acta phys. slov. 36 (1986), No. 1

VELOCITY OF ULTRASONIC WAVES IN ALKALINE EARTH FLUORIDE AND RARE EARTH FLUORIDE MIXTURE CRYSTAL SYSTEM[1])

P. HEGEDŰŠ[2]), C. MUSIL[2]), S. KOLNÍK[2]), I. ČÁP[2]), Žilina,
B. P. SOBOLEV[3]), Moscow

The paper deals with the investigation of samples of the types $CaF_2 + n(Y, La, Nd, Gd)F_3$ and $BaF_2 + n(Ce, La, Gd)F_3$. The dependence of mass densities and acoustic waves velocities on the admixtures concentration were measured at the frequency of 10 MHz at room temperature. The decrease of the parameter $c_{11} + 2c_{44}$ in $CaF_2 + nXF_3$ crystals and its increase in $BaF_2 + nXF_3$ crystals with increasing admixtures concentration was experimentally proved.

СКОРОСТЬ УЛЬТРАЗВУКОВЫХ ВОЛН В ЩЕЛОЧНО-ЗЕМЕЛЬНЫХ И РЕДКОЗЕМЕЛЬНЫХ ФТОРИСТЫХ СМЕШАННЫХ КРИСТАЛЛИЧЕСКИХ СИСТЕМАХ

В работе приведены результаты исследований образцов кристаллов типов $CaF_2 + n(Y, La, Nd, Gd)F_3$ и $BaF_2 + n(Ce, La, Gd)F_3$. Измерена зависимость массовой плотности потока и скоростей акустических волн от концентрации примесей при комнатной температуре и частоте 10 МГц. Экспериментально доказано, что с увеличением концентрации примесей параметр $C_{11} + 2\,C_{44}$ в кристаллах $CaF_2 + nXF_3$ уменьшается, а в кристаллах $BaF_2 + nXF_3$ увеличивается.

I. INTRODUCTION

Crystals of CaF_2 and BaF_2 are well known because of their varied acoustic properties in a wide temperature range. The distribution of ultrasonic velocity values in dependence on the propagation direction is shown in Fig. 1 and Fig. 2. We can see that the elastic anisotropy parameter $2c_{44}/(c_{11} - c_{12})$ differs appreciably from unity in the case of CaF_2 crystals. Also the same parameter of BaF_2 crystals equals approximately unity, which corresponds to an isotropic medium.

[1]) Contribution presented at the 9th Conference of Ultrasonic Methods in Žilina, August 23—25, 1984.

[2]) Department of Physics, University of Transport and Communications, 010 88 ŽILINA, Czechoslovakia.

[3]) Institute of Crystalography Academy of Sciences, Moscow, UdSSR.

We are interested in such materials, in which certain part of two-valent cations Ca^{2+} or Ba^{2+} are replaced by three-valent admixture cations of rare earth (lanthanides). Those systems remain monocrystalline with a typical cubic symmetry of fluoride structure at a low admixture concentration (up to 5—6 %). In case of a increased concentration these systems are not able to create a crystalline structure and become polycrystalline or amorphous. Their structure consists of a two fluoride

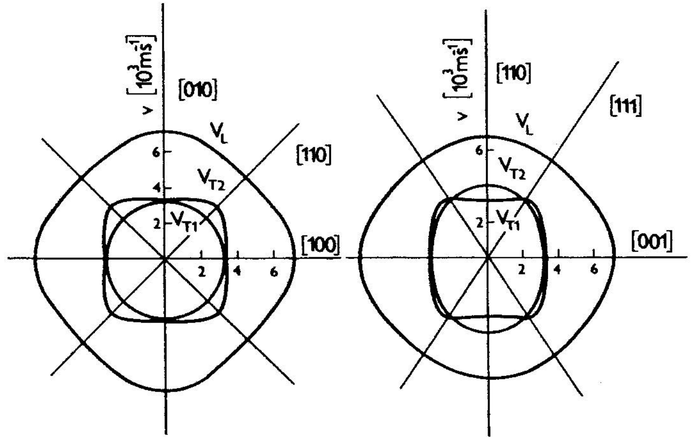

Fig. 1. Acoustic waves velocities in a CaF_2 crystal with parameters $c_{11} = 164.4$ GPa, $c_{44} = 33.7$ GPa, $c_{12} = 53.0$ GPa and velocities [100]: $v_L = 7190\ ms^{-1}$, $v_{T1} = v_{T2} = 3255\ ms^{-1}$; [110]: $v_L = 6692\ ms^{-1}$, $v_{T1} = 3255\ ms^{-1}$, $v_{T2} = 4185\ ms^{-1}$; [111]: $v_L = 6517\ ms^{-1}$, $v_{T1} = v_{T2} = 3900\ ms^{-1}$.

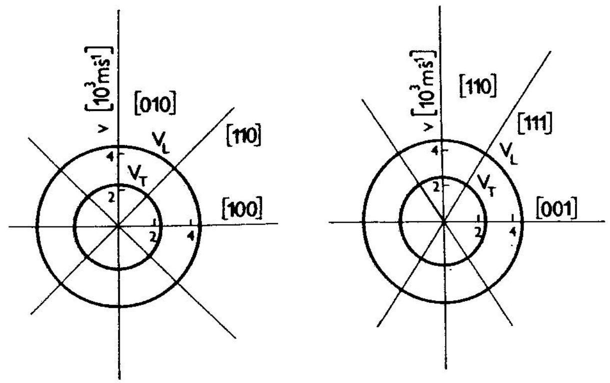

Fig. 2. Acoustic waves velocities in a BaF_2 crystal with parameters $c_{11} = 92{,}0$ GPa, $c_{44} = 25{,}7$ GPa, $c_{12} = 41.6$ GPa and velocities [100]: $v_L = 4336\ ms^{-1}$, $v_{T1} = v_{T2} = 2291\ ms^{-1}$; [110]: $v_L = 4347\ ms^{-1}$, $v_{T1} = 2291\ ms^{-1}$, $v_{T2} = 2270\ ms^{-1}$; [111]: $v_L = 4351\ ms^{-1}$, $v_{T1} = v_{T2} = 2277\ ms^{-1}$.

mixture. The phase diagrams of all cases of the rare earth cations substitution in CaF_2 and BaF_2 have been described by Fedorov [1] in a wide temperature range.

Our paper deals with acoustic waves velocities in such systems and their connection with second order elastic constants.

II. THEORY

Acoustic waves velocities are connected with the second order elastic constants. The velocity of a longitudinal acoustis wave in the [1, 1, 1] direction of the cubic crystal is given by expression [2]

$$v_{L[111]}=\sqrt{\frac{1}{3\varrho}(c_{11}+2c_{12}+4c_{44})} \qquad (1)$$

and the transversal wave velocity for all polarizations as

$$v_{T[111]}=\sqrt{\frac{1}{3\varrho}(c_{11}-c_{12}+c_{44})} \qquad (2)$$

where ϱ is the mass density and c_{ij} are second order elastic constants. The expressions (1) and (2) allow to determine the influence of admixture cations on elastic constants due to acoustic waves velocities measurements. We can obtain a more advantageous relation from the expressions (1) and (2)

$$\varrho(v_L^2+2v_T^2)=c_{11}+2c_{44}. \qquad (3)$$

This relation does not contain the c_{12} elastic constant and is walid for an arbitrary acoustic wave propagation direction in the crystal with cubic symmetry.

Mason [3] obtained the following expression for elastic constants in case of polycrystalline materials containing microcrystals of cubic symmetry

$$c'_{11}=\frac{3}{5}c_{11}+\frac{2}{5}(c_{12}+2c_{44}) \qquad (4)$$

$$c'_{44}=\frac{3}{5}c_{44}+\frac{1}{5}(c_{11}-c_{12}) \qquad (5)$$

by an average value calculation with respect to all possible orientations of microcrystals in the polycrystalline system. From the Masons formulae (4) and (5) we obtain directly the relation

$$c'_{11}+2c'_{44}=c_{11}+2c_{44}. \qquad (6)$$

This relation is very important because it can simplify experimental procedures. We

are able to study the characteristic combination (3) of the materials of cubic symmetry in monocrystalline or polycrystalline and amorphous samples.

III. EXPERIMENT

In our paper we describe the results of the experimental investigation of two different fluoride systems

$$CaF_2+n(Y, La, Nd, Gd)F_3$$
$$BaF_2+n(La, Ce, Gd)F_3$$

where n is the admixture concentration.

First we measured the materials mass density. The results can be seen in Fig. 3 and Fig. 4 versus the admixtures concentration. A mild increase of the mass density with the increase of admixtures contents occurs in all investigated cases.

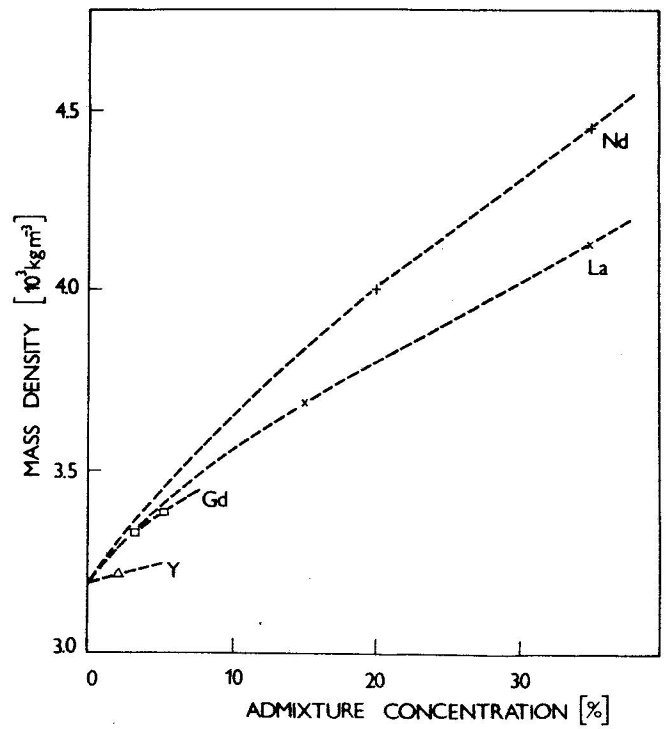

Fig. 3. Mass density of the CaF_2 materials containing different lanthanides admixtures.

Then we measured the velocities of longitudinal and transversal acoustic waves at room temperature. The standard pulse-echo method was used. The wave was generated and detected by means of a piezoelectric transducer. No significant frequency dependence of acoustic waves velocities was expected in a wide frequency region in the mentioned ionic crystals and therefore with respect to the dimensions of the samplex and transducers the frequency of 10 MHz was used in

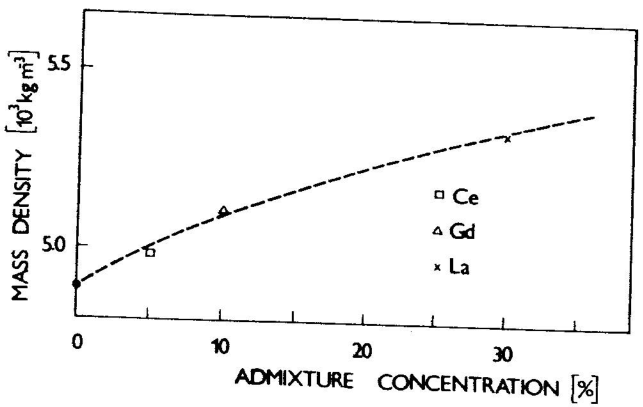

Fig. 4. Mass density of the BaF_2 materials containing different lanthanides admixtures.

Table 1

Velocities and mass density in $CaF_2 + nXF_3$ samples

Sample	Orientation	v_L [ms^{-1}]	v_T [ms^{-1}]	ϱ [10^3 kgm^{-3}]	$\varrho(v_L^2 + 2v_T^2)$ [GPa]
CaF_2	[1 1 1]	6517	3900	3.18	231.8
CaF_2 + 2 % YF_3	[1 1 1]	6500	3700	3.22	224.2
CaF_2 + 15 % LaF_3	polycrystal	5833	3189	3.69	200.6
CaF_2 + 35 % LaF_3	polycrystal	5636	3006	4.13	205.8
CaF_2 + 20 % NdF_3	polycrystal	5786	3367	4.01	225.3
CaF_2 + 35 % NdF_3	polycrystal	5557	2931	4.46	214.4
CaF_2 + 3 % GdF_3	[1 1 1]	6500	3500	3.33	222.3
CaF_2 + 5 % GdF_3	[1 1 0]	6340	4080	3.38	229.4

our experiments. The measured values and their combinations according to the expression (3) are in Tab. 1 and Tab. 2 for both $CaF_2 + nXF_3$ and $BaF_2 + nXF_3$ materials. The samples with high contents of rare earths did not show the

Table 2

Velocities and mass density in $BaF_2 + nXF_3$ samples

Sample	Orientation	v_L [ms^{-1}]	v_T [ms^{-1}]	[10^3 kgm^{-3}]	$\varrho(v_L^2 + 2v_T^2)$ [GPa]
BaF_2	[1 1 1]	4351	2277	4.39	143.4
BaF_2 + 5 % CeF_3	[1 1 1]	4385	2240	4.98	145.8
BaF_2 + 30 % LaF_3	polycrystal	4415	2380	5.33	164.4
BaF_2 + 10 % GdF_3	polycrystal	4710	2600	5.11	182.4

properties of monocrystals. This was verified by optical microscopy and ultrasonic measurements of transversal waves. With regard to this fact the data in the last column of both tables contain the values $(c_{11} + 2_{c44})$ or $(c'_{11} + 2c'_{44})$ of the measured samples.

IV. CONCLUSION

In case of $CaF_2 + nXF_3$ materials, Tab. 1, we can see that the values of $(c_{11} + 2c_{44})$ are in all investigated cases below the value of pure CaF_2. It means that the presence of rare earth fluorides causes the decrease of the elastic constant c_{11}, which in connected with the central interatomic forces [4]. The contribution of c_{11} to the total decrease of $(c_{11} + 2c_{44})$ is decisive.

In $BaF_2 - nXF_3$ materials, Tab. 2, the value of $(c_{11} + 2c_{44})$ increases compared with the value of pure BaF_2. The presence of rare earth fluorides causes the increase of the constant c_{11}.

The possibility of measuring changes of elastic constants by means of acoustic waves will be very useful for investigating the microscopic structure of the studied materials mainly at high temperatures at which fast ionic transport takes place.

REFERENCES

[1] Fedorov, P. P.: *Izučenije diagram sostojanija sistem CaF_2-(Y-La)F_3i polimorfizma trifloridov redkozemlennych elementov*. Tezisi. Moskva 1981.

[2] Mason, W. P.: *Piezoelectric Crystals and Their Application to Ultrasonics*. New York 1950 (Russian, Moscow 1952).

[3] Truell, R., Elbaum, Ch., Chick, B. B.: *Ultrasonic Methods in Solid State Physics*. (Russian transl. Moscow 1968).

[4] Born, M., Huang, K.: *Dynamical Theory of Crystal lattices*. (Russian transl. Moscow 1958).

Received December 14th, 1984

Revised version received January 2nd, 1985