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GROWTH OF TUNGSTEN BRONZE FAMILY CRYSTALS

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DARPA ORDER NO.:	4540
NAME OF CONTRACTOR:	Rockwell International Corporation
EFFECTIVE DATE OF CONTRACT:	05/02/85
CONTRACT EXPIRATION DATE:	01/30/88
AMOUNT OF CONTRACT DOLLARS:	$1,245,307
CONTRACT NO.:	N00014-85-C-2443
PRINCIPAL INVESTIGATOR:	Dr. R. R. Neurgaonkar (805) 373-4109
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A. OBJECTIVE

The objective of the present work is to develop suitable quality and size $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN) single crystals or thin films that can be used in optical device studies. The second objective of this work is to develop a phenomenological model to explain the correlation between the ferroelectric and optical properties and thereby possibly control and optimize the material performance for device applications.

B. PROGRESS

In order to extend the spectral response of Ce^{3+}-doped crystals from the visible to the infrared region, it was found necessary to change the Ce^{3+} site preference in the tungsten bronze structure. In the bronze structure, there are five sites available, namely, 15-, 12-, 9- and two 6-fold coordinated. Under normal growth conditions, Ce has shown a strong preference to occupy the 12-fold coordinated site in SBN:60 crystals. However, this situation can be changed to force the Ce ion into the 9-fold coordinated site by controlling the growth oxygen pressure and the concentration of the dopant. For such growths, it was found that the crystal color changed from pink to a greenish yellow. Spectral measurements show that the spectral absorption considerably changed, with

absorption observed from 0.68 to 0.80 μm for this arrangement. Based on these results, it is clear that the spectral response has now been extended into infrared region. This is considered a significant achievement in the present work, and efforts are underway to further optimize the concentration of Ce in the 9-fold coordinated site to obtain optimum response time.

The exchange of the crystallographic sites for cerium has not changed the growth conditions and the crystals obtained are of optical quality. Another important composition in the bronze system, $Sr_{0.75}Ba_{0.25}Nb_2O_6$ (SBN:75), is also under development, and it has been shown that Ce-doped crystals are equally excellent photorefractive material with a very high electro-optic coefficient (r_{33} = 1400 x 10^{-12} m/V). In future work, we will continue to develop both SBN:60 and SBN:75 crystals doped with 4-f and 5-d ions.

Recent work on SBN:60 single crystals has shown a value for the electro-optic coefficient, r_{51}, of 80 x 10^{-12} m/V, a value significantly greater than for SBN:75 (42 x 10^{-12} m/V) which possesses an optimum value for r_{33}. This indicates that r_{51} is also compositionally dependent on the concentration of Ba^{2+}, but in a manner opposite to the behavior of r_{33}. Since SBN:50 crystals

are now available in optical quality, we can estimate these coefficients in this composition as well. Since the longitudinal electro-optic coefficient (r_{51}) appears greater in Ba^{2+} -rich crystals, Ba^{2+} -rich end members in the bronze SBN system may have large r_{51} values similar to other important photorefractive hosts such as $BaTiO_3$. This work will be continued to analyse the behavior of other compositions as potential replacements for photorefractive $BaTiO_3$, which presently is very difficult to grow.

C. MAJOR EQUIPMENT

None.

D. CHANGE IN PERSONNEL

None.

E. TRIPS AND VISITS

In April 1986, Dr. R. R. Neurgaonkar met John Neff and R. Reynolds of DARPA and gave a briefing on the current status of this program and an outline of future work.

In May 1986, Professor L. E. Cross of Penn State University visited Rockwell for discussions on the DARPA contract, and future work was planned.

F. PUBLICATIONS AND PRESENTATIONS

1. O. Eknoyan, C. H. Bulmer, H. F. Taylor, W. K. Burns, A. S. Greenblatt, L. A. Beach and R. R. Neurgaonkar, "Vapor Diffused Optical Waveguides in Strontium Barium Niobate (SBN:60)," Appl. Phys. Lett. 48 (1), 13, (1986).
2. J. R. Oliver, R. R. Neurgaonkar and G. L. Shoop, "Structural and Ferroelectric Properties of Morphotropic Phase Boundary Systems in the Tungsten Bronze Family," accepted for publication in the Proceedings of IEEE (International Symposium on the Applications of Ferroelectrics (ISAF) (1986).
3. J. R. Oliver, R. R. Neurgaonkar, W. K. Cory, H. F. Hall, and W. W. Ho, "Tungsten Bronze Materials for High Frequency Dielectrics," presented at the 86th Annual Meeting of the American Ceramic Society, Chicago, Illinois (May 1986).

G. FUTURE WORK

Continue to establish the optimum cerium concentration in the 9-fold coordinated site of the tungsten bronze structure to extend the spectral response into the infrared region without compromising speed. The effort will be extended to grow SBN:60 single crystals doped with other transition metal cations to explore the spectral range. Continue to

examine the role of Ca^{2+} and La^{3+} in various tungsten bronze hosts to obtain superior electro-optic materials for both electro-optic waveguide and photorefractive applications.

H. FUNDING

Contract Estimated Cost	$1,155,549
Fixed Fee	$ 89,758
Total Estimated Contract Price	$1,245,307
Current Contract Funding	$ 370,000
Less Fee	$ 26,772
Available Cost	$ 343,228
Expenditure through 05/31/86 (Cost)	$ 78,795
Balance of Available Funds (Cost)	$ 264,433
Balance of Funding Required to Complete Program	$ 902,079

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