Fluoride laser nanoceramics

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Abstract. Because of the recent technology progress in the synthesis of fluoride ceramics by so-called hot-pressing method, several cooperating research groups have produced and meticulously described various polycrystalline ceramic samples with optical characteristics similar to the properties of corresponding single crystals. Their achievements made fluoride optical materials less expensive, more diverse and easier available for the use in solid-state lasers. The present review covers studies of fluoride ceramic materials and their properties in the last fifty years. It describes the most significant results obtained by leading scientific groups and indicates the most promising directions where research of fluoride laser ceramics should proceed in near future.

1. Introduction

Originally, word “ceramics” was applied to thermally treated mixtures of clay, water and some additional supplements. In the present time, this term is used for polycrystalline inorganic materials obtained by the thermal treatment of precursor batches in order to assure mechanical integrity and property continuity of the manufactured item. Ceramics can contain X-ray amorphous or glassy component, however, one would use more specific name such as “glass ceramics” only in the case of domination of non-crystalline components over crystalline ones in the described sample.

Optical ceramic materials, and in particular fluoride optical ceramics, have been known for several decades [1]. Since the time of their discovery in the middle of the 20-th century, many researchers from various laboratories have worked on the application of these polycrystalline transparent optical materials in various areas. Both American and Soviet techniques for preparing of ceramic magnesium, calcium and barium fluorides (US trademark IRTRAN and USSR trademark CO) for use in IR-optics were developed in 1960-s to 1970-s [2-5]. Bulk ceramic samples were produced by a hot pressing technique via sintering powders of the corresponding substances under pressure. The first remarkable preparations of optical ceramics for use as laser materials were carried out specifically with metal fluorides by Eastman Kodak [2, 6, 7]. This included the first hot-pressed polycrystalline CaF₂:Dy²⁺ laser body. It is worth noting that these laser materials should not have optical losses at the generation wavelength of more than $10^{-3} \text{ cm}^{-1}$, while gradients of the refractive index should not exceed $10^{-5}$-$10^{-6} \text{ cm}^{-1}$. In order to achieve such quality product, the earliest technology for manufacturing laser materials included the preparation of starting components from their melts, followed by their pulverization and pressing. Complex procedures of powder surface treatment and ceramics translucence were also utilized. These fluoride samples exhibited sustaining lasing in them, but power
of the generated beams (7 mW) was much lower than produced with single crystal laser bodies. Similar results were obtained with the use of oxide laser ceramic materials [8, 9].

A new phase of laser ceramics development begins at the end of the 20-th to the beginning of the 21-st centuries, when the high quality neodymium-doped yttrium-aluminum garnet ceramic materials were prepared [10-13]. In contrast with preceding experiments of the 1970-s, the lasing properties of these products were comparable or superior to single crystals. These results renewed interest in the study of fluoride laser ceramics, including its starting materials and preparation. Various ideas concerning the manufacture of fluoride laser ceramics, as well as raw materials for its preparation, were expressed in [14-17]. However, preparation of laser fluoride ceramics has been successfully carried out by the different research groups from A. M. Prokhorov General Physics Institute (Moscow, Russia), State Optical Institute (St. Petersburg, Russia) and INKROM Company (St. Petersburg, Russia), cooperating under the auspices of Russian Federation state contracts [18-25].

Compared to single crystals and glasses, ceramic materials possess many advantages. First of all, ceramic optical products have an essential degree of freedom in choosing the shape and the size of manufactured specimens. In particular, use of ceramics allows manufacturing of the large size samples. Secondly, one can produce ceramic materials with high and uniform (or otherwise specifically designed) distribution of dopants, whereas the similar feature is not so easily achievable (or even possible) in the case of the single crystals. Thirdly, ceramic preparations have substantial tenacity and durability, whereas crystal and glass optical materials are notoriously fragile. Single crystals become more prone to cracking at the cleavage planes with an increase in their chemical purity and perfection of their structure, while ceramics does not have this tendency.

For example, the growth of single crystals of fluorite-type \( \text{M}_{1-x}\text{R}_x\text{F}_{2+x} \) (\( \text{M} \) – alkali earth metal, and \( \text{R} \) – rare earth element) solid solutions from the melt is hampered by instability of the crystallization front. As a result, the obtained crystals have honeycombed substructure and are optically inhomogeneous.

There are some areas of chemical composition, where one cannot grow single crystals of laser quality from the melt by directed crystallization, or such growth becomes a very difficult procedure despite the existence of the corresponding thermodynamically stable phase [26, 27]. Thus fluoride ceramics technology becomes a very appealing alternative option.

2. Problems of fluoride powders’ chemistry and relevant technology processes

Achieving 100% optical density is a necessary (but insufficient) requirement for laser optic materials. It is a serious problem for oxide ceramic materials. However, physical and chemical properties of fluorides (binary and complex as well) are different from those of the corresponding oxides, and, therefore, the above target can be achieved much easier by the use of the fluoride systems. Unfortunately, there is an additional obstacle in the case of fluoride ceramics: in order to obtain highly optically transparent fluoride ceramics, one has first to overcome some very complex chemical problems.

One such difficulty stems from the fact that fluorides are prone to pyrohydrolysis, \textit{i.e.}, reaction with water and/or water vapor at elevated temperatures [26, 28], leading to the formation of the corresponding oxides and oxofluorides. These products are not isomorphous to the initial fluorides and, being accumulated in the initial material, usually form the second phase as finely dispersed inclusions. This results in the irreversible destruction of optical homogeneity in pyrohydrolyzed materials. Therefore, one must take all necessary precautions to prevent hydrolysis (pyrohydrolysis) at all stages of the manufacturing process. The well-developed surfaces of fluoride particles create additional obstacles in overcoming pyrohydrolysis because these surfaces adsorb various molecules, including water. [29] estimate that fluorides precipitated from aqueous solutions retain up to 15 adsorbed monolayers of water at their surface. These water molecules, which are strongly bound to the particle surface, are not easily removed. This situation becomes even more intractable in the case of nanoparticles with their vast surface area making their pyrohydrolysis much easier than that of macro-particles [30].
One may minimize effect of hydrolysis by using various active fluorinating atmospheres to convert the formed oxides and/or oxofluorides back to the desired fluorides [26]. Gaseous carbon tetrafluoride, CF$_4$, is the reagent most frequently used for this purpose. This or similar fluorinating technologies have been developed to improve the optical quality of fluoride ceramics by conversion of oxides impurities to fluorides (reference), but combining batch fluorination and ceramics manufacturing is a very complicated technical problem. It requires hermetically-sealed vacuum furnace and complete absence of air in the system.

In order to avoid the above complications, researchers developed different protocols to synthesize fluoride ceramics. One of much simpler process is hot pressing. This method turns polycrystalline powders into a monolithic body via particle agglomeration (Figure 1a). Usually, this process performed at $T = (0.5-0.8) \times T_{\text{melting}}$ and up to 300 MPa load under $10^{-2}$-$10^{-3}$ torr vacuum. This technique also has its shortcomings, including reducing conditions which may lead to the appearance of color centers or transition of ions-activators to their lower valence states. Such samples usually exhibit yellow, grey or even black coloration, and they may have inclusions, too. Their treatment in fluorinating atmosphere can result in discoloration and, therefore, remedy this problem.

The quality of the starting materials is one of the most important factors affecting the synthesis of the optical ceramics. Transparency data for different fluorite ceramics samples prepared from different quality batches are presented in Figure 2a: a proper choice of the initial ingredients allowed the creation of products of the same quality as in [2].

Laser materials usually need doping with activator admixtures (unless they work exclusively utilizing color centers). Therefore, authors [31-34] attempted synthesis of two-component activated batches that provided activated ceramics of the appropriate quality.

Preliminary experiments [34] have shown that mixing powders of calcium and erbium fluorides does not lead to products which have an acceptable level of composition homogeneity, for diffusion in the samples is incomplete. Product samples are optically inhomogeneous and do not undergo lasing. This highlights the obvious obstacle with samples of complex chemical composition and batches with multiple precursor components Kuznetsov [32, 33], and Bensalah [31] simultaneously attempted similar approaches to address the latter problem by implementing a co-precipitation from aqueous solutions via slow dropwise addition of starting nitrate solutions to aqueous hydrofluoric acid:

![Figure 1. Two methods of ceramics preparation: hot pressing with agglomeration of powder particles (a) and hot forming via crystal deformation (b). 1 – cylindrical chamber, 2 – heating jacket, 3 – piston, 4 – sample](image-url)
0.95 Ca(NO$_3$)$_2$ + 0.05Yb(NO$_3$)$_3$ + 2.05 HF → Ca$_{0.95}$Yb$_{0.05}$F$_{2.05}$ + 2.05 HNO$_3$.

Figure 2. Optical transparency of CaF$_2$ ceramics prepared by hot-pressing from different starting materials [34] (a); appearance of high optical quality ceramics (external outlook) [2] (b).

Whereas target single-phase M$_{1-x}$R$_x$F$_{2+x}$ solid solutions have been easily precipitated by addition of HF to the aqueous systems containing calcium and/or strontium ions along with lanthanide ions, similarly treated barium-lanthanide fluoride samples appeared to be a mixture of BaF$_2$ and Ba$_4$R$_3$F$_{17}$ phases instead [35]. The latter circumstances prohibited the synthesis of optically homogeneous ceramics due to the fluctuation of the chemical composition within the sample. In contrast, Ca$_{1-x}$R$_x$F$_{2+x}$ batches – after necessary treatment – produce transparent ceramics (Figure 3a and 3b). Some of these Ca$_{1-x}$R$_x$F$_{2+x}$ specimen, e.g., CaF$_2$:Yb ceramics (Figure 3a and 3b), in accordance with their UV spectra, accommodate significant Yb$^{2+}$ concentrations.
Figure 3. CaF$_2$:Yb ceramics prepared by hot-pressing according to [34, 36] (a) and [37] (b)
However, ceramics, prepared from batches initially co-precipitated from aqueous solutions, do not generate lasing because of the strongly adsorbed water layer on the surface of the batch particles [34, 37]. This layer can be hardly removed under a fluorinating atmosphere or under translucence treatment. Lanthanide fluorides undergo hydrolysis much more easily than alkali earth metal fluorides [26, 30], generating oxygen-containing phases between particles and thus causing the light beam scattering.

The deformation of heated crystal under pressure, or hot-forming process for the synthesis of ceramics mentioned above, led to successful avoidance of product contamination with oxygen via pyrohydrolysis (Figure 1b). Whereas Hatch, Carnall et al. [2, 6, 7] hot-pressed preliminary pulverized melts, Basiev, Fedorov et al. [19-25] used the single crystals as starting materials for our hot-pressing protocols. Indeed, parameters of the above hot-forming and hot-pressing processes are different due to the different physical mechanisms of single crystal deformation and consolidation of powder particles in the course of the formation of polycrystalline optic materials.

3. Microstructure

Microstructure of ceramics samples depends on their method of synthesis (Figures. 4 and 5).

Hot-pressing fluoride powders leads to homogeneous microstructure with relatively large (80-150 nm) domains. This has been observed for pure CaF$_2$ as well as for doped ceramics, such as CaF$_2$:Yb. The layered fine nanostructure within these domains has been detected by electron microscopy and atomic force microscopy (AFM): fine layer width for CaF$_2$ is ca. 25 nm [38]. The most probable guess is that this nanostructure stems from crystal twinning within the grains of sample. Deformed at higher temperatures, single crystal samples have different microstructure. For low degrees of deformation, one can observe a fractal crack-type structure of the borders of crystalline domains (Figure 5a). This structure is most likely not stable and should relax with sample aging. When the degree of deformation is increased, sample microstructure becomes inhomogeneous and...
contains relatively large areas (ca. 1 mm) with single crystal-type structure along with areas of grain-type structure, typical for classic ceramics. Only at higher degrees of deformation does the structure of the deformed single crystal turns into a completely homogeneous typical ceramic structure. One can observe layered nanostructure of the ceramics domains of the deformed single crystals very similar to the nanostructure of the hot-pressed powders [38] (Figure 5c).

The above observation can be illustrated with a typical correlation between the average size of BaF₂ crystalline domains and degree of deformation of the single crystal (Figure 6); only highly-deformed samples correspond to the “completely” ceramic state of the studied material.
4. Fluoride ceramics as optical medium

Samples of CaF$_2$ optical ceramics prepared by hot-pressing were studied by [24, 34, 39-43] as the model object. Their CaF$_2$ samples appeared to be practically the same as in [2] (Figure 2b). For comparison, [39-43] have also used standard CaF$_2$ single crystals from the State Optical Institute, St. Petersburg, Russia, and CaF$_2$ natural optical ceramics specimen (Suranskoe deposit, Urals Mountains; average crystalline domain size about 37 nm). The latter ceramic sample was unique natural object formed approximately one billion years ago.

UV/visible and IR absorption spectra of the synthesized and natural CaF$_2$ ceramics (curves 1 and 2) as well as CaF$_2$ single crystal (curves 3) are presented in Figure 7(a, b). The transmission of the ceramics samples is somewhat inferior to that of the single crystal in the near-UV part of the spectrum, however, at visible and IR wavelengths, the corresponding transmission values coincide or almost coincide.
Figure 6. Size of crystalline domains vs. deformation degree of BaF$_2$ single crystal (δ) at 800°C; δ = (h$_0$–h)/h·100, %, where h$_0$ – height of the initial sample and h – height of the formed plate.

Figure 7. Optical transparency of synthesized CaF$_2$ ceramics (thickness = 8.8 mm) (1, 2) and CaF$_2$ single crystal (thickness = 8.3 mm) (3) [34].

Two different methods were used to measure small optical losses in synthesized CaF$_2$ ceramics under monochromatic laser radiation. One method was specifically designed to estimate the losses in optical fibers and was based on measuring the evolving heat from the weakly absorbing medium when a laser beam passed through it [24]. The second method, used by Palashov et al. [41, 42], measured the thermal depolarization of laser radiation in an absorbing medium. Both types of measurements were carried out at 1.06 micron wavelength. The first method gave a loss value of 9•10$^{-3}$ cm$^{-1}$, whereas the second method produced a value of (1.1-1.5)•10$^{-3}$ cm$^{-1}$. Both numbers have indicated a high transparency of the prepared ceramic samples suitable for laser materials. Low values of the optical losses in synthesized CaF$_2$ ceramics was determined by the specific structure of the boundaries between crystalline grains.

The study of transport of sub-THz heat acoustic phonons in CaF$_2$ single crystals and ceramics showed the length of their free path at 3.82 K to be equal to 1.2•10$^{-1}$; 6.6•10$^{-2}$; 1.4•10$^{-2}$ cm respectively for single crystal, synthesized and natural ceramic samples [43]. The actual thickness of the above boundary layers between crystalline domains in natural ceramics has been estimated to be
about 1.5 ± 0.3 nm. At the same time, actual samples of the synthesized CaF$_2$ ceramics exhibited properties with zero or almost no boundary layer.

A comparative study of the thermal conductivity of CaF$_2$ single crystal, synthesized and natural ceramic samples has shown that all have practically the same properties over the 50-300 K temperature interval [39] (Figure 8).

Figure 8. Thermal conductivity of CaF$_2$ samples: natural sample from Suranskoe deposit, Urals Mountains (1), single crystal (2) and synthesized optical ceramics (3) [40].

Carnall [2] has found that the refraction and optical dispersion coefficients of CaF$_2$ single crystal and synthesized ceramic specimens were practically the same. This was confirmed for the pure CaF$_2$ as well as doped CaF$_2$ single crystals and ceramics samples [19].

In order to characterize mechanical properties of the prepared CaF$_2$ ceramic samples, their microhardness and fracture toughness were studied by Akchurin et al. [23, 39] (Table 1). These samples were subjected to the mechanical load, followed by measuring the linear size of the formed radial cracks ($C$), which appeared near the site of load application, as a function of the load on the indenter. Calculations of the coefficient of stress intensity (fracture toughness) $K_{IC}$ exhibited the following correlation:

$$K_{IC} = 0.016(E/H)^{1/2}P/C^{3/2},$$

where $H$ is the microhardness, $P$ is the load, and $E$ is Young’s modulus (Table 1). $K_{IC}$ values for the synthesized and natural CaF$_2$ ceramic specimens were more than 3 and 4 times higher than $K_{IC}$ values for single crystals.

In general, fluoride ceramic samples appear to have sufficiently good optical properties for use in laser manufacturing, while their mechanical properties absolutely exceed those of single crystals.

5. Spectral luminescence and generation properties

Lithium fluoride crystals with aggregate color centers are among the most promising laser materials for smoothly tunable generation of pico- and femto-second pulses in the near-IR region. The broad enhancement band in the 1-1.3 micron range, high cross-section of luminescence transition (ca. 10$^{-17}$ cm$^2$), broad absorption band for pumping by lasers irradiating near 1 micron and high thermal conductivity make these crystals virtually ideal for application in tunable lasers and lasers with mode synchronization. Since laser diodes with radiation wavelength of 960-980 nm have become accessible
recently, efficient and compact solid state tunable lasers can now be created with the use of lithium fluoride crystals. However, the latter crystals have some serious drawbacks, including, first of all, their low mechanical strength that restricts the limiting power of generated radiation. The creation of lithium fluoride optical ceramics with color centers can eliminate this obstacle, and LiF laser materials with the F\textsubscript{2}\textsuperscript{-} color centers were produced by the irradiation of pre-synthesized LiF optical ceramics.

Comparison of lasing of LiF-F\textsubscript{2}\textsuperscript{-} ceramics and single crystals of the similar optical density was carried out [20, 21]. Absorption, luminescence and generation spectra of LiF-F\textsubscript{2}\textsuperscript{-} ceramics are shown in Figure 9. Figure 10 shows the dependence of the average lasing output power of ceramic and single crystal LiF F\textsubscript{2}\textsuperscript{-} samples [21]. Ceramic samples were characterized by lower lasing thresholds than single crystals. The maximum differential lasing efficiency of 26\% has been observed for a 4 mm thick ceramic sample (vs. 18\% for the single crystal sample).

Absorption and luminescence spectra of fluoride ceramics and single crystals doped with rare-earth ions (Er, Yb, Tm) are essentially identical [34, 44] (Figure 11). Their optical centers’ spectral compositions, lifetimes of the excited states, absorption coefficients, wavelengths of absorption bands...
and luminescence lines are very close for the samples of the same chemical composition. Excellent quality of rare earth-doped fluoride ceramic specimens, prepared by hot-forming of crystals, allows achieving lasing parameters almost equivalent to the properties of the single crystals of the same chemical composition (Figure 12).

![Optical scheme for studying of the generation properties](image)

**Figure 12.** Lasing of CaF$_2$:Yb$^{3+}$ (5%) samples [19]. Optical scheme for studying of the generation properties (a). Output power vs. input (utilized) power for single crystal (b) and ceramics (c) for various reflection coefficients of the output mirror.

Generation properties of CaF$_2$:Yb$^{3+}$ single crystals and ceramics were studied by Doroschenko [19] with the use of IPG laser diode pumping (100 micrometer fiber radiation output; impulse mode; 2 msec duration of impulse at 10 GHz repetition frequency). Radiation wavelength (967 nm at room temperature), generated by laser diode, was thermally adjusted to coincide with the absorption maximum of Yb$^{3+}$ ions in CaF$_2$ matrix (972 nm). Output beam was focused by the single lens (focus distance = 5 mm). Semispherical resonator for measuring of generation properties was formed by flat dichroic mirror (maximum transparency at the generation wavelength of 972 nm and maximum reflection at the generation wavelength of 1020-1080 nm) and spherical output mirror (50 mm radius) (Figure 12a). Ca$_{0.95}$Yb$_{0.05}$F$_{2.05}$ experimental sample, used for studying lasing generation, was doped with 5 mol. % Yb$^{3+}$ ions [19].

Output parameters of Ca$_{0.95}$Yb$_{0.05}$F$_{2.05}$ single crystal (Figure 12b) and ceramic (Figure 12c) specimens for the different reflection coefficients (as a function of the absorbed pump power) are very close. The highest differential efficiency coefficient of 35% has been obtained for Ca$_{0.95}$Yb$_{0.05}$F$_{2.05}$ ceramics at 95% reflection coefficient of the output mirror.

Usually, the grains of fluoride ceramics are too large to produce some kind of size effects and affect spectral kinetic properties related to path lengths and trajectories of electrons, excitons and phonons. However, borders between domains as well as twinning borders within crystalline grains...
can cause the difference in the properties of ceramic and crystal samples. Such differences have been observed for LiF lasing [21], CaF₂ color center formation [45], and scintillation features of pure BaF₂ and Ce-doped BaF₂:Ce: ceramic materials produced higher photon yield in the case of X-ray luminescence [46, 47].

6. CaF₂:Yb³⁺ System

By now, lasing has been observed for CaF₂:R³⁺, where R = Yb, Nd, Tm [19, 25, 44, 48], SrF₂:R³⁺, where R = Nd [49], Pr [50] and Ca₀.₆₅Sr₀.₃₀Yb₀.₆₅F₂.₀₅ [23] ceramic (polycrystalline) samples. However, most efforts are concentrated on CaF₂:Yb³⁺ ceramics. Ytterbium(III) ions, compared to the widely utilized neodymium(III) ions, have numerous advantages as ions-activators, when they are used in diode-pumped laser materials [51]:
- Yb³⁺ ions have lower difference between pumping wavelength and lasing wavelength (980 and 1,030 nm), than Nd³⁺ (808 and 1060 nm, respectively), i.e., lower “quantum defect”, and as a result heat losses are typically lower for Yb³⁺ materials;
- electron energy levels of ytterbium used in lasing are simpler than those of neodymium, so the former has fewer competitive pathways (“parasite channels”) for energy loss;
- ytterbium exhibits wider lines and absorption bands than neodymium in electron spectra, which is better for short impulse generation and for use in adjustable lasers;
- lifetime of the highest excitation energy level is higher for ytterbium than for neodymium.

Whereas laser applications (especially in the powerful laser systems) of CaF₂:Yb³⁺ single crystals have been actively studied recently [52 - 64], one of the first spectroscopic investigations of ytterbium admixtures in CaF₂ crystals was done as early as in 1969 [65].

Phase diagram of CaF₂-YbF₃ system (Figure 13) has been built according to Fedorov, Sobolev, Greis et al. data [66-69] and by using an analogy with CaF₂-YF₃ system ([70] in the area of lower temperature. It contains area of Ca₁₋ₓYbₓF₂₋ₓ solid solution, that stretches up to 41 mol.% YbF₃ at its maximum width. Experimental measurements have confirmed that ytterbium melt-crystal distribution coefficient is about 1 for the area with the lower YbF₃ concentration in the aforementioned system. Increase of ytterbium concentration makes melting of the solid solution clearly incongruent; whereas ytterbium distribution coefficient turns to be less than 1. Once YbF₃ content exceeds 10-15 mol.%, growth of Ca₁₋ₓYbₓF₂₋ₓ single crystals of laser quality becomes very problematic due to concentration overcooling and instability of the crystallization front [27].

Crystal lattice parameter of Ca₁₋ₓYbₓF₂₋ₓ solid solution cubic phase depends on the sample composition in a linear manner [66]:
\[ a = 5.463 + 0.112x \ [\text{Å}] \]
where x is a molar part of YbF₃ in CaF₂-YF₃ system. Changes in the crystal lattice parameters of Ca₁₋ₓYbₓF₂₋ₓ solid solution phase are determined by heterovalent isomorphic substitution of calcium cations with yttrium accompanied with charge compensation via insertion of additional fluoride anions
\[ \text{Ca}^{2+} \Rightarrow \text{Yb}^{3+} + \text{F}^{−} \]

Replacement of the relatively large calcium cations with smaller ytterbium cations is compensated by insertion of fluoride anions and leads to the smaller change of the crystal lattice parameter under variation of the chemical composition.

For the lower concentrations of ytterbium (ca. 0.01 mol.%), lattice defects of the opposite charge form dipole couples [69, 70] [71]; [72].

Ca₁₋ₓYbₓF₂₋ₓ solid solution decomposes at the lower temperatures with formation of Ca₂YbF₇, Ca₁₀Yb₂F₁₃, Ca₁₇Yb₁₀F₆₄ and Ca₄Yb₃F₁₁ fluoride-derived phases existing in 33-42 mol.% YbF₃ composition interval. Ca₂YbF₇, Ca₁₀Yb₂F₁₃, Ca₁₇Yb₁₀F₆₄ and Ca₄Yb₃F₁₁ phases contain YbₓF₇ clusters naturally and coherently built in their crystal lattices [73-77] (Figure 14), as it has been proven by ESR technique [78]. Cations in these clusters maintain the same coordination number 8 as they had in the original fluorite crystal lattice before the replacement of the regular cubes by Thompson’s antiprisms. Difference in size between YbₓF₇ cluster and replaced by it corresponding part of fluoride-type crystal lattice leads to the internal local strain and deformation within composite material. Difference
between the cluster formal charge and formal charge of the replaced part of fluorite lattice causes addition of extra fluoride anions to the crystal matrix along with formation of Yb$_{37}$F$_3$ fragment:

$$(M_6F_{32})^{20^-} \rightarrow (R_6F_{37})^{19^-} + F_{int^-}$$  \hspace{1cm} (3)

Figure 13. Phase diagram of CaF$_2$-YbF$_3$ system [66-70]: L- melt, F – Ca$_{1-x}$Yb$_x$F$_{2+x}$ solid solution, T – Yb$_{1-y}$Ca$_y$F$_{3-y}$ solid solution, T’ – Yb$_x$Ca$_2$F$_{27}$, R – Ca$_y$R$_3$F$_{31}$.

Figure 14. CaF$_2$ crystal lattice unit (a), Yb$_{37}$F$_3$ cluster (b) and its positioning in fluorite crystal lattice (c).

Absorption bands in Ca$_{1-x}$Yb$_x$F$_{2+x}$ solid solution spectra, assigned to association of the couples of Yb$^{3+}$ ions or combination of several complex optical centers [56, 65], more likely shall be attributed to the spectral properties of Yb$_{37}$F$_3$ cluster, for these bands stay unchanged in a very wide concentration interval of ytterbium. The latter also supports suggestion regarding relatively high Yb$_{37}$F$_3$ cluster stability.
Preparation of $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$ ceramics and single crystals under reducing conditions (e.g., by contacting graphite crucible surface) is accompanied with partial conversion of $\text{Yb}^{3+}$ to $\text{Yb}^{2+}$ ions and subsequent appearance of the corresponding absorption bands in UV segment of electron spectrum [54, 79] and possible thermal non-radiative losses under lasing [62].

It is very important to keep in mind that according to the existing $\text{CaF}_2$-$\text{YbF}_3$ phase diagram $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$ solid solution exists under non-equilibrium conditions at room temperature. Usually, transformations in these solid solutions with a few mol. % of lanthanide trifluoride are extremely slow, so no changes in the samples could have been detected over several decades. This may be related to very low values of the cations’ diffusion coefficients and relatively high activation energy barriers for the formation of the centers for crystallization of the new phase. These factors, however, can cause certain problems for the ceramic materials designated for the use under high energy flow conditions. Phase transformation also can be initiated at the boundaries between twinning domains. One can describe border between twinning domains in fluorite-type crystal lattice as 2-layer cation pack instead of the regular 3-layered matrix, corresponding to the closest packing of cations in fluorite-type crystal lattice. These borders can play role of the nucleation centers for the formation of the new tysonite-type phase (low temperature orthorhombic modification of $\beta$-$\text{YF}_3$), but this suggestion requires further studying.

Earlier, alleged equal thermal conductivity of both laser ceramics and pure fluorite was considered as an important advantage of ceramic materials [53, 58, 60]. However, actual measurements of this parameter disproved this assumption and demonstrated that introduction of heterovalent admixture to fluorite structure leads to the dramatic decrease of the thermal conductivity, especially, at lower temperature. The reason of such essential decrease of thermal conductivity in the case of samples with heterovalent isomorphic doping vs. specimens with isovalent substitutions is that scattering of acoustic phonons occurs at defect clusters for materials with heterovalent doping instead of the single atoms in the isovalent-substituted samples (Figure 14).

Ceramics with the relatively high concentration of trifluoride dope exhibits glass-type temperature dependency of its thermal conductivity [80]. Comparison of the thermal conductivity of $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$ solid solution and ytterbium-doped Al-Y garnet [12] (Figure 15) shows that fluoride ceramics is inferior to oxide material. Decrease of ytterbium content in $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$ leads to the increase of its thermal conductivity, but relatively insufficient improvement of this property significantly limits prospective use of $\text{CaF}_2$-$\text{Yb}^{3+}$ materials, including ceramics, for the powerful lasers.

Properties of various $\text{CaF}_2$-$\text{Yb}$ ceramics are presented in Table 2.

![Figure 15. Thermal conductivity of $(Y_{1-x}Yb_x)Al_5O_{12}$ [12] and $\text{Ca}_{1-x}\text{Yb}_x\text{F}_{2+x}$ (P.A.Popov, [80] and private communication) solid solutions at 300 K.](image)
7. Synthesis of prospective materials

Crystal symmetry of laser ceramics plays a decisive role in prospective application of these materials. Both fluoride and oxide laser ceramics have cubic crystal lattices. Oxides have structure of garnet (Ia3d space symmetry group, or SSG) or yttrium oxide (Ia3 SSG), whereas fluorides are represented by CaF$_2$, SrF$_2$ or their combinations (fluorite-type solid solutions) and lithium fluoride (all of fluorides belong to Fm3m SSG). These cubic crystals are very likely to form boundaries between crystalline domains that correspond to polysynthetic twinning and, therefore, produce low optical losses. From this point of view, cubic KY$_3$F$_{10}$ (Fm3m SSG) could be a very good candidate for the same laser application.

Similar suggestion can be true for CaF$_2$:Yb,Na solid solution, too [57]. Fluorite, double-doped with sodium and ytterbium, does not produce good quality single crystals (as per phase diagram for NaF-CaF$_2$-YbF$_3$ system [81], thus ceramic CaF$_2$:Yb,Na looks like a very promising alternative.

Compounds with non-cubic crystal lattices do not form laser-quality ceramic materials. Because of anisotropic refraction coefficients and light scattering at the incoherent boundaries between crystalline domains, their samples exhibit essential optical losses. One could produce acceptable values of light transmittance for Y$_2$O$_3$-based Yttralox crystals, but similar result was impossible to achieve for Al$_2$O$_3$-based Lukalox ceramics. Oxosulfides of the rare earth elements also cannot be used for manufacturing of transparent laser ceramics [34]. The same is true for MgF$_2$ (tetragonal system, P42/mnm SSG), YF$_3$ (orthorhombic system, Pnam space group), LiRF$_4$ (tetragonal system, I4$_1$/a SSG), BaR$_2$F$_8$ (monoclinic system, C2/m SSG) fluorides, too.

As it has been already mentioned above, CaF$_2$-based ceramics exhibits twinning at the nano-level and, therefore, generates low optical losses because of perfectly well-structured boundaries between crystalline domains. Polysynthetic twinning is known for the phase transitions of the second type (or close to the second type), when lower-temperature modifications are slightly distorted in comparison with more symmetric higher-temperature modifications. This type of twinning with lowering crystal lattice symmetry is especially common for the phase transitions of the higher-temperature cubic phases. As an example of this phenomenon, one can mention ferroelectrics [82]. In particular, A$_2$BRF$_6$ elpasolites (A, B- alkaline metals with $r_A > r_B$, R – rare earth elements) undergo multiple phase transitions at different temperatures [83], and Rb$_3$NaAlF$_6$ transparent ceramics has been synthesized in [84] by cold-pressing of elpasolite precursor produced by sol-gel method. Another example of the same kind is neighborite NaMgF$_3$ [85]; [86]. This compound (melting point 1020°C) has an orthorhombic crystal lattice at room temperature, but at 700°C it undergoes phase transition and forms high-temperature cubic modification. Preliminary studies have shown an opportunity to synthesize transparent twinned polycrystalline samples at room temperature [19].

Ordered fluorite-type phases in MF$_2$-RF$_3$ systems [28, 66, 73] also have slightly-distorted CaF$_2$ structures (Fig. 13) and, therefore, they may be considered as prospective materials for transparent laser ceramics. For example, optically homogeneous crystal domains of trigonally-distorted fluorite-type Ca$_8$R$_5$F$_{31}$ have been observed in polished cross-sections of two-phase samples in CaF$_2$-RF$_3$ systems by [87].

However, one can make highly transparent ceramics from non-cubic crystalline substances only of crystalline domains will be less than the wavelength of the used electromagnetic radiation [88].

8. Conclusion

The reviewed publications show that modern fluoride ceramics technology provides materials with high optical transparency and homogeneity, so they can be widely used as laser materials.

40+ years ago Kodak scientists published their first studies in this area, and recently researchers from A. M. Prokhorov General Physics Institute (Moscow, Russia), State Optical Institute (St. Petersburg, Russia) and INKROM Company (St. Petersburg, Russia) developed new synthetic methods to manufacture fluoride laser ceramics with properties similar to the properties of corresponding single crystals, thus making fluoride laser ceramics the most prospective and easily available material for the solid-state lasers of various types and different designation.
Polycrystalline fluoride laser materials were prepared by hot-forming of single crystals instead of more conventional methods. However, use of thermal treatment of starting batches and similarity of the structure of the obtained polycrystalline samples and corresponding properties of the substances prepared by “classic” protocols makes possible application of “ceramic laser materials” term to the products of hot-deformation synthesis.

Pure CaF$_2$ ceramics possesses excellent mechanical and perfect optical properties. Therefore, making doped fluorites of the comparable properties becomes a priority. The co-precipitation from water medium does not produce satisfactory results, so one can consider preparation of their precursor materials from non-aqueous solutions.

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