PRODUCTION AND EXAMINATION OF BARIUM-SODIUM NIOBATE SINGLE CRYSTALS. PART 1

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1. Introduction

Ferroelectric double niobates having the structure of tetragonal potassium-tungsten bronze have been produced recently with properties that enable them to be used in nonlinear optics [1-3].

The structure is of perfect tungsten-bronze type, and therefore these three crystals are less damaged than other niobates by laser radiation. The best of these appears to be barium-sodium niobate Ba$_2$NaNb$_5$O$_{15}$ (BSN) [4]. A BSN crystal in a cavity of a YAG:Nd$^{3+}$ laser produces a green emission with 100% conversion of the infrared radiation [5]. The material has also provided an improved continuous-wave parametric laser [6]. BSN crystals are also of value in optoelectronic devices. The half-wave field is 1500-1570 V/cm, which is much less than the value for LiNbO$_3$ [3, 7], so BSN may prove to be a good optical modulator [3, 8].

2. Crystal Growth

The crystals were made by Czochralski's method, which has been used before with BSN [4, 9-11]. The distinctive features of our technique are described below.

A universal oven type PTsP-2 was used, which was developed at the Institute of Crystallography, Academy of Sciences of the USSR. A VChI-25 high-frequency oscillator was used to heat the crucible directly. The temperature was stabilized and monitored with a VRT-2 regulator linked to the transformer driving the rectifier in the oscillator via an autotransformer type LATR, which provided manual control of the output power as well as automatic power reduction during annealing and cooling. A thermopile with a sapphire light guide monitored the temperature of the melt.

A Donets-1 equipment has also recently been used to grow the crystals.

The initial materials were barium and sodium carbonate along with niobium pentoxide, all of special-purity grade. Two compositions were used for the initial mixture: Ba$_{2.083}$Na$_{0.711}$Nb$_5$O$_{15}$ (it is claimed [11] that this mixture crystallizes congruently) and Ba$_2$NaNb$_5$O$_{15}$ (stoichiometric). Each mixture was prefired at about 1200°C in a platinum cup to decompose the carbonates and produce the barium-sodium niobate.
The crystals were grown in air in platinum crucibles 70 x 70 mm, wall thickness 7 mm. The seed crystal was oriented on the c axis and mounted in a platinum holder, which provided reasonably good cooling. However, this metallic holder may result in electrical breakdown through the seed, which consequently melts, because the crystal is of comparatively high electrical conductivity, as is the BSN melt at the growth temperature, while the potential of the crucible is fairly high (about 500 V). The crucible was therefore grounded. The optimum pulling rate and rotation speed were 5 mm/hr and 20 rpm respectively. Figure 1 shows the design of the crucible and the axial temperature gradient.

Crystals of both compositions were grown under identical conditions. The stoichiometric composition gave crystals with less tendency to crack than did the Ba$_{2.085}$Na$_{0.7}$UNb$_5$O$_{15}$ composition, possibly because nonstoichiometric crystals contain many defects [12], which result in high internal stresses and therefore cracking.

BSN crystals of diameter 10-12 mm and length 30-40 mm have been grown; Fig. 2 shows one such crystal.

The crystals immediately after production were colorless, but they rapidly became pink on exposure to light; the coloring and the photosensitivity were suppressed by prolonged annealing in oxygen. Also, crystals grown in dry air (with a boat containing P$_2$O$_5$ in the closed oven) did not become colored on exposure to light. The photosensitivity appears to be associated with the presence of OH$^-$ groups in the crystal.

3. Macroscopic and Microscopic Defects

Twins, domain structure, and defects were observed by cutting the BSN crystals perpendicular to the growth axis into wafers 1-2 mm thick. These were carefully ground and polished with diamond paste.

Fig. 1. (a) Crucible assembly: (1) platinum rod; (2) alundum screen; (3) seed; (4) viewing port; (5) crystal; (6) BSN melt; (7) platinum crucible 70 x 70 mm; (8, 9) alundum vessels; (10) coil; (11) alundum ring. (b) Axial temperature gradient.