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ULTRASONIC PROPERTIES OF A SUPERIONIC GLASS : B_2O_3 , 0.5 Li_2O , 0.7 $LiCl$

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Abstract. - We measured the attenuation and the phase velocity variations of longitudinal ultrasonic waves in a superionic glass of composition : B_2O_3 , 0.5 Li_2O , 0.7 $LiCl$. The experimental curves show at least three different mechanisms of sound attenuation. Comparison with the result for a less conductive compound (B_2O_3 , 0.5 Li_2O) is done. Two of the mechanisms are attributed to the glassy nature of the compound. One is believed to be due to the superionic properties of the material.

Among the superionic conductors there is a class of compounds which are glassy materials. These are very interesting because it is relatively easy to prepare them with a fairly large size (typically a cubic centimeter). But up to now they are not as good conductor at room temperature as the crystalline superionic. Thus there is a need for studying their properties in order to improve them.

We have measured the attenuation and the phase velocity variations of ultrasonic waves in a superionic glass with the chemical formula : B_2O_3 , 0.5 Li_2O , 0.7 $LiCl$. These materials were synthesized by A. LEVASSEUR and his co-workers, from the University of Bordeaux I. Their room temperature conductivity is between 10^{-5} and $10^{-6} \Omega^{-1} \text{ cm}^{-1}$. It is generally believed that the increase of lithium oxide will change mainly the microscopic structure of the glass when the increase of lithium chloride will increase the conductivity of the material. Thus it seemed worth to us to study a glass with the same content of lithium oxide but without lithium chloride, i.e. B_2O_3 , 0.5 Li_2O . In this way we expected to be able to separate the variations due to the structure of the material (glassy type variations) from those due to the superionic nature of the glass. The experimental results are displayed in Figure 1 for the attenuation and in Figure 2 for the velocity. In these figures the data for the glass with $LiCl$ are shown with full lines when the ones for the glass without $LiCl$ are shown with dashed lines.

At low temperatures (below 15 K) both materials have the same kind of variations. They are glassy types. The variations for the compound with $LiCl$ have been analysed in details and the result reported elsewhere [1]. The attenuation changes as T^3 up to about 1 K, then it bends around towards a plateau the height of which varies linearly with the frequency.

Between 15 K and 100 K a second mechanism of attenuation arised. It seemed clear from the results for the compound without $LiCl$, this mechanism is due to the relaxation of a distribution of two level systems (TLS) with a relaxation time changing with a distributed Arrhenius type law versus the temperature. Such a peak is

often found for glassy materials [2]. This behavior is less obvious for the LiCl compound. But, since an increase of the attenuation arises in the same range of temperature, we believe that the main reason for it is an Arrhenius type relaxation.

Finally, at higher temperatures ($T > 100$ K) a new mechanism of attenuation appears in the LiCl compound. It is certainly much weaker in the other compound since we begin to see such an increase only above 250 K. This mechanism seemed to be of a new type and probably related to the lithium concentration since it exists in both materials and it is much stronger in the compound with the higher lithium concentration.

The velocity variations does not show so well defined temperature behavior. However at low temperature they are characteristic of a glassy compound. At temperatures lower than 4 K, the velocity increases as the logarithm of the temperature and is frequency independent. The slope of the curves for the LiCl doped compound is slightly lower than the ones of the other compound. These variations are known to be due to the resonant interaction between the ultrasonic waves and the TLS [1-3]. Then the curves bend around and a decrease almost linear is observed. It has been shown in Ref. [1] this variations can be explained by the relaxation interaction between the waves and the TLS. The bending appears at higher temperature and the temperature decrease is weaker in the compound without LiCl than in the other.

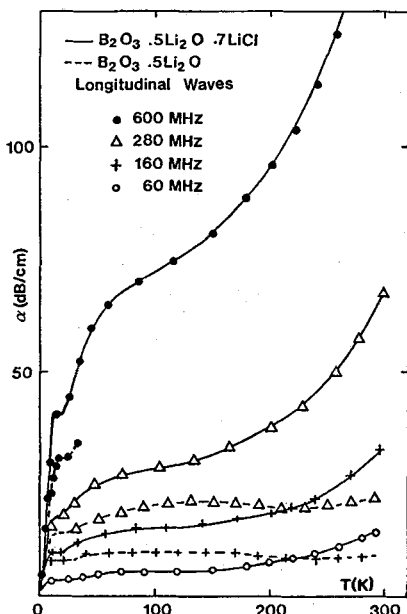


Figure 1 - Experimental variations of the attenuation of longitudinal waves in both compounds. The lines are guide for the eyes. The full lines are relative to B_2O_3 , 0.5 Li_2O , 0.7 LiCl and the dashed lines to B_2O_3 , 0.5 Li_2O .

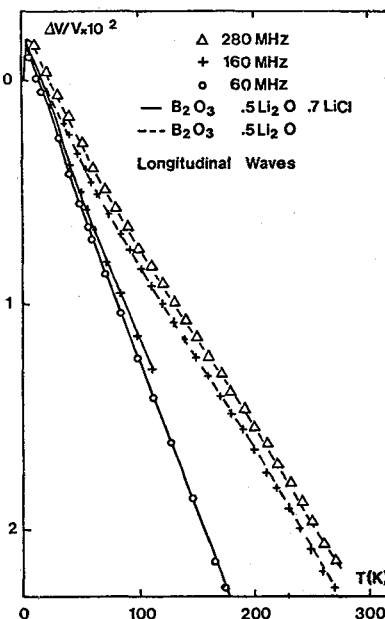


Figure 2 - Experimental velocity variations of longitudinal waves in both compounds. The lines are guide for the eyes. The full lines are relative to B_2O_3 , 0.5 Li_2O , 0.7 LiCl and the dashed lines to B_2O_3 , 0.5 Li_2O .

Around 60 K the slope of the decrease diminishes and a region with a slight dispersion starts. It is in the temperature range near the maximum of the Arrhenius peak. Then we think this change is related to the peak.

On a quantitative point of view, we must remember that the attenuation variations for any effect are at least proportional to the inverse of the third power of the sound velocity. Thus we measured the absolute sound velocity for longitudinal and transverse waves in both compounds. We found $V_L = 6.2 \cdot 10^3$ m/sec and $V_T = 3.75 \cdot 10^3$ m/sec in the LiCl compound, and $V_L = 6.92 \cdot 10^3$ m/sec , $V_T = 3.97 \cdot 10^3$ m/sec in the other. Thus the attenuation of the latter must be multiply by 1.25 before comparison with the LiCl doped compound.

If we do so, the height of the plateau is the same in both compounds. This seemed to show that the coupling constant is independent of the LiCl concentration. The slight difference in the slope of the velocity curves can be taken into account by changing the distribution of two level systems as it was done in Ref. [3].

It has been shown in [1] using the theory of Ref. [3] that the attenuation and the velocity variations in the LiCl compound can be explained quantitatively by introducing, besides the deformation potentials, two constants labeled K_3 and K_7 . K_3 K_7 are expected to be roughly proportional respectively to V_T^{-5} and V_T^{-10} . Then with the velocity measured, K_3 and K_7 should be stronger by a factor of 1.3 and 1.8 in the LiCl doped compound. The accuracy is too small on the attenuation curves to see such a weak factor. But it is clear on the velocity curves that the height of the maximum is lower and the slope of the decrease, higher for the LiCl doped compound than for the other. This is exactly what is expected from the theory developed in Ref. [3].

The quantitative comparison is more difficult at higher temperature since there is no satisfying theory developed up to now to explain the Arrhenius peak. A simple way to analyse the results will be to subtract from the LiCl curve the conveniently scaled variations for the other compound. But this leads to some rather strange variations for the extra attenuation around 40 K. Then we think that the introduction of LiCl changes possibly the distribution of the barrier height. This called for a more careful analysis. Finally we note that the extra attenuation increases very roughly as the frequency.

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