Analysis of Neutron Induced Defects in Silver Doped Lithium Tetraborate

B. E. Kananen, A. T. Brant, D. A. Buchanan, M. K. Murari, J. W. McClory, *Member, IEEE*

***Abstract*—Neutron-induced defects in silver doped lithium tetraborate ($Li_2B_4O_7$:Ag) are identified and characterized using electron paramagnetic resonance (EPR) spectroscopy and thermoluminescence (TL). Neutron irradiation induced two unique defects detectable by EPR. Both of these neutron-induced defects are substantially more thermally stable than as-grown crystal defects. Models for the neutron-induced defects are proposed.**

I. INTRODUCTION

The drive to detect small quantities of the neutron by-products of fission motivates the exploration of boron and lithium containing compounds such as lithium tetraborate ($Li_2B_4O_7$). In addition to containing ^{6}Li and ^{10}B, isotopes with relatively high probabilities of neutron interaction, $Li_2B_4O_7$ in single crystal form may provide a medium in which to time integrate neutron induced defects. Potential signal integration over time leverages the time available en route to a final destination to detect special nuclear material. In addition, the thermoluminescent (TL) and optical properties of $Li_2B_4O_7$ may provide inexpensive methods of assessing the number of neutron interactions in a single crystal sample. Any inexpensive, ready method of assessing neutron interactions would yield a lower cost detector in turn facilitating fielding detectors in greater numbers. As is the case for radiation detector materials, it is important to identify the point defects in the crystal, both intrinsic (vacancies and interstitials) and extrinsic (intentional or unintentional impurities), that may affect device performance.

This research focuses on characterizing both as grown and neutron irradiated defects in silver enriched lithium tetraborate ($Li_2B_4O_7$), hereafter called LTB. Our research shows promise in using LTB as a possible inexpensive dosimeter. LTB crystals used in this experiment were grown by the Czochralski technique at the Institute of Physical Optics (L'viv, Ukraine), where silver was an as grown ingredient, i.e. not diffused after crystal growth. This research has been motivated by earlier detailed investigations of copper ions in LTB crystals, and the behavior of Cu^{2+} ions in the crystal structure. [1]-[3]

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B. E. Kananen is with the Air Force Institute of Technology, Wright Patterson AFB, OH 45431 USA (email: brant.kananen@jtfcs.northcom.mil)

A. T. Brant is with West Virginia University Morgantown, WV USA 26506 (email: brant.adam@gmail.com)

D. A. Buchanan is with the Air Force Institute of Technology, Wright Patterson AFB, OH 45431 USA (email: douglas.buchanan@afit.edu)

M. K. Murari is with the University of Cincinnati, Cincinnati, OH USA 45221 (email: madhavkrishna.murari@uc.edu)

J. W. McClory is with the Air Force Institute of Technology, Wright Patterson AFB, OH 45431 USA (email: john.mcclory@afit.edu)

II. EXPERIMENT

Samples were initially characterized by EPR and thermoluminescence. A Bruker EMX spectrometer was used to obtain the EPR data. Spectra presented were taken between 25 and 40 K in the spectrometer using a microwave frequency close to 9.5 GHz (X-band) and magnetic fields between 300 to 400 mT. EPR spectra shown are taken with the magnetic field parallel to the [001] crystal direction. Prior to any collection of EPR spectra, samples were exposed to 30 mA, 60 kV x rays for 10-15 minutes. This energy source populates the electron and hole trap sites. Thermoluminescence data was collected using a Harshaw TLD Reader with a 1°C per second heating rate. This heating rate is different than a pulsed annealing procedure utilized in evaluating the stability of the electron and hole traps using EPR. The pulsed anneals (PA) for EPR evaluation involved raising the temperature to the desired anneal temperature and holding for three minutes. After three minutes, the samples were quickly exposed to room temperature. The sample was left in the spectrometer for annealing temperatures up to 50 °C and placed in a furnace for temperatures between 50 °C and 400 °C. The procedural difference between thermoluminescence and pulsed anneals results in thermoluminescent glow curves shifted to slightly higher temperatures due to the continuous heating rate and the fact that samples are not being held at constant temperatures for longer periods of time, where more recombination of electrons and holes would occur. This is reflected in the data presented in this investigation.

The as grown defects of LTB:Ag were characterized using EPR in concurrent study. [4] The as grown defect of interest in this study is a silver electron center that appears in EPR spectra centered at 338 mT. Silver has two common isotopes, ^{107}Ag and ^{109}Ag, with relative abundances of 51.8% and 48.2% and slight differences in their magnetic moments that explain the relative peak intensities and assigned isotopes in Fig. 1. Silver has a spin of 1/2 and would split into two sets of 4 peaks when interacting with a spin of 3/2. The interacting nuclei would most likely be a neighboring boron or lithium ion, both having a 3/2 spin. The ^{107}Ag and ^{109}Ag hyperfine patterns have very large splitting and little angular dependence. Together, these are general characteristics of a Ag^0 atom ($4d^{10}5s^1$) that forms when a Ag^+ ion traps an extra electron. The difference between our silver electron trap and those reported in the literature [5]-[7] is the hyperfine splitting, predicted to be 2109 MHz for the ^{109}Ag isotope.[8] The reduction in splitting is best described by considering that

some of the unpaired spin density may also be distributed on the nearby oxygen ions. [4] This silver electron center is paired with a silver hole center, not shown. Both anneal out by 200 ºC and decay in parallel as shown in Fig. 2. The thermoluminescent glow curve also shown in Fig. 2 corresponds to the electron-hole recombination of the as grown defect. Again, the slight upward shift in temperature is due to the heating difference between EPR pulsed anneal heating and TL heating rates.

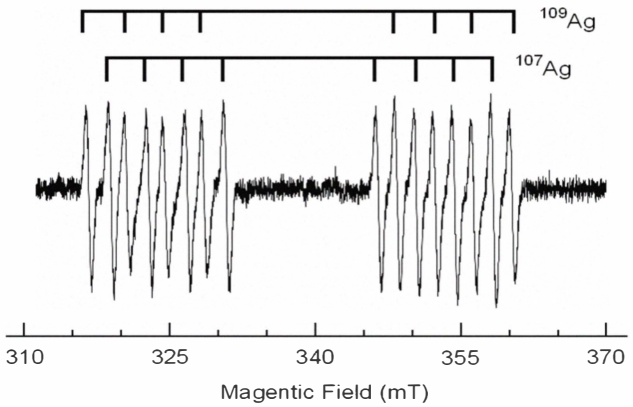

Fig. 1. LTB:Ag EPR spectra of the as grown silver electron trap site. Stick figures above the spectra show isotope assignment. Spectra was collected with magnetic field aligned with [001] crystal direction.

Silver has been shown to be a good dopant as a possible dosimeter. Our research has shown that it has a unique characteristic to act as both an electron and hole trap. [8] The as-grown crystal contains both interstitial Ag^{+} ions and Ag^{+} ions substituting for the Li^{+} ions of the crystal structure, shown in Fig. 3. During irradiation, substitutional ions trap holes, becoming Ag^{2+} ions while the interstitial Ag^{+} trap electrons and become Ag^{0}. These defects in LTB:Ag are much more thermally stable than the as grown undoped LTB defects, that anneal out at much lower temperatures. [9]

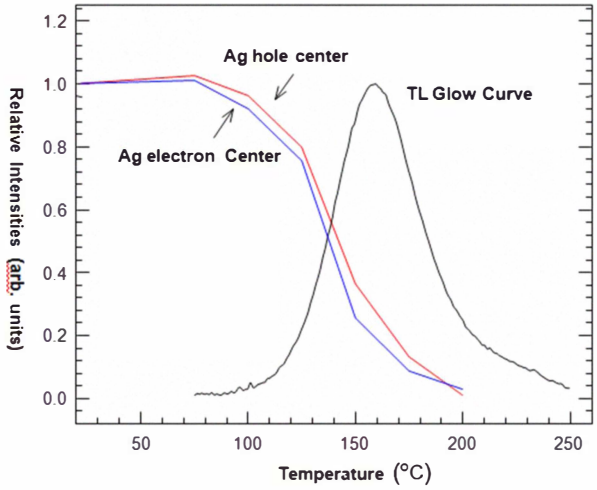

Fig. 2. Pulsed anneal (red and blue curves) and thermoluminescence glow curve of as grown defects in LTB:Ag.

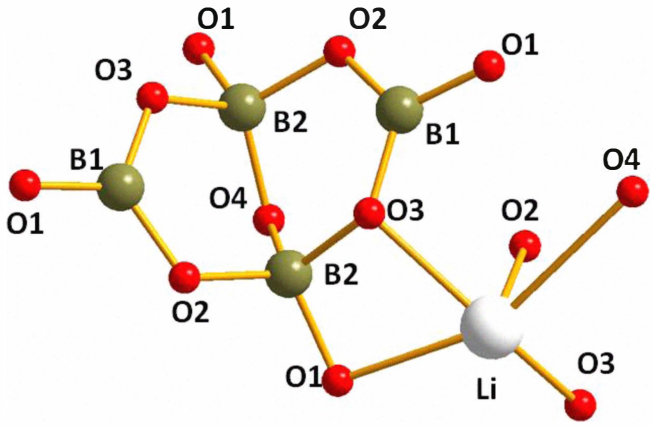

Fig. 3. LTB basic crystal structure. In LTB:Ag the lithium locations would be the only logical position for a substitutional silver ion.

The goal of our experiment was to investigate the effect of neutron irradiation on LTB:Ag. Samples used in this investigation were not enriched above natural abundance of ^{6}Li or ^{10}B, 6% and 20% respectively. After initial characterization, samples were irradiated at the Ohio State University Research Reactor while it ran at 90% capacity, approximately 500 kW. With sample placement close to the reactor core, calculated exposure times of approximately one hour was predicted to yield 10^{15} cm^{-3} thermal neutron (< 1 MeV neutron) exposure. Only $n(^{6}Li, \alpha)^{3}H$ and $n(^{10}B, ^{7}Li)\alpha$ reactions were considered in calculating neutron-induced defect densities.

III. EXPERIMENTAL RESULTS

With neutron irradiation being the only variable in our experiment, results found in EPR and TL can be assigned due to neutron "knock on" damage or a byproduct of neutron irradiation. Neutron irradiation induced two new defects of interest, a single EPR peak centered at 337 mT and a pair of triplets centered at 340 mT shown in Fig. 4. The as grown silver electron center is also shown in Fig. 4 but the peaks are much lower in intensity, the periodic structure in the noise region is the silver electron center. These new peaks will only be referred to as single and triplet peaks because a specific defect assignment can only be posited.

During isochronal pulsed annealing, the singlet and triplet increase in signal intensity from 125 – 225 ºC, while the silver electron center decreases and becomes unobservable above 200 ºC. The singlet and triplet signals are anisotropic. Once the sample was raised above 300 ºC, the two spectra were no longer observable. When annealed above 400 ºC, the triplet spectra could no longer be produced, meaning the neutron induced defects were completely annealed out of the sample.

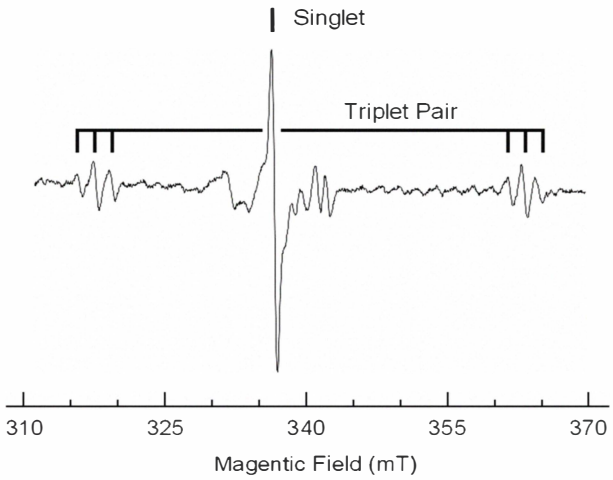

Fig. 4. LTB:Ag EPR spectra after neutron irradiation. The singlet and triplet are both due to neutron irradiation effects.

Post neutron thermoluminescence glow curves, shown in Fig. 5, also coincided with the EPR results. The glow curve showed an upward shift centered around 250 ºC, compared to 170 ºC pre-neutron irradiation. A similar thermoluminescence experiment investigating beta-irradiated LTB:Ag noted luminescence peaks at 170 ºC and 255 ºC. [10]

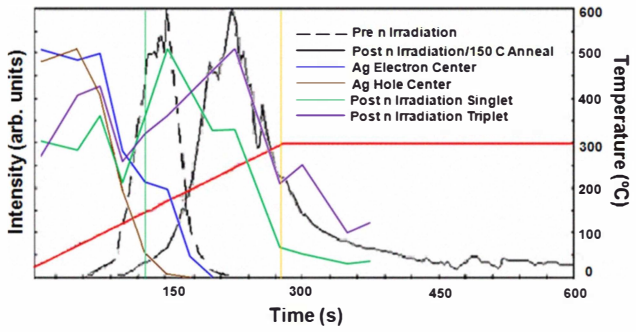

Fig. 5. LTB:Ag Thermoluminescence pre (dashed) and post (solid) glow curves. Pulsed anneal post-neutron irradiation (in color). Red line correlates time and temperature axis.

The samples also changed in color at specific points, noted by the vertical lines in Fig. 5. Prior to neutron irradiation the samples were clear. When exposed to x-rays the samples would turn green and would lose coloration above 175 ºC. After neutron irradiation the samples took on a slight brown color but again turned green upon exposure to room temperature x-rays. When neutron irradiated samples were annealed above 150 ºC, the sample changed from a green to an orange color. When irradiated samples were annealed above 300 ºC, the sample returned to colorless. Finally, when irradiated samples were annealed above 400 ºC, the orange color could no longer be reproduced.

IV. Conclusions

Combining previous studies with our experiment, we can make several conclusions about neutron induced defects using EPR and thermoluminescence.

First, the neutron induced singlet and triplet defects were electron centers. Two points in our experiment lead us to this conclusion. As the as grown silver electron center annealed out, the signal intensity due to the induced singlet and triplet spectra increased in intensity. The electrons being released from the as grown trap sites were getting trapped at the neutron induced sites. This concurs with their increased temperature stability. Secondly, the effective g value for the spectra typically correspond to electron centers which is in agreement with the as grown silver electron spectra existing near the same location of magnetic field.

Second, the singlet and triplet defects are responsible for the shift in the thermoluminescent peak at 250 ºC. Considering the temperature shifts in the pulsed anneal defects, the shift is almost identical in the thermoluminescent glow curve.

Third, the orange color can be assigned to the neutron irradiation effects, the triplet defect. The color change concurred with the presence of the EPR spectra and annealed out the same as the EPR spectral intensity.

Further investigation is required to identify the exact defects causing the singlet and triplet peaks in the spectra. The singlet is most likely due to an unpaired electron that is interacting with a nucleus of zero spin. Considering the crystal, oxygen would be the most likely candidate. Unintentional materials that may be present in the crystal structure could not be of great enough numbers to produce the large spectra observed. The triplet spectra could possibly be identified using Electron Nuclear Double Resonance (ENDOR). A possible assignment to this triplet could be an electron interacting with two spin 1/2 nuclei, silver being a likely candidate.

Overall, the results of this research shows that silver doped lithium tetraborate may be a possible material for neutron detection and shows promise in dosimeter applications. Also, as the trapped electrons and holes recombine upon annealing, LTB:Ag defects show promise in providing new and highly efficient radiative recombination pathways.

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