

ELASTIC ANISOTROPY OF ALCALINE EARTHS FLUORIDES WITH RARE EARTHS FLUORIDES INGREDIENTS¹⁾

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The paper deals with the experimental investigation of solid solutions of alkaline earths fluorides with rare earths fluoride ingredients. The new method of elastic anisotropy and second order elastic coefficients experimental investigation was developed to avoid the necessity of an exact crystallographic sample orientation. It was applied to the investigation of a set of crystalline materials based on CaF_2 and BaF_2 at room temperature by means of the standard acoustic pulse-echo method at the frequency of 11 MHz.

1. INTRODUCTION

Elastic properties of CaF_2 , SrF_2 and BaF_2 crystals were investigated by many authors at room temperature [1], [2], at very low [3] and at high temperatures [4], [5]. Little attention, however, was devoted to the investigation of their anisotropy. Recently, the development of the preparation of new materials derived of alkaline earths fluorides by means of rare earths ingredients in a wide concentrations range [6] has made the investigation of the whole system of the acoustic properties of such new materials very actual in obtaining a survey of the ingredients influence on the second-order elastic coefficients and the elastic anisotropy quantities. The knowledge of such influences is decisive not only for the solution of the technology problems of the preparation of these perspective materials, but also for the estimation of the absorption coefficient of the surface acoustic waves, which is significantly connected with elastic anisotropy [7].

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II. ELASTIC ANISOTROPY OF CUBIC CRYSTALS

Elastic anisotropy is mainly connected with different velocities of acoustic waves of the same mode in various crystallographic directions. The anisotropy can be characterized by means of an elastic coefficients c_k matrix taking the properties of isotropic medium into account [8]. In connection with the symmetry of the mentioned materials we shall describe in more detail cubic crystals.

In the case of crystals with cubic symmetry the difference of longitudinal acoustic waves in the [110] and the [100] directions is directly connected with the crystal anisotropy

$$V_L = V_{L(100)} - V_{L(110)}$$

where

$$V_{L(100)} = \sqrt{\frac{c_{11}}{\rho}} \quad V_{L(110)} = \sqrt{\frac{c_{11} + 2c_{44} + c_{12}}{2\rho}}$$

are the corresponding longitudinal waves velocities, c_k the second-order elastic coefficients and ρ mass density. From the practical point of view it is more convenient to characterize the crystal anisotropy as

$$A_L = V_{L(100)}^2 - V_{L(110)}^2 = \frac{1}{2\rho} \sqrt{(c_{11} - c_{12} - 2c_{44})}. \quad (1)$$

Similarly we can use transversal modes velocities in significant propagation directions

$$V_{T(110)} = \sqrt{\frac{c_{11} - c_{12}}{2\rho}} \quad V_{T(110)} = V_{T(100)} = \sqrt{\frac{c_{44}}{\rho}}$$

where V_T and V_{T1} are fast and slow transversal modes, $V_{T(110)}$ corresponds to the polarization in the (110) plane and $V_{T(110)}$ is polarized normally to this plane. In the [100] direction both modes have the same velocity $V_T = V_{T1} = V_T$. From these expressions there follows another anisotropy quantity

$$A_T = V_{T(110)}^2 - V_{T(100)}^2 = \frac{1}{2\rho} (c_{11} - c_{12} - 2c_{44}). \quad (2)$$

It is seen that both quantities A_L and A_T have the same value. There exists a significant second-order elastic coefficients combination characterizing the elastic anisotropy called anisotropy given by

$$D \triangleq c_{11} - c_{12} - 2c_{44} \quad (3)$$

which reaches the zero value for an isotropic medium. Parameters of another

relative anisotropy are in many cases more convenient. The Zener parameter is given by [10]

$$p = \frac{V_{T(110)}^2}{V_{T(100)}^2} = \frac{2c_{44}}{c_{11} - c_{12}} \quad (4)$$

and the relative parameter

$$\xi = \frac{V_{L(100)}^2}{V_{T(100)}^2} = \frac{c_{11}}{c_{44}}. \quad (5)$$

The measured anisotropy parameters enable us to calculate the second-order elastic coefficients by means of relations following from (3), (4), and (5)

$$c_{11} = \frac{p\xi}{2(1-p)} D \quad c_{44} = \frac{p}{2(1-p)} D \quad c_{12} = \frac{p\xi - 2}{2(1-p)} D. \quad (6)$$

These relations are suitable for describing strongly anisotropic media. In quasi-isotropic crystals they give very inaccurate results because of the $D \rightarrow 0$ and the $p \rightarrow 1$ limits of both parameters. In such case the invariant quantity

$$I = \rho(V_L^2 + V_{T1}^2 + V_T^2) = c_{11} + 2c_{44} \quad (7)$$

independent of the acoustic waves propagation direction in the cubic crystal is very advantageous for the elastic coefficients investigation. After eliminating the anisotropy D from (6) by applying (7) we obtain

$$c_{11} = \frac{\xi}{\xi + 2} I \quad c_{44} = \frac{1}{\xi + 2} I \quad c_{12} = \frac{p\xi - 2}{2(\xi + 2)} I. \quad (8)$$

These relations allow us to calculate exactly elastic coefficients values up to the isotropic state.

The presented formulae (8) are very useful for the elastic coefficients investigation in the case of mixture crystals with low concentrated rare earths ingredients. It will be seen that the elastic coefficients c_{12} and c_{44} are quasi-independent on the ingredients concentration. Only the coefficient c_{11} is significantly influenced by their presence. Under the mentioned assumption and the first-order c_{11} approximation the relations (4) and (5) can be expressed due to an invariant (7) relative variation

$$\xi = (\xi_0 + 2) \left(1 + \frac{I - I_0}{I_0} \right) - 2 \quad (9)$$

$$p = p_0 \left[1 + \frac{p_0}{2} \left(\xi_0 + 2 \right) \frac{I - I_0}{I_0} \right]^{-1} \quad (10)$$

where ξ_0, ρ_0, I_0 are the values of the pure crystal and ξ, ρ, I correspond to the mixture crystal. In the case of a well-known pure crystal parameters only the invariant I measurement is necessary to the elastic anisotropy investigation. From the experimental point of view there is no need of the accurate crystallographic orientation of the sample for the invariant quantity (7) evaluation. The obtained relative anisotropy parameters (9) and (10) allow us to calculate the second-order elastic coefficients of the mixture crystals by means of the relations (8).

III. ELASTIC PROPERTIES OF CaF_2 , SrF_2 and BaF_2 CRYSTALS

The elastic properties of alkaline earths fluoride crystals with cubic symmetry as CaF_2 , SrF_2 and BaF_2 have been investigated by many authors at very low [1], [2], [3] and high temperatures [4], [5], [6] up to 1500 K. The results of these publications have been completed with our measurements in the room temperature region and plotted in Fig. 1. We have extrapolated the plotted dependences above the 1500 K point up to melting temperatures under the assumption that all crystals approach the values given by the relations $c_{44} \rightarrow 0$ and $c_{11} \rightarrow c_{12}$ which are typical for an isotropic liquid medium in the vicinity of the melting temperature. The pointed curves follow the lower temperatures behaviour, whereas the thin curves correspond to the expected actual dependence near the melting points. It is seen from these extrapolations that the most drastic change of the coefficient c_{11} occurs near the transition to the liquid state. In the case of CaF_2 the difference between the A and A' points (Fig. 1.) is $\Delta c_{11} \approx 65$ GPa, in the case of SrF_2 it is $\Delta c_{11} \approx 25$ GPa between the B and B' points and in the case of BaF_2 it is $\Delta c_{11} \approx 18$ GPa between points the C and C'. The coefficient c_{44} reaches zero values in all cases and c_{12} is quasi constant. Such elastic properties are in accordance with the mechanism of interatomic forces. Another conclusion following from the plotted dependences is connected with the successive decrease of the second-order elastic coefficients in a wide temperature range up to 1500 K due to the interchange of Ca^{2+} , Sr^{2+} and Ba^{2+} cations in these isostructural crystals. We expect a similar behaviour above the temperature of 1500 K up to melting points. The most expressive change occurs in the case of the c_{11} coefficient, whereas both c_{12} and c_{44} change only slightly. It means that the changes caused by isovalent cation interchanges influence significantly only the c_{11} elastic coefficient.

The elastic coefficient changes are connected with different cation diameters. Their values are given by [12] as 2.28×10^{-10} m (Ca^{2+}), 2.54×10^{-10} m (Sr^{2+}) and 3.00×10^{-10} m (Ba^{2+}) for the fluoride compositions. It follows from Fig. 1. that the increasing of the cation diameter in the system of alkaline earths fluorides leads to the decrease of all second-order elastic coefficients. If we take

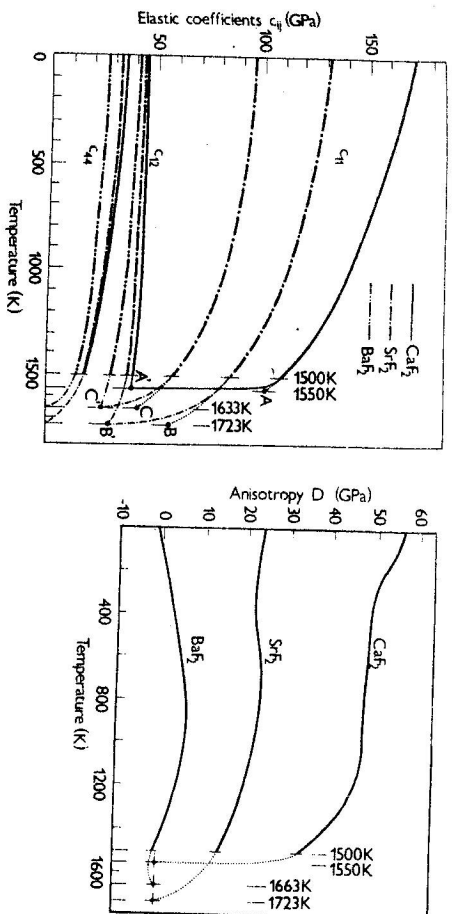


Fig. 1. — Temperature dependence of elastic coefficients c_{11} , c_{12} and c_{44} of CaF_2 , SrF_2 and BaF_2 crystals.

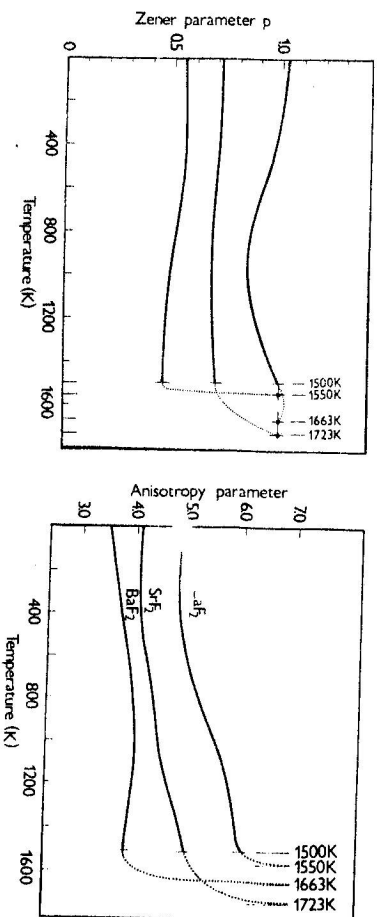


Fig. 2. — Temperature dependence of anisotropy D of CaF_2 , SrF_2 and BaF_2 crystals.

Fig. 3. — Temperature dependence of anisotropy parameter p of CaF_2 , SrF_2 and BaF_2 crystals.

Fig. 4. — Temperature dependence of anisotropy parameter ξ of CaF_2 , SrF_2 and BaF_2 crystals.

the Vegard rule [13] into account according to which the isovalent cations can substitute one another without changing the crystal structure, mainly in the case of not very different cation diameters, it follows that the crystals with arbitrary elastic coefficients limited in the whole range by the plots in Fig. 1. should be obtained due to successive cation exchange.

The temperature dependences of the anisotropy parameters D , p and ξ are plotted in Fig. 2., Fig. 3. and Fig. 4. for all the discussed alkaline earths fluorides. The corresponding values of the parameters have been calculated from

the second-order elastic coefficients given in Fig. 1, from low temperatures up to 1500 K and extrapolated up to melting points to the values of the isotropic liquid state. The most pronounced anisotropy is that of the CaF_2 crystal. The crystal of BaF_2 , on the other hand, presents quasi isotropic properties in all investigated parameters in a wide temperature region of the solid phase. It is remarkable that the Zener parameter p has values near unity from very low temperatures up to room temperature and the anisotropy D crosses the zero value in this range. The relative parameter ξ reaches the value of 3.6 in this region of the cubic crystal "elastic isotropy". We can see the parameters D and p do not significantly change in the vicinity of the melting point in case of BaF_2 , whereas the CaF_2 crystal presents the most expressive change of both parameters near the phase transition to the liquid state, Fig. 3 and Fig. 4.

IV. ELASTIC PROPERTIES OF MIXED CRYSTALS

We have shown that the BaF_2 crystal with its lowest elastic anisotropy is typical of the system of alkaline earths fluorides. It connects with increasing anisotropy due to the substitution of the Ba^{2+} cation by those isovalent Sr^{2+} and Ca^{2+} with smaller cation diameters. Another problem are elastic anisotropy changes due to aliovalent cation substitution in the crystals of the CaF_2 structure.

In [6] phase diagrams of the systems $MF_2 + xZF_2$, are dealt with where M represents the alkaline earths (Ba, Sr and Ca), Z the rare earths (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and x is the concentration. We can conclude from the results in [6] that the rare earths ingredients influence mainly the c_{11} elastic coefficient and so the invariant I of the thus created solid solutions. The coefficients c_{12} and c_{44} change only slightly in a wide concentration range owing to their preserving practically the type of the CaF_2 structure up to ingredients concentrations of several tens of percent.

We have investigated many materials of the mentioned structure based on the CaF_2 and the BaF_2 crystals at room temperature. The obtained results are in Tab. 1 and Tab. 2. We have supposed the coefficients c_{12} and c_{44} to be quasi independent of the ingredients concentration. It allowed us to evaluate the anisotropy parameters and successively the elastic coefficients by means of the relations (9) and (10). The parameters of pure CaF_2 and BaF_2 crystals were measured on the samples with an accurate crystallographic orientation according to the definitions (4), (5) and (7). The obtained values are in the first lines of Tab. 1. and Tab. 2. In the case of the mixed crystals we have measured only the invariant quantity (7) without the need of special crystallographic orientation.

Table 1

Elastic properties of some solid solutions on the base of BaF_2 at room temperature					
Sample	ρ [$10^3 \text{ kg} \cdot \text{m}^{-3}$]	I [GPa]	ξ	p	c_{11} [GPa]
BaF_2	4.89	143.4	3.58	1.02	92.0
$\text{BaF}_2 + 5\% \text{ LaF}_3$	4.97	145.0	3.64	0.99	93.6
$\text{BaF}_2 + 10\% \text{ LaF}_3$	5.02	147.0	3.72	0.95	95.6
$\text{BaF}_2 + 30\% \text{ LaF}_3$	5.33	164.0	4.39	0.72	112.7
$\text{BaF}_2 + 5\% \text{ CeF}_3$	4.98	145.8	3.67	0.98	94.4
$\text{BaF}_2 + 10\% \text{ GdF}_3$	5.11	182.4	5.10	0.58	131.1

Table 2

Elastic properties of some solid solutions on the base of CaF_2 at room temperature					
Sample	ρ [$10^3 \text{ kg} \cdot \text{m}^{-3}$]	I GPa	ξ	p	c_{11} [GPa]
CaF_2	3.18	231.8	4.87	0.56	164.2
$\text{CaF}_2 + 2\% \text{ YF}_3$	3.22	224.0	4.67	0.59	156.6
$\text{CaF}_2 + 15\% \text{ LaF}_3$	3.69	200.6	3.95	0.75	133.2
$\text{CaF}_2 + 35\% \text{ LaF}_3$	4.13	205.8	4.11	0.71	138.4
$\text{CaF}_2 + 20\% \text{ NdF}_3$	4.01	225.3	4.69	0.60	157.9
$\text{CaF}_2 + 35\% \text{ NdF}_3$	4.64	214.4	4.36	0.65	147.0

The presented results have been obtained from the acoustic waves velocities measurement by means of the standard pulse-echo method at a frequency of 11 MHz at room temperature on samples about 1 cm long.

We can see in Tab. 1 that the ingredients cause in the BaF_2 crystal an increase of the invariant quantity I , which is connected with the increasing elastic coefficient c_{11} and the increasing crystal anisotropy. Solid solutions based on CaF_2 , Tab. 2., are typical of their decrease of the invariant quantity I connected with the decrease of c_{11} and crystal anisotropy in confront with the pure CaF_2 crystal.

V. CONCLUSION

The investigation of elastic anisotropy of crystalline materials gives us very important information on their complex elastic properties. The most serious difficulty consists in the necessity of an exact crystallographic sample orientation connected with the anisotropy quantities definitions. We have developed an effective method for the case of the investigation of a set of samples derived from the same basic crystal by means of isovalent or aliovalent cations exchange, typical with a very slight influence on the elastic coefficients c_{12} and c_{44} and a

significant variation of c_{11} . We have proved in such a case that the anisotropy quantities variations depend only on their relative variation of the invariant quantity I independent of the acoustic wave propagation direction. This fact is important from the experimental point of view, because it allowed us to accomplish the whole experiment by means of a sole measurement of all three acoustic modes velocities on a sample with an arbitrary crystallographic orientation.

After a detailed analysis of the alkaline earths fluoride properties we have used this method for the investigation of the elastic anisotropy of a set of samples of alkaline earths fluorides with rare earths ingredients. The suggested method proved to be very effective.

REFERENCES

- [1] Goerlich, D.: Phys. Rev. 135 (1964), A 1331.
- [2] Wong, C., Schuele, D. E.: J. Phys. Chem. Solids 29 (1968), 1225, 1309.
- [3] Saškolskaja, M. P.: *Akustičeskie kristally*. Izd. Nauka, Moskva 1982.
- [4] Catlow, C. R. A., Comins, J. D., Germano, F. A., Harley, R. T., Huest, W.: J. Phys. C—Solid State Phys. 11 (1978), 3179.
- [5] Monarech, M. O., Pederson, D. O.: J. Acoust. Soc. Amer. 75 (1984), 1766.
- [6] Fedorov, P. P.: *Izučenje diagram sostojanja sistem CaF_2 — ($\gamma-La$) F_3 i polimorfizm trifloridov redkozemelnykh elementov*. Tezisi, IKAN, Moskva 1981.
- [7] Royer, D., Dieulesaint, E.: J. Acoust. Soc. Amer. 76 (1984), 1438.
- [8] Fedorov, F. I.: *Teorija uprugich voln v kristallach*. Izd. Nauka, Moskva 1965.
- [9] Truell, R., Eibaum, Ch., Chick, V. B.: *Ultrasonic methods in solid state physics* (in Russian). Izd. Mir, Moskva 1972.
- [10] Dieulesaint, E., Royer, D.: *Ondes elastiques dans les solides*. (in Russian), Izd. Nauka, Moskva 1982.
- [11] Kolnik, S., Čap, I., Hegediš, P., Musil, C., Sobolev, V. P.: *Ultrasonic Investigation of Elastic Anisotropy of Crystals with CaF_2 Structure*. Preceed. of Ultrasound 86 DT ČSVTS, Bratislava, 1986, 15.
- [12] Kaminskij, A. A.: *Lazernye materialy*. Izd. Nauka, Moskva 1975.
- [13] Kašpar, J., Šmid, J., Eckstein, J.: *Monokristaly*. (in Czech). SNTL, Praha 1957.

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АНИЗОТРОПИЯ УПРУГИХ СВОЙСТВ ШЕЛОЧНОЗЕМЕЛЬНЫХ ФТОРИСТЫХ СОЕДИНЕНИЙ С РЕДКОЗЕМЕЛЬНЫМИ ФТОРИСТЫМИ КОМПОНЕНТАМИ

В работе приводятся результаты экспериментальных исследований твердых растворов щелочноземельных фтористых соединений с редкоземельными фтористыми компонентами. Разработана нового метода экспериментального исследования анизотропии упругих свойств и модулей упругости второго порядка были проведены так, чтобы избежать необходимости точной ориентировки кристаллографического образца. Метод был использован для исследования совокунности кристаллических веществ, основанных на CaF_2 и BaF_2 , при комнатной температуре посредством стандартного акустического импульсного метода с отраженным сигналом при частоте 11 МГц.