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Citation: AIP Conf. Proc. **1544**, 70 (2013); doi: 10.1063/1.4813462

View online: http://dx.doi.org/10.1063/1.4813462

View Table of Contents: http://proceedings.aip.org/dbt/dbt.jsp?KEY=APCPCS&Volume=1544&Issue=1

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Synthesis and TL Characterization of $Li_2B_4O_7$ Doped with Cooper and Manganese

C. Guarneros-Aguilar[1], E. Cruz-Zaragoza[2,*], J. Marcazzó[3], R. Palomino-Merino[1], J. E. Espinosa[1]

[1]*Posgrado en Física Aplicada, Facultad de Ciencias Físico-Matemáticas, Benemérita Universidad Autónoma de Puebla, Av. San Claudio y 18 Sur, Col. San Manuel, 72570, Puebla, México*
[2]*Unidad de Irradiación y Seguridad Radiológica, Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, A.P. 70-543, 04510 México D.F., México*
[3]*IFAS, Universidad Nacional del Centro de la Provincia de Buenos Aires, Pinto 399, 7000 Tandil, Argentina*

Abstract. Copper (Cu) and manganese (Mn) doped tissue equivalent $Li_2B_4O_7$ were prepared by solid state sintering. The glow curves shows a high temperature peak at 222 °C for $Li_2B_4O_7$:Cu and for $Li_2B_4O_7$:Mn at 218 °C. Linear dose response is observed up to 140 Gy. With a thermal treatment at 125 °C, the first peak of the phosphors doped with copper (95 °C) and manganese (90 °C) disappears and the main TL peaks remain isolated. The dose rate dependence was studied by exposing the samples at doses of 25 Gy and 250 Gy. At low dose it was observed that the $Li_2B_4O_7$:Cu TL response has non-dependence on dose rate, and at higher dose was observed that there is a dependence of the TL response with the different dose rate until of 30%. For the case of $Li_2B_4O_7$:Mn, the TL response has non-dependence on dose rate at low dose or high dose.

Keywords: Thermoluminescence; dosimeters; radiation; copper; manganese.

PACS: 87.53.Bn

1. INTRODUCTION

Tissue equivalence is an important property for thermoluminescent (TL) dosimeters for estimation of absorbed dose in tissue because the absorbed dose in soft biological tissue exposed to ionizing radiation can be determined more accurately, if the dosimetric material has a similar atomic composition as that of human tissue (7.42); and lithium borate based TL dosimeters are best with an effective atomic number of 7.3 [1, 2]. The introduction of a small quantity of dopant into the lithium tetraborate enables its sensitivity to ionizing radiation influence to be increased substantially; the materials show some desirable features for TL in terms of linearity and storage and many of the earlier problems of fading, light sensitivity and poor humidity behavior have been avoided. The most promising from this point of view are the copper and manganese dopants, for which the best photoluminescence characteristic indices were achieved [3, 4]. Therefore, single crystals of this material doped with copper (Cu) and doped with manganese (Mn) are promising for dosimetric applications and as radiation proof material for optical devices.

2. EXPERIMENTAL PROCEDURE

In the present study, lithium tetraborate ($Li_2B_4O_7$) doped with Cu (0.5 wt %) have been obtained using as dopant $CuCl_2$. In this case, Li_2CO_3 and H_3BO_3 were mixed and melted at 950° C during 180 minutes in a ceramic crucible using a muffle furnace in air. The sample was slowly cooling to room temperature and then reheated at 650° C during 120 minutes to complete the crystallization. $Li_2B_4O_7$:Cu was obtained by adding the $Li_2B_4O_7$ powder into a solution of $CuCl_2$ in acetone/alcohol and subsequently dried. The dried mixture was treated at 900° C in air during 60 minutes. $Li_2B_4O_7$:Mn was prepared by mixing stoichiometric compositions of lithium carbonate (Li_2CO_3) and boric acid (H_3BO_3) and moistened with a solution containing manganese (II) chloride ($MnCl_2$) to yield a product with dopant concentration of 0.5 wt %. The mixture was

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dried for 12 hours at 100° C. The dried mixture was heated at 950° C during 180 minutes in a ceramic crucible using a muffle furnace in air too. Powder X-ray diffraction (XRD) patterns were recorded using Cu-Kα radiation to corroborate the phase purity of the samples synthesized. The phosphors were ground and the powders were irradiated by different doses in the range 10 - 2000 Gy from ^{60}Co gamma source and TL glow curves were obtained and analyzed. For low doses the gamma dose ratio was 0.02294 Gy/min and for high doses was 128.392 Gy/min.

3. RESULTS AND DISCUSSION

3.1 XRD pattern

Powder X-ray diffraction (XRD) patterns were recorded using Cu-Kα (1.5406 Å) radiation in an X-Ray Bruker D8 Discover Diffractometer, operated at 40 kV and 40 mA, to corroborate the phase purity of the samples synthesized. The slow scan was performed in the 2θ range from 10–80° with a scan step of 0.026°. The results obtained were matched with the standard data available (card no. 01-079-0963) for $Li_2B_4O_7$. Figure 1 shows the X-ray diffraction pattern of the synthesized $Li_2B_4O_7$:Cu with (hkl) values [5].

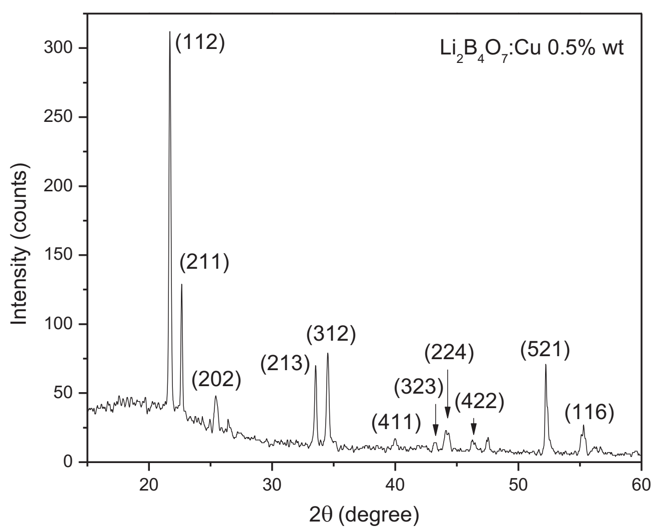


FIGURE 1. X-ray diffraction pattern of $Li_2B_4O_7$:Cu

The XRD pattern of the $Li_2B_4O_7$:Mn synthesized is shown in Figure 2. It is observed the peaks corresponding to the lithium tetraborate doped with manganese and other corresponding to boric acid reagent, due to the temperature and reaction time was no enough for the $Li_2B_4O_7$:Mn synthesis [6]. For the two samples, the peak positions match well with that of standard pattern (data 00-011-0408). It was found that the phosphors are chemically stable and moisture resistant.

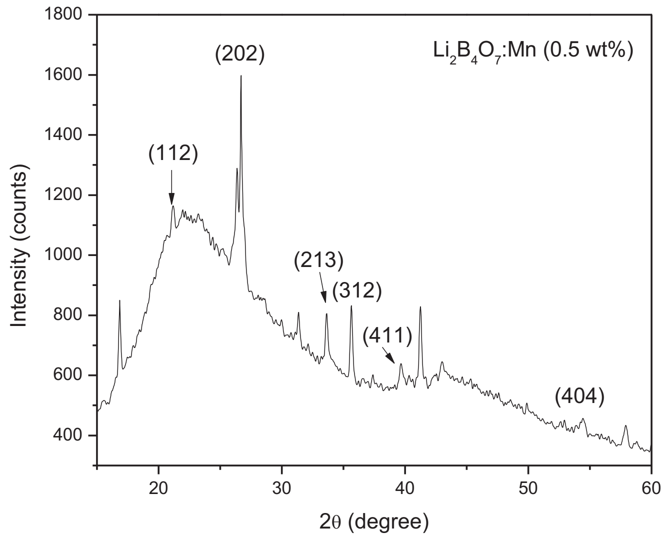
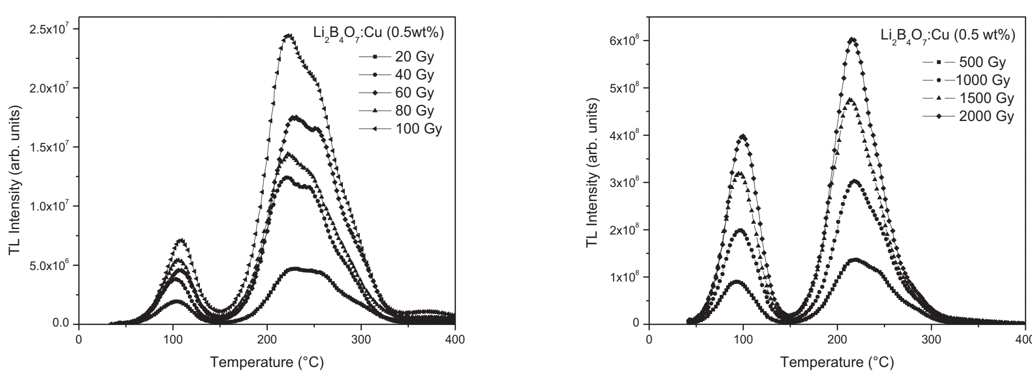


FIGURE 2. X-ray diffraction pattern of $Li_2B_4O_7$:Mn

3.2 Glow curve

To study TL properties, the samples were exposed to gamma rays using ^{60}Co source for different doses 10 - 2000 Gy (Gammacell 200 for low doses and Gammabeam 651 PT for high doses). Thermoluminescence measurements were carried out using Thermo Scientific Harshaw TLD 3500 reader at a linear heating rate of 2°C/s. The TL glow curves of the both phosphors synthesized were recorded after low doses of gamma irradiation.

TL glow curves for $Li_2B_4O_7$ doped with Cu for various absorbed doses (Figure 3) are composed of two well-separated and one shoulder peaks, with the main one situated at about 222 °C and the low-temperature peak at about 108 °C.



a) b)

FIGURE 3. TL glow curves of $Li_2B_4O_7$:Cu synthesized and irradiated at a) low doses and b) high doses, with gamma radiation using a ^{60}Co source.

The TL $Li_2B_4O_7$:Mn glow curves for various absorbed doses (Figure 4) are composed of a dominant dosimetric peak around 218 °C and a composite low-temperature peak around 98 °C at 40 Gy and 60 Gy, while at 20 Gy and 80 Gy the dosimetric peak is so weak.

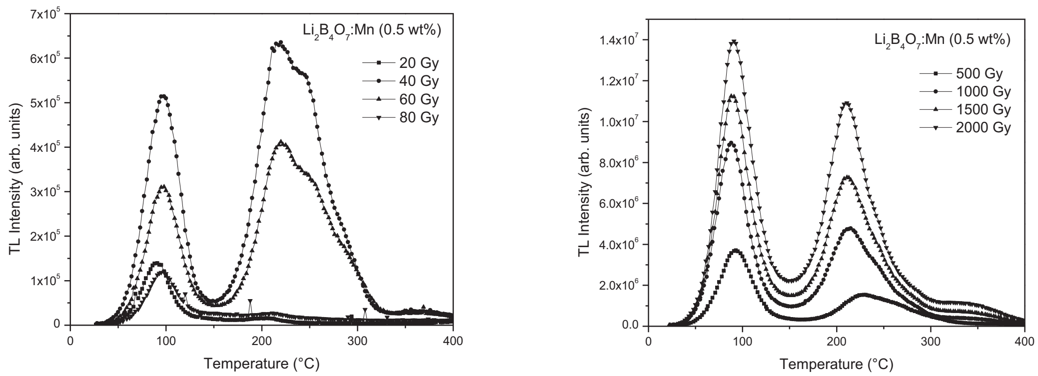


FIGURE 4. TL glow curves of $Li_2B_4O_7$:Mn synthesized and irradiated at a) low doses and b) high doses, with gamma radiation using a ^{60}Co source.

3.3 Dose vs TL response

The dose vs TL response of the $Li_2B_4O_7$:Cu and $Li_2B_4O_7$:Mn is shown in Figure 5 and Figure 6. At low doses the phosphors synthesized not show a linear pattern. When the samples were exposed for high doses, TL response is found to be linear in the dose range 140 Gy – 2000 Gy. Therefore, the phosphors can be used as TL material within this range.

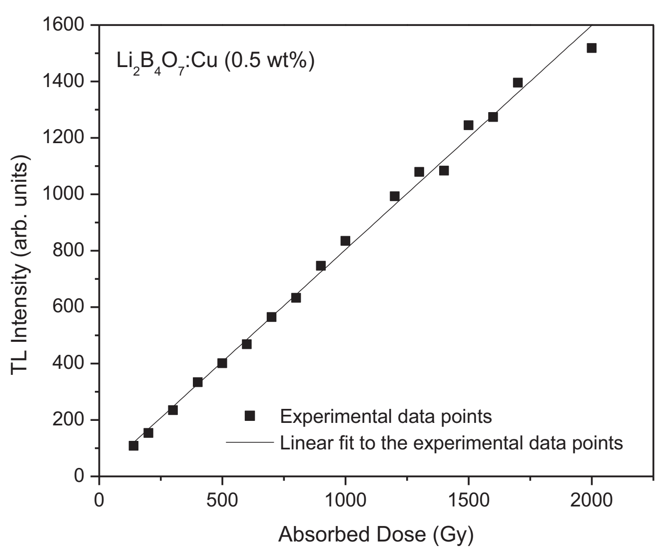


FIGURE 5. TL response vs. absorbed dose of the $Li_2B_4O_7$:Cu in the dose range 140 Gy – 2000 Gy.

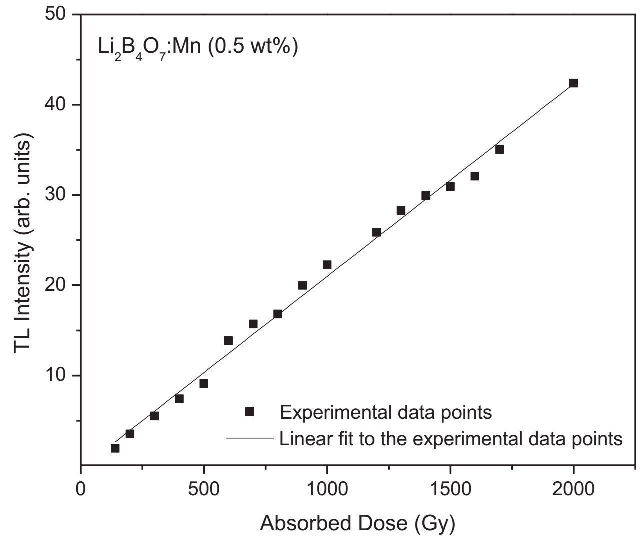


FIGURE 6. Absorbed dose vs. TL response of the $Li_2B_4O_7$:Mn in the dose range 140 Gy – 2000 Gy.

In order to evaluate the reproducibility for the dose measurements of synthesized materials, were carried out experiments twelve times at the same dose of 200 Gy each. It was found that the TL response for $Li_2B_4O_7$:Cu has some variations while the TL response for $Li_2B_4O_7$:Mn remains almost the same even. With the purpose of analyzing the dose rate effect, it was considered the follow rates, 0.2148 Gy/min, 2.692 Gy/min, 7.957 Gy/min, 19.0517 Gy/min, 77.30 Gy/min, and 187.1 Gy/min. Both samples were exposed at the same doses (25 Gy and 250 Gy). At 25 Gy it was observed that the $Li_2B_4O_7$:Cu TL response has non-dependence on dose rate. At the mayor dose, it was observed that there is a dependence of the TL response with the different dose rate until of 30%. For the case of $Li_2B_4O_7$:Mn, the TL response has non-dependence on dose rate at low dose or high dose.

A thermal bleaching was carried out for isolate the main peak located at 224 °C, for the $Li_2B_4O_7$:Cu sample exposed at a dose of 200 Gy, from the effect of the first TL peak located at 95 °C. The interval temperature treatment was from 50 °C to 350 °C in steps of 25 °C. It was found that the mean peak can be isolated with a thermal treatment at 125 °C, which is useful for a protocol of use of those materials with dosimetric properties in radiation dosimetry. Figure 7 shows the thermal bleaching for the phosphor doped with copper and the behavior of TL response with the thermal treatment, the TL response was multiply by a factor of $1x10^{13}$ to observe it better.

Figure 8 shows the thermal bleaching for lithium tetraborate doped with manganese exposed at a dose of 200 Gy. In the same way that in the previous case, the thermal treatment was carried out in an interval of 50 °C to 350 °C, but only one temperature is presented (125 °C). At this temperature, the main peak located at 222 °C can be isolated from effect of the first TL peak located at 90 °C.

In order to determine the fading characteristics of synthesized materials, the samples were irradiated to a dose of 200 Gy and stored in dark conditions a room temperature for a period of fourteen hours, and then for twenty-four hours. The glow curves obtained for lithium tetraborate doped with copper are presented in Figure 9, the TL response initial was 146.4 μC and the final TL response was 0.139 μC. The fading on the fourteen hours is 0.095%. For the period of twenty-four hours, the TL response initial was 148.9 μC and the final TL response was 0.263 μC; the fading is 0.177%.

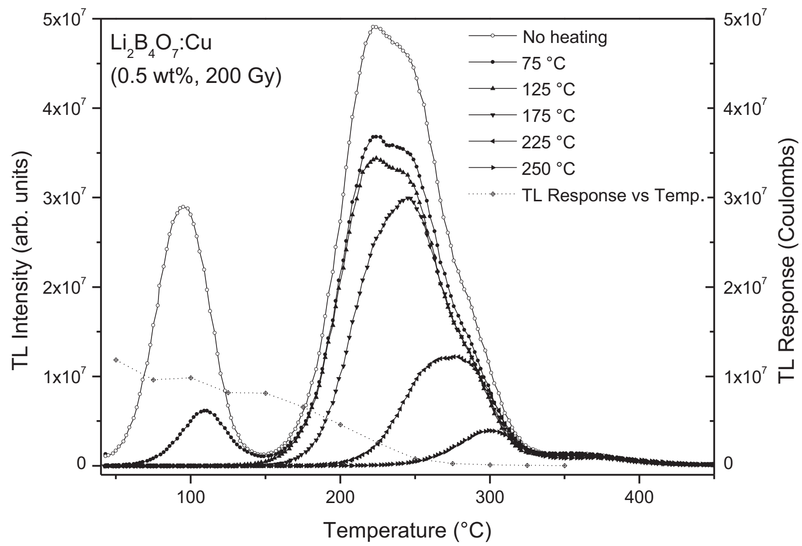


FIGURE 7. $Li_2B_4O_7$:Cu thermal bleaching for a dose of 200 Gy, the thermal treatment was varied from 50 to 350° C. TL response was multiply by a factor of $1x10^{13}$.

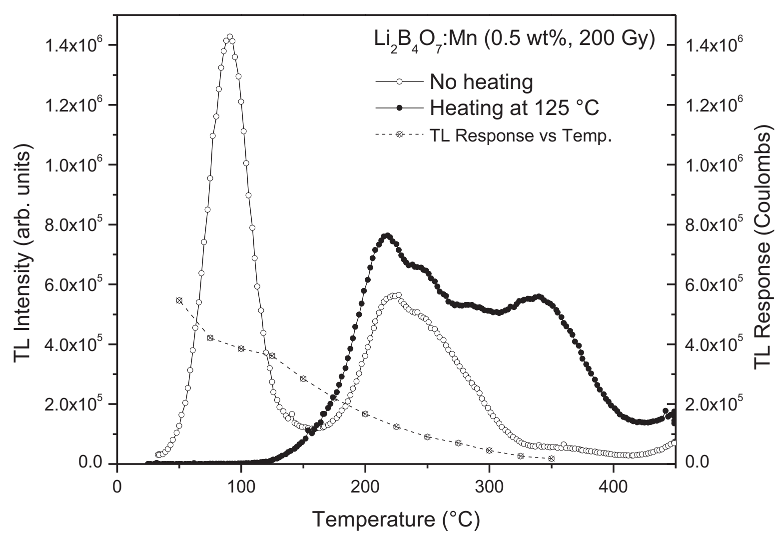
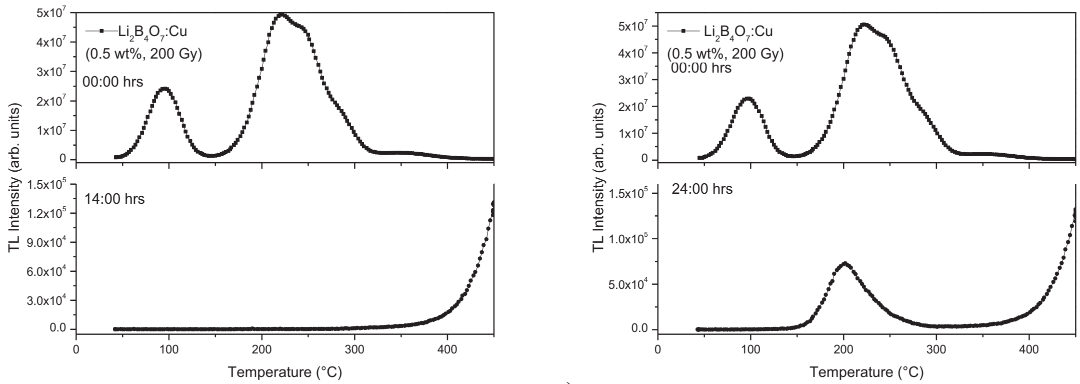


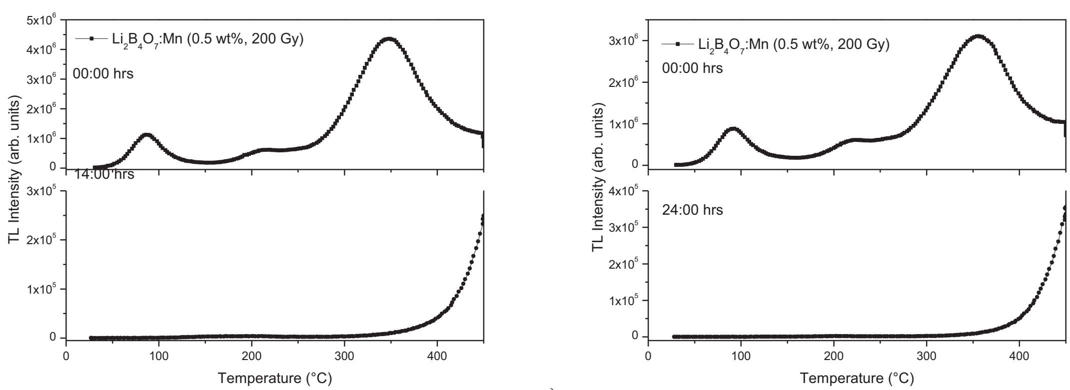
FIGURE 8. $Li_2B_4O_7$:Mn thermal bleaching for a dose of 200 Gy, the thermal treatment was varied from 50 to 350° C. TL response was multiply by a factor of $1x10^{11}$.



a) b)

FIGURE 9. Glow curves of $Li_2B_4O_7$:Cu, a) for a period of fourteen hours, and b) for a period of twenty-four hours.

The glow curves obtained for lithium tetraborate doped with manganese are presented in Figure 10, the TL response initial was 15.8 μC and the final TL response was 0.297 μC for a period of fourteen hours; the fading is 1.88%. For a period of twenty-four hours, the TL response initial was 12.3 μC and the final TL response was 0.39 μC, the fading is 3.17%.



a) b)

FIGURE 10. Glow curves of $Li_2B_4O_7$:Mn, a) for a period of fourteen hours, and b) for a period of twenty-four hours.

4. CONCLUSIONS

Dosimetric materials $Li_2B_4O_7$:Cu and $Li_2B_4O_7$:Mn were obtained by solid state sintering. According to the X-ray diffraction pattern, the phosphor doped with copper has good crystalline quality; however, the diffraction pattern of phosphor doped with manganese shows the presence of boric acid. The TL response of the phosphor doped with copper was higher than the phosphor doped with manganese. Both materials present complex glow curves related to trap distribution. An advantage of this preparation is that the samples show a dose wide interval from 140 Gy to 2000 Gy. With the thermal treatment, the first peak of the phosphors doped with copper (95 °C) and manganese (90 °C) disappears at 125 °C and the main TL peaks remain isolated. A better reproducibility of the TL signals could be obtained with this thermal treatment. Low fading makes it useful for applications in gamma radiation dosimetry at doses higher than 140 Gy.

Acknowledgments

We are grateful to Dr. E. Rubio and M.C. R. Agustín of Centro Universitario de Vinculación (BUAP) for providing necessary facilities to carry out the XRD studies.

4. CONCLUSIONS

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