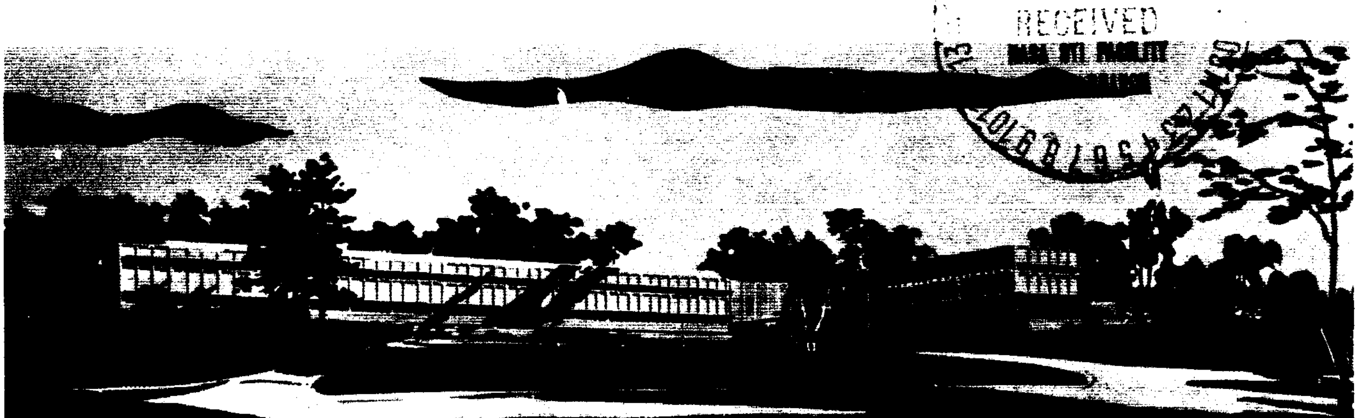

SPERRY RAND
RESEARCH CENTER

SUDBURY, MASSACHUSETTS

SPERRY RAND
CORPORATION

SRRC-CR-68-7

SEMIANNUAL PROGRESS REPORT

on

INVESTIGATION OF SINGLE CRYSTAL MICROWAVE ACOUSTICAL DELAY LINE MATERIALS

R. W. Kedzie and M. Kestigian

Period Covered: July 1, 1967 to December 31, 1967

Contract No. NAS 12-571
Electronics Research Center
National Aeronautics and Space Administration

SPERRY RAND RESEARCH CENTER
SUDBURY, MASSACHUSETTS 01776

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Investigation of Single Crystal Microwave Acoustical Delay Line Materials

I. SUMMARY

The Czochralski direct melt crystal growth technique is employed to study the growth of MgO doped and undoped $LiNbO_3$ and $LiTaO_3$ single crystals. Growth procedures are discussed in addition to methods for annealing, poling and obtaining single domain piezoelectric materials. Differences between the niobate and tantalate systems are discussed with specific references being made to control of the problem of coloration which is related to oxygen deficiencies in the melt.

The as-grown crystals were fabricated into rods and polished for evaluation as microwave acoustical delay line materials. Acoustic attenuation measurements have been performed on both the doped and undoped samples and the results compared. It is found that the temperature independent attenuation is less in the MgO doped samples than in the undoped samples. These results are discussed in terms of the scattering of acoustic waves by crystal imperfections and of the influence MgO doping has on crystal quality.

II. INTRODUCTION

The preparation and evaluation of acoustic materials for delay line applications has had rapid growth since the early work of Jacobsen and that of Woodruff and Ehrenreich.[1] Following their work Oliver and Slack[2] developed a correlation between the thermal properties of single crystals (i.e., thermal conductivity and Debye temperature) and their acoustic attenuation. By means of their work the search for materials possessing low acoustic attenuation has become more systematic.

A particularly interesting aspect of their work is the possibility of reducing the acoustic attenuation in low loss materials by selective doping or alloying of single crystals. In some cases the reduction in attenuation is due to the interaction of the acoustic wave with the energy levels of a paramagnetic impurity and in other cases the reduction is due to impurity scattering of the thermal phonons themselves. This shortens the time in which thermal phonons interact with an acoustic wave and thus effectively reduces the attenuation. In addition, impurities may also reduce inhomogeneity scattering of the sound wave by decreasing the number of oxygen vacancies and other imperfections present in the crystal due to the growth process.

The purpose of this report is to describe the work performed during the first half of NASA contract number NAS 12-571. This work includes crystal growth experiments and the effect which MgO impurity doping has upon the acoustic attenuation of $LiNbO_3$ and $LiTaO_3$ single crystals.

III. DISCUSSION

A. Crystal Growth

1. Lithium Metaniobate

Lithium metaniobate single crystals were prepared from the direct melt by the Czochralski technique. A high frequency generator was used as the heat source in these crystal growth experiments. Typical crystal growth parameters include seed rotation rates of 50 to 100 rpm and seed withdrawal rates of 0.125 to 0.25 in/hr. Although single crystals of good quality have been grown at rates exceeding 0.5 in/hr, detailed measurements of the properties of these crystals have revealed that better crystals are prepared at the slower withdrawal rates.

Clear, transparent, colorless single crystals are obtained if sufficient oxygen surrounds the growing crystal and objectionable impurities are absent in the raw materials. For example, the presence of divalent cations will preclude obtaining a colorless single crystal since these impurities stabilize the formation of lower oxidation states of niobium.

The as-grown lithium metaniobate single crystals exhibit random ferroelectric domains. Single domain material has been obtained by three different methods. These are:

(a) addition of impurity oxides to the melt from which the crystal is grown;

(b) application of an electric field to the growing crystal;

(c) a two-step process in which the single crystal is grown and subsequently subjected to an electric field while being heated at a high temperature.

Techniques (b) and (c) have been shown to yield material of comparable high quality. However, the electric poling procedure in which the single crystal is annealed is more efficient. In addition, this process minimizes the thermal stresses that may cause the raw boule to fracture in the fabrication of rods for acoustic studies.

2. Doped Lithium Metaniobate

Doped lithium metaniobate single crystals were grown by the Czochralski process from a melt which contained 0.01 mole percent magnesium oxide. The crystals were annealed and subjected to an electric field while maintained at a high temperature to obtain single domain material.

Molybdenum oxide doped lithium metaniobate single crystals have also been grown. The presence of molybdenum has been reported by Bell Labs to yield single domain lithium metaniobate single crystals. The incorporation of molybdenum in $LiNbO_3$ invariably yields a single crystal of poorer quality. The growth of molybdenum oxide doped lithium niobate single crystals was discontinued because the two other methods of obtaining single domain single crystals are highly successful.

3. Lithium Metatantalate

Single crystals of lithium metatantalate were prepared from the direct melt by slowly withdrawing a rotating seed through an appropriate temperature gradient. An rf generator is used as the heat source in these experiments. The lithium metatantalate single crystals prepared by this approach are of good optical quality; however, colorless single crystals have not been obtained except for small samples which are a few millimeters in cross-sectional area. The color of the single crystals currently being grown is light yellow to light tan. Prolonged annealing in an oxygen atmosphere at various temperatures has not reduced the coloration.

There are several differences in the lithium metaniobate — lithium metatantalate systems which may prevent us from obtaining a colorless metatantalate single crystal. A higher temperature is required to obtain a tantalate melt causing increased thermal decomposition. The higher operating temperature enhances the formation of tantalum valence states less than five. The presence of lower oxidation states of tantalum would be associated with an oxygen deficiency in the single crystal and as a result yield a colored material.

It has been shown that only a limited variation in composition is possible for lithium metaniobate single crystals; however, this is not the case for the metatantalate system. The stoichiometry of the lithium metatantalate melt plays a major role in the composition of the single crystal that is grown. Any variation in composition from the 1:1:3 atomic ratios favors the formation of single crystals which are not colorless.

4. Doped Lithium Metatantalate

Lithium metatantalate single crystals were grown from iridium crucibles maintained in an oxidizing environment. Stoichiometric melts were prepared which contained 0.1, 0.2 and 0.3 mole percent magnesium oxide. Single crystals of magnesium oxide doped lithium metatantalate were also grown from melts which contained up to five mole percent excess lithium oxide and tantalum oxide, respectively.

B. Acoustic Attenuation

1. Lithium Metaniobate

The attenuation of sound waves in solids depends upon the quality of the single crystals in which the wave is propagating. The conversion of acoustic energy to lattice heat depends upon the presence of crystal imperfections since small perturbations in growth conditions can scatter microwave frequency sound waves directly. Thus, the propagation of sound waves in solids may be used as a measurement of the changes in overall crystal quality which occur when growth conditions are varied.

The attenuation measurements were made by a new pulse echo technique[3] which consists of comparing the attenuation of a particular echo with another echo, usually the first in a series. By this relative method, it is possible to observe the customary temperature dependent attenuation in addition to variations in attenuation due to the amplitudes of the echoes themselves. In this report we will only be concerned with the temperature and frequency dependent attenuation of longitudinal and shear wave echoes in lithium niobate and tantalate grown under different conditions.

An example of the striking difference in sound wave propagation which occurs under slightly different growth conditions is shown in Fig. 1. The temperature dependent attenuation of longitudinal acoustic waves propagating at X-band frequencies in two samples of Czochralski grown $LiNbO_3$ are compared in the figure. The solid curve at the upper left in the figure is due to the undoped sample, and the two curves drawn through the open circle data points are obtained from a $LiNbO_3$ single crystal doped with 0.01 mole percent MgO. Note that the temperature independent attenuation ($4^oK - 30^oK$) of the doped sample is 75 percent less than that of the undoped sample. The temperature dependent attenuation increases rapidly above 35^oK for both samples and does not appear to be altered by the MgO dopant. However, since the total acoustic attenuation is the sum of temperature independent and temperature dependent terms, the reduction in low temperature attenuation enables us to observe an echo in $LiNbO_3$ at room temperature for the first time at X-band frequencies. Although we are unable at this time to obtain relative attenuation data at room temperature and at X-band frequencies, a comparison between the two samples was made at L band. The results of this experiment for longitudinal acoustic waves is plotted in Fig. 2. No significant difference in attenuation is found for the two samples. This is to be expected if only the temperature independent contribution to the attenuation is reduced by the growth process and the loss is dominated by the temperature dependent contribution at room temperature.

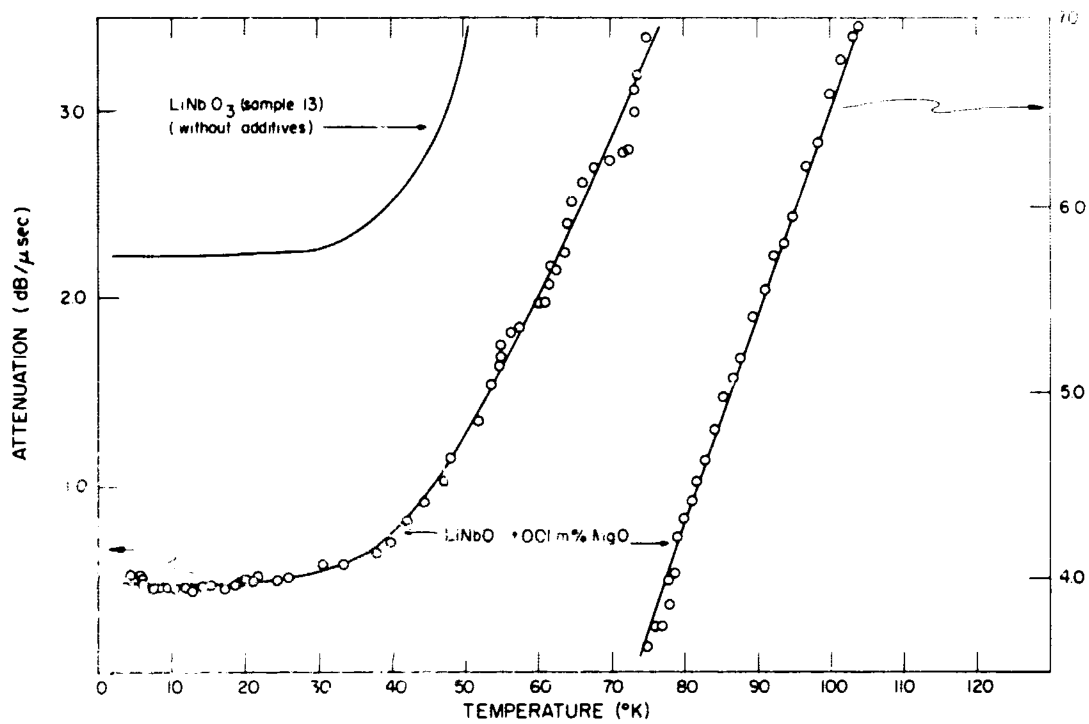

FIG. 1 Longitudinal acoustic wave attenuation in two samples of c-axis oriented $LiNbO_3$ as a function of temperature at X-band frequencies. The upper solid curve is due to $LiNbO_3$ without added impurities and the other curves drawn through the open circles are due to $LiNbO_3$ doped with 0.01 m% MgO. Two separate ordinates are used for the data on the doped crystals.

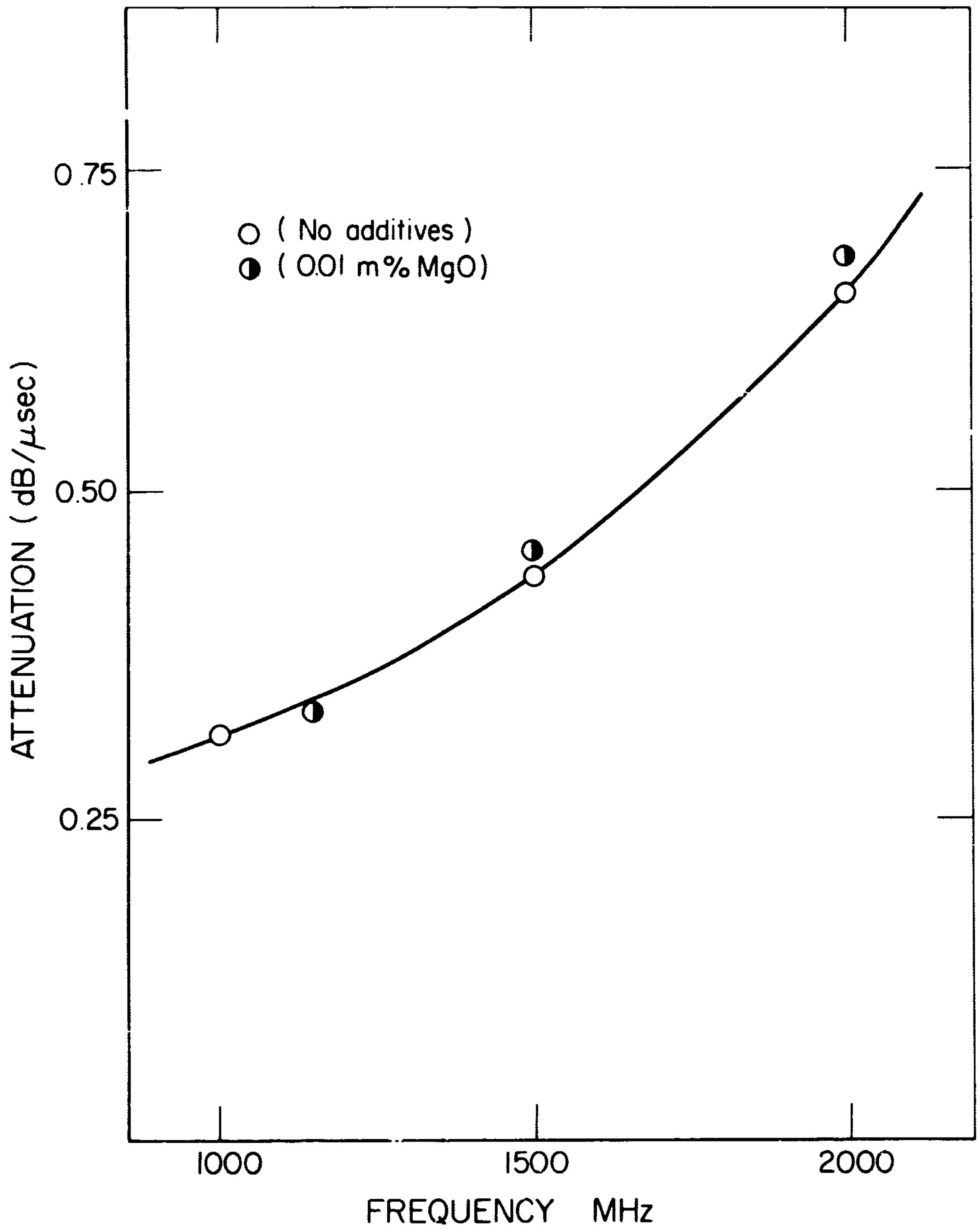

FIG. 2 Frequency dependent (L-Band longitudiral acoustic wave attenuation in c-axis oriented $LiNbO_3$ rods at room temperature. The open circles are due to $LiNbO_3$ without additives and the half-filled circles were obtained from $LiNbO_3$ rods containing 0.01 m% MgO.

Temperature dependent shear wave attenuation was also compared for the MgO doped and undoped $LiNbO_3$ crystals. The best undoped samples are compared with the doped sample in Fig. 3. Shear wave attenuation at low temperatures in the MgO doped single crystal is found to be 20 percent less than the attenuation of the better of the two undoped crystals. This rather small reduction in low temperature attenuation coupled with the more rapid rise in temperature dependent attenuation precludes the observation of a room temperature shear wave echo. These results strongly suggest that the quality of the $LiNbO_3$ has been improved by the MgO doping. This result will be tested further by extension to a homologous crystal.

2. Lithium Metatantalate

Acoustic attenuation measurements were performed on single crystals of $LiTaO_3$ suitably fabricated for microwave transmission experiments. The results of longitudinal acoustic wave generation in several single crystal rods are compared in Fig. 4. The solid lines were drawn through data obtained from single crystals grown without additives. The open circles are the data points obtained for $LiTaO_3$ doped with 0.1 mole percent MgO and a 5 mole percent excess of Ta_2O_5. Note that, although a much smaller temperature independent attenuation region exists at low temperatures, the attenuation between 4^oK and 18^oK is less than the better sample without additives. Several other interesting features of the data are readily apparent. The rate of increase in attenuation with increasing temperature is more rapid for the MgO doped sample than it is for the undoped samples. This seems to indicate a possible shift in thermal phonon distribution which may produce a greater interaction with the sound waves. In addition, a sharp reduction in the attenuation rate occurs for both the doped and undoped samples between 35^oK and 58^oK. This effect may be due to the $LiTaO_3$ crystal structure itself, but more work will be required before its nature is understood. The reduction in temperature independent attenuation has allowed us to observe a single longitudinal echo at room temperature for the first time at X-band frequencies.

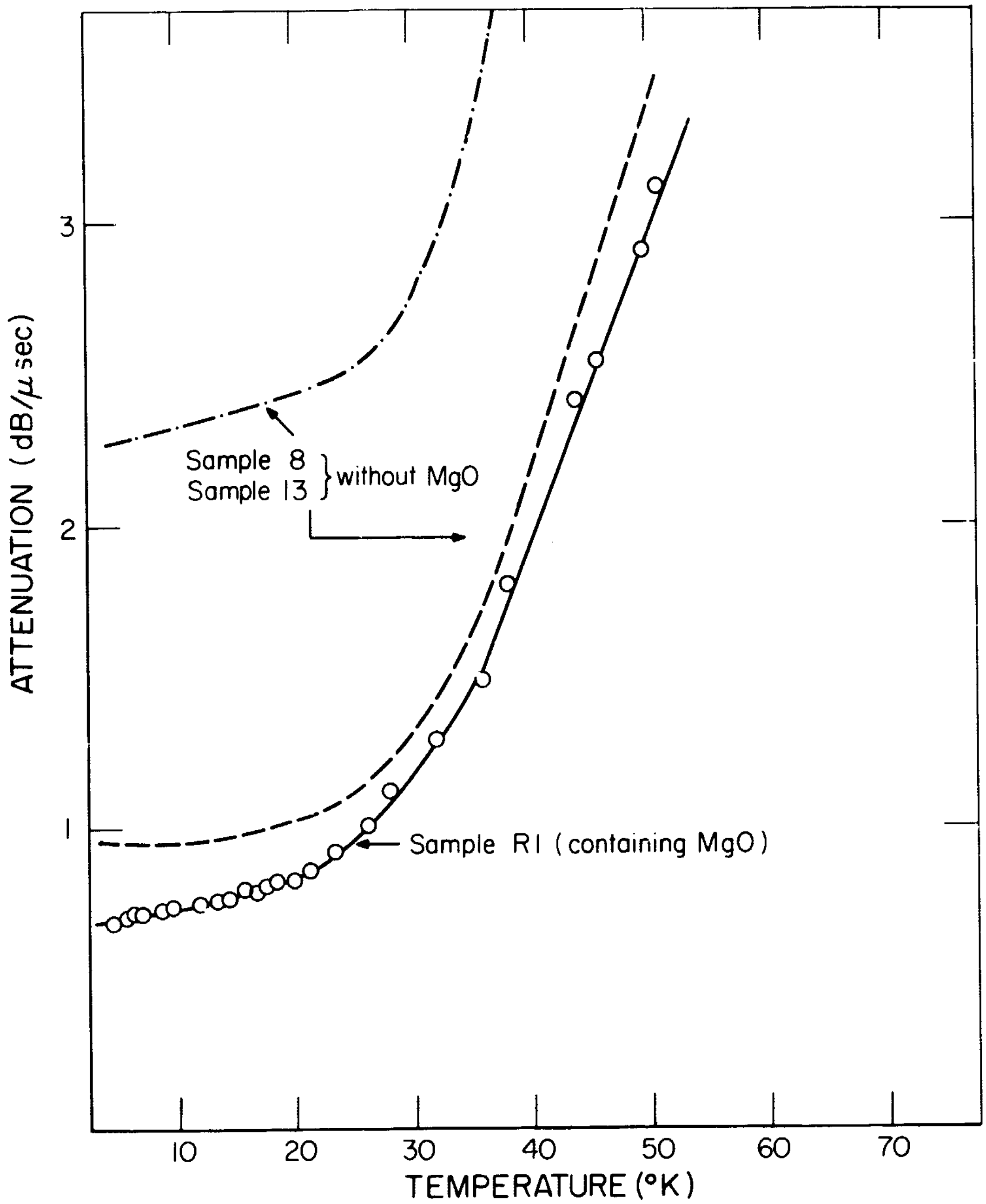

FIG. 3 Temperature dependent attenuation of shear elastic waves compared at X-band frequencies for MgO doped and undoped $LiNbO_3$ single crystal rods. The broken curves are drawn through the data points obtained for two undoped crystals. The open circles are the data points obtained from a $LiNbO_3$ single crystal rod doped with 0.01 m% MgO.

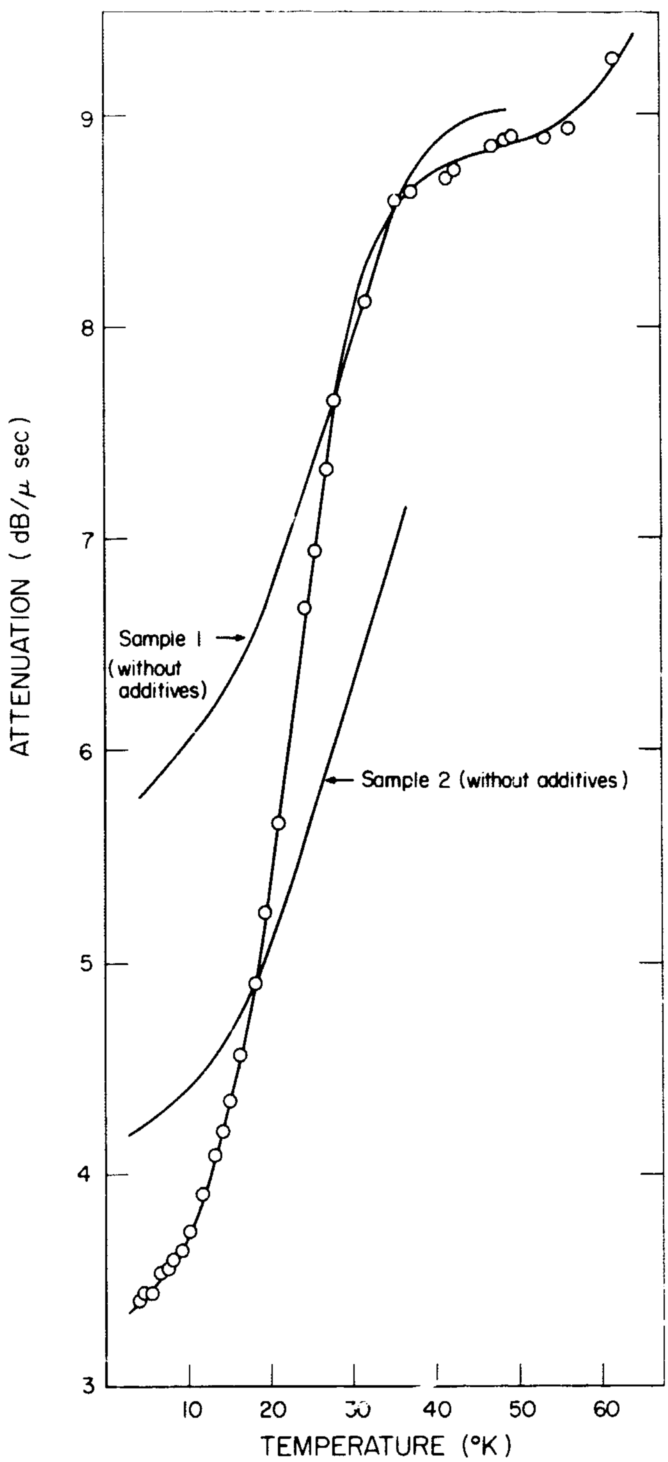

FIG. 4 Temperature dependent longitudinal acoustic wave attenuation in c-axis oriented $LiTaO_3$ rods at X-band frequencies. The solid curves are due to the attenuation of single crystals of $LiTaO_3$ grown without additives. The open circles are the data points obtained for $LiTaO_3$ doped with 0.1 m% MgO and a 5 m% excess of Ta_2O_5.

Previous attempts to generate a resolvable series of shear wave echoes in $LiTaO_3$ were unsuccessful. The acoustic attenuation in these samples was large and a rather complicated echo pattern, as is shown at the top of Fig. 5, resulted. The doped sample, however, yielded a readily resolvable series of shear wave echoes as is shown at the bottom of Fig. 5. We ascribe the difference between the doped and undoped crystals to a reduction in oxygen vacancies in the former and therefore to a more perfect structure. This hypothesis requires further study but these initial results show significant differences between the two types of crystals.

The reduction in inhomogeneity scattering by the addition of MgO has allowed the first temperature dependent shear wave attenuation study to be made. The results of this experiment are shown in Fig. 6. Note that a region of temperature independent attenuation does not exist and a very rapid rise in attenuation occurs with increasing temperature. These encouraging results on the doped $LiNbO_3$ and $LiTaO_3$ systems suggest that more crystal growth experiments should be done in order to improve the over-all crystal quality and by this means reduce the acoustic attenuation. In addition, substitution of rare earths such as terbium and holmium for niobium and tantalum may decrease the attenuation by decreasing the thermal phonon relaxation time. This occurs by selective scattering of thermal phonons by energy levels associated with the paramagnetic rare earth ion. The results described in this report should add impetus to future experiments to obtain better materials for microwave delay line applications.

REFERENCES

1. E. H. Jacobsen, Phys. Rev. Letters 2, 249 (1959); T. O. Woodruff and H. Ehrenreich, Phys. Rev. 123, 1553 (1961).

2. D. W. Oliver and G. A. Slack, J. Appl. Phys. 37, 1542 (1966).

3. R. W. Kedzie, submitted for publication to IEEE Trans. on Sonics and Ultrasonics.

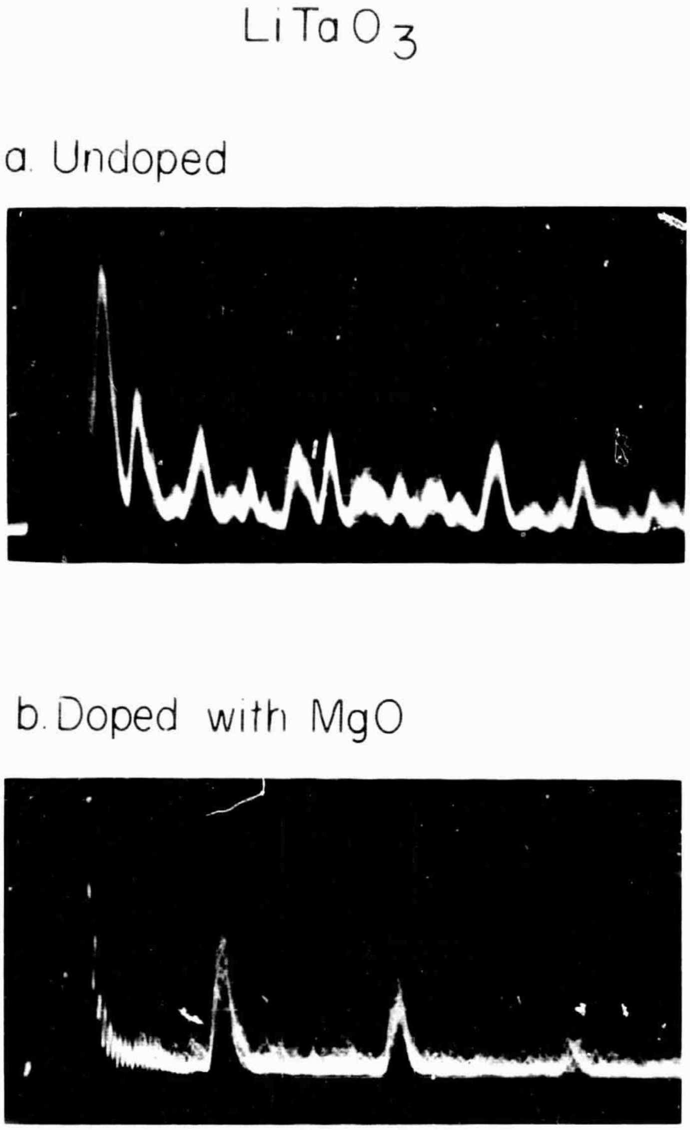

FIG. 5 Oscilloscope photographs of acoustic waves generated in the shear wave configuration of an X-band microwave reentrant cavity. The top photograph was observed in an undoped $LiTaO_3$ crystalline rod at 4.2°K and the bottom photograph was observed at the same temperature in $LiTaO_3$ doped with 0.1 m% MgO and a 5 m% excess of Ta_2O_5.

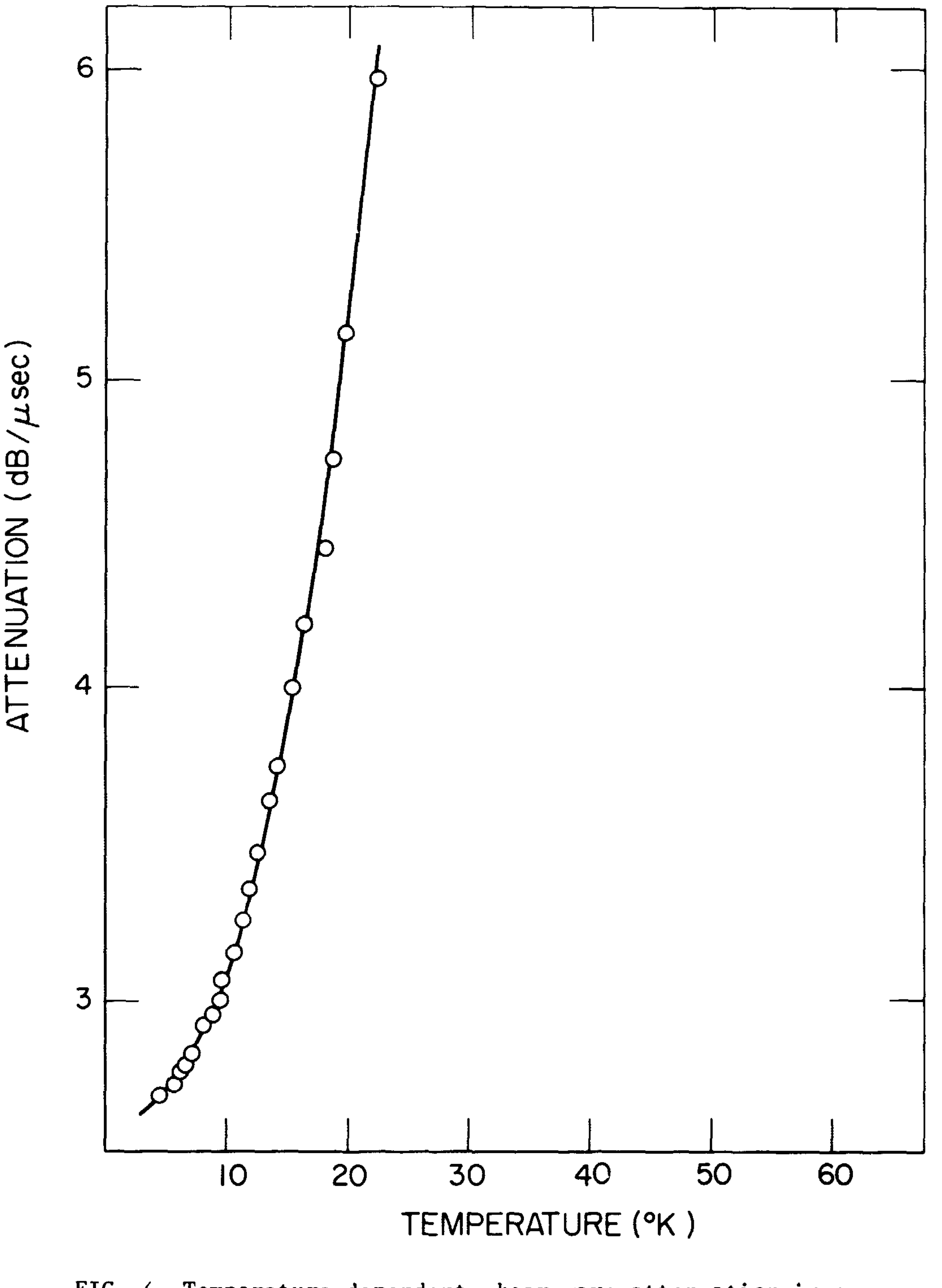

FIG. 6 Temperature dependent shear wave attenuation in a c-axis oriented $LiTaO_3$ single crystalline rod doped with 0.1 m% MgO and a 5 m% excess of Ta_2O_5.