperature Co^{60} γ-ray exposures to 1.15×10^8 R. Hayakawa and Ikushima[2] irradiated single-crystalline $BaTiO_3$ at room temperature with Co^{60} γ rays to a total dose of 10^7 rad. Post-irradiation measurements indicated the spontaneous polarization had nearly disappeared, and the hysteresis loop was almost linear. The authors suggested an oxygen-displacement mechanism as the cause of the observed changes in the hysteresis loop. Glower and Hester[3] have reported a detailed investigation of the effects of reactor irradiation on the hysteresis loop of $BaTiO_3$ single crystals. In this investigation, the crystals were etched prior to irradiation to remove the surface layer, which is known to exist on as-grown crystals of $BaTiO_3$.[4] A neutron ($E>0.1$ MeV) dose of $10^{18}n/cm^2$ and the associated γ dose of 10^{10} rad caused the remanent polarization to decrease and the coercive field to increase significantly. The irradiation temperature was believed to be about 70°C. A radiation-damage model, incorporating observed changes in the domain structure of the crystals as a result of the irradiation, was suggested to explain the changes in the hysteresis loop. A comparative study of the effects of monoenergetic electrons and Co^{60} γ irradiation on single crystals of $BaTiO_3$ has been reported by Solov'ev *et al.*[5] The results indicated that Co^{60} γ-rays and monoenergetic electrons with energy sufficient to displace the oxygen atoms produced similar effects in $BaTiO_3$. In each case, the spontaneous polarization increased with initial irradiation and then decreased with continued irradiation. The maximum value of polarization corresponded to a γ dose of about 4×10^7 rad. The irradiations were performed at room temperature, and it was found that the effects of electrons and Co^{60} γ irradiation could be entirely annealed out at 150°C. The authors suggested that the results could be explained by assuming oxygen atoms to be displaced from their normal lattice sites, but remaining in their unit cell.

Changes in the color-center content produced by oxygen nonstoichiometry[6] and changes in the domain structure[7,8] are both known to alter significantly the hysteresis loop of crystals that were originally *c* domain. Previous research has shown that $BaTiO_3$ crystals become colored by γ irradiation,[1] and also that reactor irradiation causes large domains to break up into smaller 90° and 180° domains.[3]

[2] S. Hayakawa and H. Ikushima, J. Phys. Soc. Japan **17**, 1198 (1962).
[3] D. D. Glower and D. L. Hester, J. Appl. Phys. **36**, 2175 (1965).
[4] W. Kanzig, Phys. Rev. **98**, 549 (1955).
[5] S. P. Solov'ev, I. I. Kuzmin, and V. A. Kharchenko, in *Proceedings of the International Meeting on Ferroelectricity, Prague, 1966*, edited by V. Dvorak, A. Funskova, and P. Glogar (Czechoslovak Academy of Sciences, Prague, 1966), Vol. 2, pp. 277.
[6] H. Arend, V. Cierny, and P. Coufova, Czech. J. Phys. **B11**, 379 (1961).
[7] E. A. Little, Phys. Rev. **98**, 978 (1955).
[8] B. Brezina and J. Fousek, Fiz. Tverd. Tela **4**, 1400 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1030 (1962)].

TABLE I. Crystal data.

Crystal No.	Original thickness (μ)	Final thickness (μ)	Maximum γ dose received (rad)
2	390	134	1.60×10^9
4	298	150	1.60×10^9
5	362	150	1.60×10^9
8	322	149	1.32×10^9
9	120	120	2.91×10^8
12	160	160	2.91×10^8

The experimental work reported in this paper was directed toward three objectives. The first was to obtain data showing changes in the ferroelectric hysteresis loop, the optical-absorption spectrum in the wavelength range 0.43–0.70 μ, and the domain structure of etched $BaTiO_3$ crystals as a function of Co^{60} γ dose. The second objective was to explore whether the basic mechanisms of radiation effects in γ-irradiated $BaTiO_3$ involved oxygen displacements (as revealed by changes in color-center concentration) or involved changes in domain structure. The third objective was to compare the effects of radiation upon the properties of etched $BaTiO_3$ with the effects upon crystals which did not have the original surface layer removed.

II. EXPERIMENTAL METHODS

The six specimens used in this study were undoped $BaTiO_3$ crystals of the classic butterfly-wing type produced commercially by the potassium-flux method. Four of the crystals had the surface layer removed by etching in H_3PO_4 at 145°C, and two crystals were used in the as-grown condition. The original and final thicknesses and the maximum γ dose received by each crystal are shown in Table I.

The ferroelectric hysteresis loop was obtained using the basic Sawyer-Tower circuit,[9] modified to include a low-frequency signal generator and an X-Y plotter. The sine-wave output of the signal generator had magnitude maxima of ±19 V. The signal frequency used to produce the hysteresis loop (0.15 Hz) was selected so that annealing of radiation damage[3] could be observed. All of the hysteresis-loop measurements were made at 23°C. Lithium chloride was used as the electrode material, and the electrode diameter was determined using a measuring microscope. The hysteresis-loop measurements were started at least 15 min after the electrode material was applied in order to minimize a time-dependent influence of the electrode material on the coercive field.[10]

The optical-absorption spectrum measurements were made using a Beckman Model DU Spectrophotometer. The photomicrographs of the domain structure were obtained using a polarizing microscope and attached camera. The crystals were subjected to a γ-dose rate of 3.65×10^6 rad/h as determined using a standard ferrous

[9] C. B. Sawyer and C. H. Tower, Phys. Rev. **35**, 269 (1930).
[10] P. Glogar and V. Janovec, Czech. J. Phys. **B13**, 261 (1963).

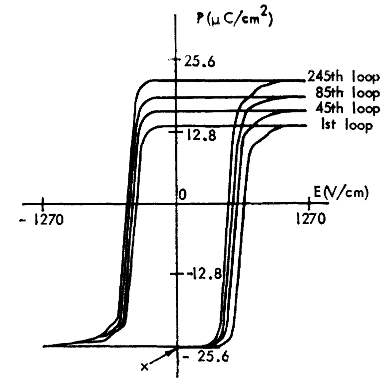

FIG. 1. Annealing of radiation effects in $BaTiO_3$ by the field used to develop the hysteresis loop.

sulfate dosimeter. During the irradiations, the temperature of the air surrounding the crystals was maintained at 20°C by a coolant loop.

III. RESULTS

A. Etched Crystals

All of the etched crystals were irradiated in the poled condition. The manner in which the hysteresis loop changed with repeated cycling of the crystal following irradiation is shown in Fig. 1. The data presented are for crystal 4 after a γ dose of 1.60×10^9 rad and are typical of annealing effects observed in other crystals. The crystal was in the poled state indicated by the point x in Fig. 1 during the irradiation. The annealing of remanent polarization and coercive field by the cycling is readily seen from the plotted hysteresis loops. A total of 245 cycles was required to stabilize the loop in this instance.

The manner in which the stabilized hysteresis loop of poled $BaTiO_3$ single crystals is affected by Co^{60} γ irradiation is shown in Fig. 2. The data are plotted for crystal 4, however, all the etched crystals showed a similar behavior. Curves 1–3 represent the stable loop configurations prior to the irradiation, after 6.83×10^8 and after 1.60×10^9 rad, respectively.

Figures 1 and 2 indicate that the incident γ radiation affected the unoccupied ferroelectric state while the occupied state remained essentially unchanged. Similar results have been reported by Chynoweth[11] for poled ferroelectric triglycine sulfate which was irradiated with x rays. The effects of Co^{60} γ irradiation on the remanent polarization P_r and on the coercive field E_c of single-crystalline $BaTiO_3$ are shown in Figs. 3 and 4, respectively. These data were obtained after each crystal had been cycled a sufficient number of times to stabilize the hysteresis loop.

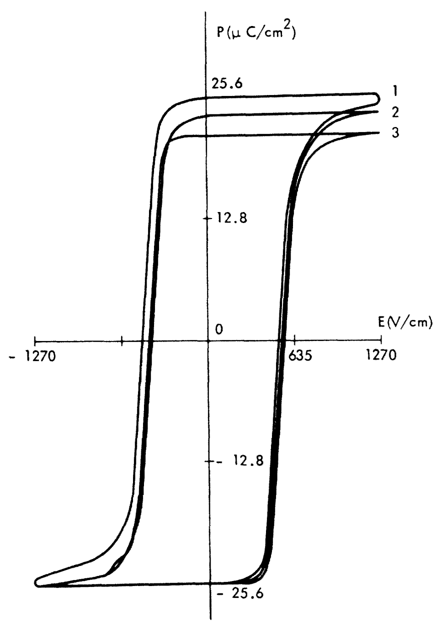

FIG. 2. The effect of Co^{60} γ radiation on the stable hysteresis loop of etched $BaTiO_3$ crystals.

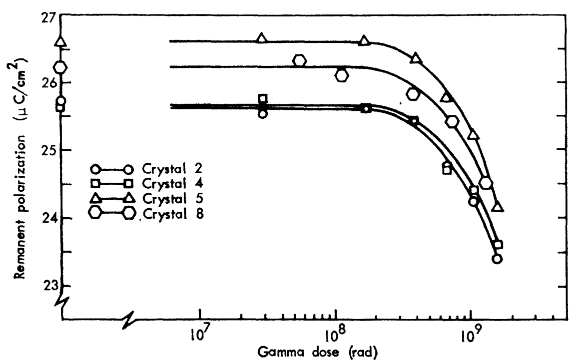

FIG. 3. Remanent polarization versus Co^{60} γ dose.

The values of P_r for the unirradiated crystals are in good agreement with the accepted values for good $BaTiO_3$ crystals. Figure 3 indicates that P_r is essentially unchanged until a γ dose of about 2×10^8 rad has been reached. P_r decreases with continued irradiation beyond this dose.

Figure 4 shows that E_c is generally reduced with increased γ dose. For crystals 2, 4, and 8 the values of E_c go through a minimum at a dose of about 5×10^8 rad and then begin to increase for continued irradiation. The irregularity of behavior exhibited by crystal 5 is unexplained.

The effects of the γ irradiation on the optical-absorption spectrum are shown in Figs. 5 and 6. Figure 5 shows the spectra for crystal 8 prior to irradiation and also after a γ dose of 3.95×10^8 rad. The curves plotted represent the maximum difference obtained in the absorption coefficients for all the doses used for this particular crystal. In general, the absorption coefficients

[11] A. G. Chynoweth, Phys. Rev. 113, 159 (1959).

for all crystals decreased with increasing γ dose to a total dose of about 6×10^8 rad. Continued irradiation beyond this dose resulted in a gradual increase in the coefficients as shown in Fig. 6, where the absorption coefficients at a wavelength of $0.64\ \mu$ are plotted against the γ dose. This wavelength corresponds to the position of the absorption peak observed experimentally in reduced $BaTiO_3$ by Coufova and Arend[12] and to the position calculated by Dvorak[13] for the absorption peak produced by oxygen vacancies with a single trapped electron. In the present study, the optical-absorption spectrum measurements did not reveal any absorption peaks in the wavelength range 0.43–0.70 μ. The absence of an absorption peak at 0.64 μ indicates that the point defect consisting of an oxygen vacancy with a single trapped electron is not produced in $BaTiO_3$ by Co^{60} γ irradiation. The changes observed in the hysteresis loop are thus due to some other defect mechanism.

Photomicrographs taken before and after each irradiation indicate that the domain structure of etched $BaTiO_3$ crystals is unaffected by γ irradiation to a total dose of 1.60×10^9 rad. No *a* domains were introduced into the *c*-domain crystals, and no changes in polarization direction were observed. This latter result was confirmed by the hysteresis-loop measurements because the polarization annealed only in the direction opposite to that in which it was oriented during the irradiation. This effect can be seen in Fig. 1.

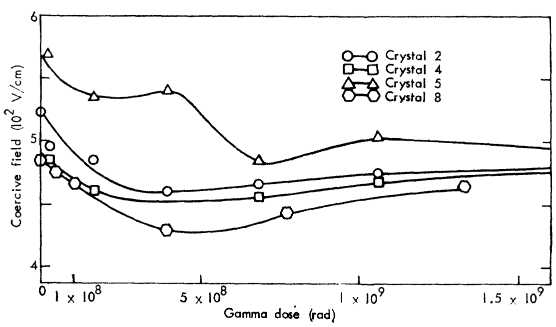

FIG. 4. Coercive field of $BaTiO_3$ versus Co^{60} γ dose.

B. Unetched Crystals

The radiation effects in $BaTiO_3$ crystals which did not have the surface layer removed by etching are different from those observed in etched crystals. The changes in P_r with Co^{60} γ dose for crystals 9 and 12 are shown in Fig. 7. Crystal 9 had a thickness of 120 μ and crystal 12 a thickness of 160 μ. The maximum electric fields applied to these crystals were 1580 and 1190 V/cm, respectively. It is noted that the preirradiated values of P_r for the unetched crystals are much lower than those shown in Fig. 3 for the etched crystals. Apparently,

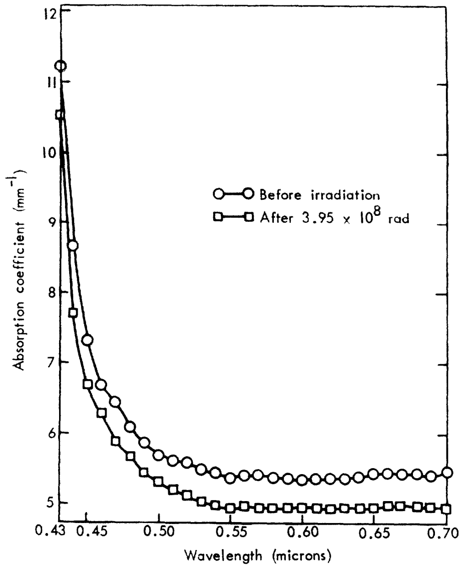

FIG. 5. Optical-absorption spectrum of crystal 8 prior to and after a γ dose of 3.95×10^8 rad.

saturation polarization was not attained in the unetched crystals, even though the electric fields applied to the crystals were much higher than the coercive field. This problem is discussed by Merz[14] and by Kanzig[4] and it is attributed to the influence of the surface layer.

Figure 7 shows that P_r increases initially with increasing γ dose and at a dose of about 2×10^7 rad it starts to decrease. P_r continues to decrease with increasing γ dose to the maximum dose of 2.91×10^8 rad. In all cases, P_r was determined after the crystals had been cycled for approximately 3 h and the hysteresis loop was no longer changing. These results are in general agreement with the results of Solov'ev *et al.*[5] for electron and Co^{60} γ irradiation of $BaTiO_3$.

The effect of Co^{60} γ irradiation on the coercive field of unetched crystals is shown in Fig. 8. The unirradiated values of E_c for the two crystals reflects the crystal thickness dependence of E_c.[10] After irradiation to a dose

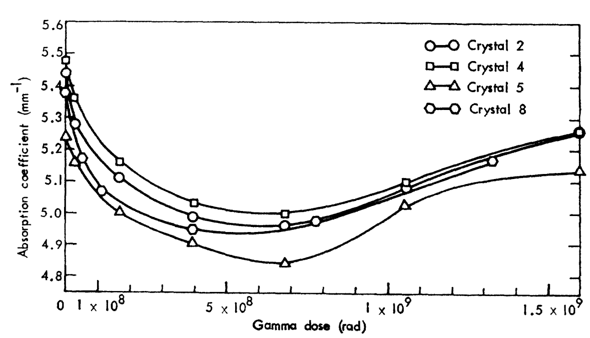

FIG. 6. Optical-absorption coefficient ($\lambda=0.64\ \mu$) versus Co^{60} γ dose.

[12] P. Coufova and H. Arend, Czech. J. Phys. **B11**, 416 (1961).
[13] V. Dvorak, Czech. J. Phys. **B11**, 253 (1961).
[14] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

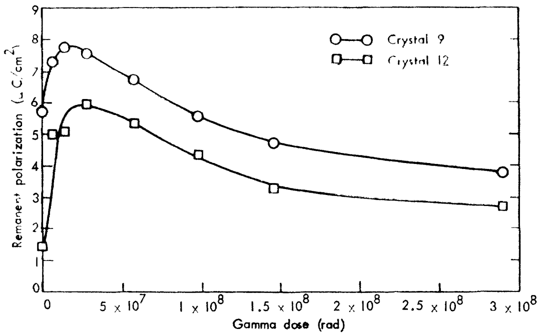

FIG. 7. Remanent polarization versus Co^{60} γ dose for unetched $BaTiO_3$ crystals.

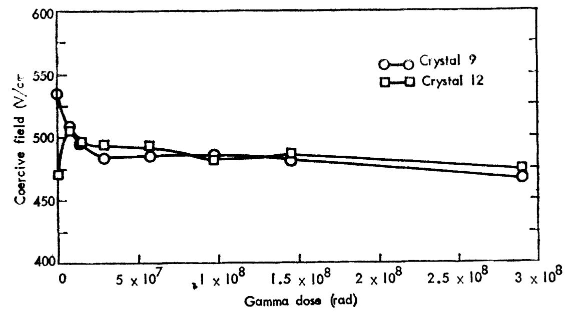

FIG. 8. Coercive field versus Co^{60} γ dose for unetched $BaTiO_3$ crystals.

of 7.56×10^6 rad, the values of E_c for the two crystals are nearly the same. Additional irradiations caused a decrease in E_c for both crystals, with the values being nearly the same after each irradiation. The domain structure of crystals 9 and 12 was unaffected by γ irradiation to a total dose of 2.91×10^8 rad.

IV. SUMMARY

The experimental results obtained using the etched crystals may be summarized as follows.

(1) Co^{60} γ irradiation to a total dose of 1.60×10^9 rad causes a decrease of about 8.7% in the remanent polarization. P_r is essentially unaffected below a total dose of 2×10^8 rad.

(2) The coercive field decreases with initial irradiation. At a dose of about 5×10^8 rad, a minimum value is reached and E_c then increases with continued irradiation.

(3) The electric field used to develop the hysteresis loop causes annealing of the radiation-induced effects. This annealing, which occurs as the crystal is continuously looped, results in an increase in P_r and a decrease in E_c as compared to the values determined from the first loop after an irradiation.

(4) The optical-absorption spectrum measurements show a reduction in the absorption coefficients with initial irradiation. At a dose of about 6×10^8 rad the coefficients reach a minimum and then increase with continued irradiation. No absorption peaks were observed in the wavelength range 0.43–0.70 μ. In particular, no peaks were observed which would indicate the presence of point defects consisting of an oxygen vacancy with a single trapped electron.

(5) No changes were found in the domain structure of etched $BaTiO_3$ irradiated to a total dose of 1.60×10^9 rad.

Unetched crystals were irradiated to a total dose of 2.91×10^8 rad. The experimental results for unetched crystals are summarized as follows.

(1) The value of remanent polarization increases initially with increasing γ dose. A maximum in P_r is found at a dose of about 2×10^7 rad. Continued irradiation causes a reduction in the values of P_r.

(2) The coercive field decreases with increasing γ dose.

(3) The domain structure of unetched $BaTiO_3$ crystals is unaffected by Co^{60} γ irradiation to a total dose of 2.91×10^8 rad.

The radiation damage model developed by Glower and Hester[3] for reactor-irradiated, etched $BaTiO_3$ crystals does not explain the results found in the present study. Their model considers ionization as the major radiation-damage mechanism for reactor irradiation, and it suggests that changes in the hysteresis loop with irradiation are associated with changes in the domain structure of the crystals. The results of the present study, where ionization effects are indeed the most significant, reveal no changes in domain structure with increasing γ dose.

The radiation-induced changes in the hysteresis loop of etched crystals also cannot be attributed to the presence of point defects consisting of an oxygen vacancy with a single trapped electron. The absorption peak corresponding to this particular defect was not observed in this study, although it is known to fall within the range of wavelength studied.

There is a significant difference in the response of etched and unetched $BaTiO_3$ single crystals to Co^{60} γ irradiation. The unetched crystals show a much higher radiation sensitivity than do the etched crystals.

ACKNOWLEDGMENTS

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