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The effect of $LaBr_3$:Ce single crystal aliovalent co-doping on its mechanical strength

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ABSTRACT

Lanthanum bromide cerium doped single crystals are a transparent scintillator material that offers outstanding scintillation properties with high light yield, excellent energy resolution, fast emission and excellent proportionality. Although properly packaged detectors are robust enough to withstand operating conditions during geophysical oil logging operations, the material itself is brittle and exhibits low fracture toughness. We attempted to modify the composition of the crystals through aliovalent co-doping by Ba, Ca, Hf, Sr, Zn and Zr. These elements have been added in concentrations from 100 ppm to 5000 ppm to the growth bath. Ratio of co-doping in the crystalline matrices ranged from no incorporation (for Hf, Zn, and Zr) up to 200 ppm for Sr and 10–20 ppm for Ca. The effect of the aliovalent co-doping on the mechanical properties of the crystals and in particular on their mechanical strength, hardness and toughness has been measured. As the crystals are extremely hygroscopic this demanded designing customized experiments in anhydrous environment in order to obtain reliable and accurate results. The ultimate strength has been measured by four points bending. Hardness has been measured by indentation and by the same technique we attempted to have some information on the fracture toughness. No improvement of the mechanical properties of the co-doped crystals with respect to the reference standard lanthanum bromide cerium doped could be found.

1. Introduction

Lanthanum bromide cerium doped single crystals are a transparent scintillator material that offers outstanding scintillation properties with high brightness ($>65\,000$ ph. MeV^{-1}), excellent energy resolution ($\sim 3\%$ full-width at half-maximum (FWHM) at $E_\gamma = 662$ keV), fast emission ($\tau_d < 20$ ns) and excellent proportionality [1].

Although properly packaged detectors are robust enough to withstand operating conditions during geophysical oil logging operations, the material itself is brittle and exhibits low fracture toughness [2].

In order to increase the fracture toughness of $CeBr_3$ single crystals, aliovalent co-doping was proposed as a solution [3]. In the cited work, polycrystalline samples were obtained by melting of powders in sealed quartz tubes. Photo-excitation and scintillation tests were performed on the polycrystalline samples to determine which kind of aliovalent doping did not degrade these properties. It was found that, with the exception of Pb, all the other elements tested qualitatively did not quench or reduce the fluorescence.

$CeBr_3$ is very similar to $LaBr_3$. Their crystallographic structures belong to the same family: the uranium trichloride family (UCl_3) [4,5] which is an hexagonal structure belonging to the $P6_3/m$ space group. The cell parameters of the two crystals are also similar ($a = 7.951$ Å, $c = 4.501$ Å for $LaBr_3$ [4] and $a = 7.952$ Å and $c = 4.444$ Å for $CeBr_3$ [5]).

It is thus expected that aliovalent codoping of lanthanum bromide single crystals will have the same effect on the fracture toughness and mechanical resistance as for $CeBr_3$. Unfortunately the claimed effect of aliovalent doping in increasing the fracture toughness of $CeBr_3$ has been advanced in other published works [6–8] but to our knowledge no experimental evidence has been published to support the claims.

The brittleness of cerium and lanthanum bromide is a critical point for the further development of large and high quality scintillating crystals. It is then critical to verify experimentally the assumption of the fracture toughness increase because of aliovalent doping. Therefore aliovalent co-doped $LaBr_3$:Ce single crystals have been grown and the mechanical resistance has been measured by mechanical tests.

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2. Experiments

2.1. Co-doped crystals growth

$LaBr_3$:Ce co-doped crystals have been grown by adding to the growth bath the bromine phases corresponding to co-doping element (Ca, Hf, Sr, Zn and Zr). These elements have been added in concentrations from 100 ppm up to 5000 ppm. Ingots with good optical quality and completely crack-free were grown. Higher concentrations in co-doping were also tested but resulted in cracked or hazy crystals. The molar Ce concentration was kept constant at the standard value of 5% in the melt. Concentration of the dopant and co-dopant elements was measured by dissolving samples of the crystals in slightly acidic water and analysing the solution by ICP-AE. The results on co-doping are given in weight concentration.

2.2. Mechanical resistance by 4-points bending

Mechanical resistance has been measured by 4-points bending. For this purpose a "house-made" testing machine has been built with dimensions allowing operation in a dry-box (approximately 30 cm × 70 cm × 5 cm). The moisture level inside the drybox has been constantly monitored and all the experiments have been conducted at a dew point < -85 °C. The machine is operated by a step-motor and the force is measured with a 500 N load cell (by AEP, TCA model). The calibration of the load cell has been checked by using a dedicated set-up. The distance between the outer rollers has been fixed to 45 mm while the distance between the inner rollers has been fixed to 15 mm. The rollers have been built in Teflon in order to decrease the Hertz contact stresses between the rollers and the probe. Outer rollers had a diameter of 8 mm, inner rollers had a diameter of 5 mm.

Probes have been cut from the grown ingots with dimension 50 mm × 5 mm × 5 mm according to two distinct crystallographic orientations (shown in Fig. 1). The "*a-axis*" oriented probes (cut parallel to the crystallographic *a-axis*) are expected to be weaker as the cleavage plane will be put in tension, on the lower face, during the mechanical test, while the "*c-axis*" oriented probes (cut parallel to the crystallographic *c*-axis) are expected to be stronger as the cleavage plane will be parallel to the neutral axis during the bending and it will almost not be stressed in tension (except for Poisson's effect).

Probes have been charged by moving the cross head at 0.5 mm min^{-1} until the breakage of the probe. The breaking force is recorded as the maximum of the force on the load cell. At least 10 samples were measured for each set of samples in order to obtain a satisfactory statistic. If the breakage origin was originated outside the inner span the value has been rejected and not used for the analysis.

2.3. Microindentation

Microindentation experiments have been performed in dry box too, with constant humidity control and a dew point < -85 °C. As these surface mechanics experiments are very sensitive to surface state, special care was taken to work on polished surfaces and making sure that the surface state did not degrade during the experiments. Anyway the environment in the used dry box is such that the optically polished surface state can be preserved during several months without visible evolution (by naked eye or optical microscopy).

Micro-indentation experiments were performed by using a Future Tech micro-hardness tester piloted by a software and equipped with a camera by Clemex. Loads were applied from 25 gf to 500 gf by using a Berkovich and a Vickers tip. Only the data obtained with the 25 gf and the Berkovich tip are presented and analysed in this paper as indentation with higher loads led to excessive cracking around the indentation print. The symmetry of the Berkovich tip is more easily compatible with the symmetry of the crystal. The load was hold during 60 s before unloading. The shape of the residual print and the length of the induced surface cracks have been measured just after the test and after 24 h. No measurable evolution was observed.

Samples for the microindentation experiments have been prepared by "slicing" the ingots in slices with a thickness of 10 mm. One of the two surfaces has been accurately polished. The orientation of this surface, on which the indentation measurements were performed, is parallel to the crystallographic plane (0 0 0 1).

Indentations were performed in radial direction, from the centre to the periphery every 5 mm and along a circular path every 10° (at a distance of 5 mm from the periphery).

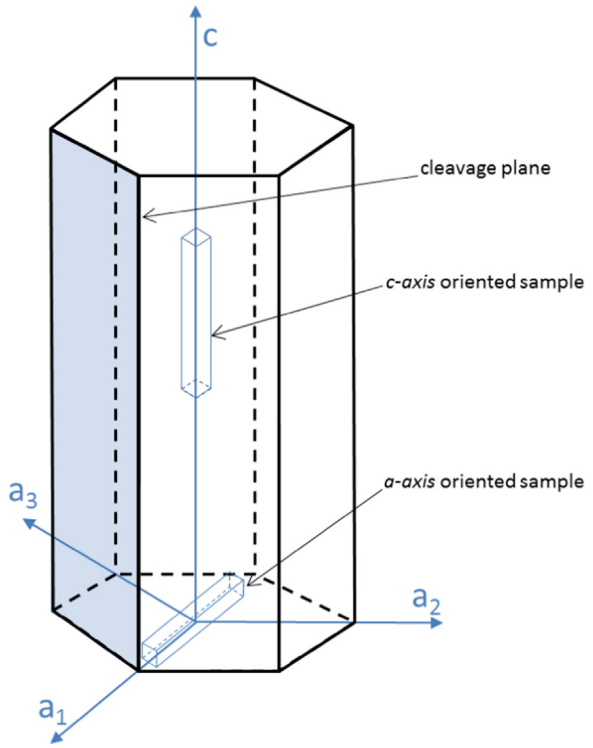

Fig. 1. Orientation of the probes tested in 4-points bending tests with respect to the crystallographic axis. Two kinds of probes have been cut: "*a-axis*" oriented probes have been cut parallel to the *a*-axis, "*c*-axis" oriented probes have been cut parallel to the *c*-axis thus the cleavage plane $(1\,0\,\bar{1}\,0)$ is parallel to the longest direction and to the neutral axis during the bending test. The cleavage plane $(1\,0\,\bar{1}\,0)$ is shaded in the figure. (The figure is inspired from [9]).

3. Results

The co-doping elements added to the bath are not always easily incorporated in the matrix of the grown crystals. Table 1 reports the amount of co-doping element in the growth bath as well the effective ICP-AE measured concentration in the crystal. It can be seen, that between the tested elements, Sr, Ca, Hf, Zn and Zr only the first two, Sr and Ca could be incorporated effectively in the crystal, although their concentration was much lower than the concentration in the bath. The concentration of Hf, Zn and Zr is below the detection limit of the ICP-AE, we can thus assume that these elements are not incorporated into the crystal.