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Size–strain line-broadening analysis of the calcite-type borates ABO₃ (A=Fe, In, Ga)

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Abstract. In this paper, the microstructure of metal borates grown by the solution-melt crystallization method was determined by X-ray diffraction broadening analysis. XRD measurements of the calcite-type borates were carried out using X-ray diffractometers SmartLab Rigaku and DRON-3 with Cu K_{α} radiation. The Williamson–Hall analysis and Debye–Sherrer method were used to study the individual contributions of crystallite sizes and strain on the peak broadening of FeBO₃, InBO₃ and GaBO₃. The crystallite sizes of the FeBO₃ and GaBO₃ calculated on the Williamson–Hall plots are in good agreement with the Scherrer method. We have also investigated the temperature dependence of crystallite size and strain in FeBO₃. It was found that the temperature increased in the value of crystallite size and strain, indicating that the ordering of the crystal structure in iron borate with heat processing.

1. Introduction

The distribution of microstructure depends on the manufacturing techniques, sintering process, raw materials used, equilibrium reactions, kinetics and phase changes. The characterization of crystalline microstructure contributes to the control of the manufacturing process.

In this paper we report study of the microstructure of gallium, iron, and indium borates by X-ray diffraction line broadening analysis. These compounds have attracted attention because of their potential applications as photoluminescence materials, laser media, scintillating materials and magnetic materials [1]. Broadening of diffraction peaks arises mainly due to three factors viz. instrumental effects, crystallite size and lattice strain. Crystallite size is a measure of the size of coherently diffracting domains. The crystallite size of the particles is not generally the same as the particle size due to the formation of polycrystalline aggregates. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocations. Other sources of strain include the grain boundary triple junction, contact or sinter stresses, stacking faults and coherency stresses [2].

The aim of this work: a study of the crystallite size and strain by XRD broadening analysis of the calcite-type borates ABO₃ (A=Fe, In, Ga).

2. Object and method of research

Calcium carbonate, CaCO₃, exists in three different polymorphs: The calcite, vaterite, and aragonite structures [3]. Triangle planar BO₃ ^{3–} groups can replace CO₃ ^{2–} to form metal orthoborates with the nominal formula A^{III}BO₃ which have been determined to be isostructural with different forms of CaCO₃. Usually, small cations of A³⁺ lead to the crystallization of A^{III}BO₃ in a calcite type structure which belongs to the trigonal space group R-3c. The A³⁺ cations occupy octahedral positions and can be substituted by Gal³⁺, In³⁺ and Fe³⁺ [4].

For structural studies, samples of polycrystalline indium, gallium and iron borates were ground into powder by standard technology.

XRD measurements of InBO₃ and FeBO₃ were carried out using SmartLab Rigaku X-ray diffractometer with Cu K_{α} radiation. The instrument was set up in Bragg-Brentano geometry on the line focus side with a graphite monochromator in the diffracted beam arm. XRD pattern of GaBO₃ was obtained by X-ray diffractometer DRON-3 equipped with Cu K_{α} radiation. The voltage and the current of the X-ray tube were 25 kV and 25 mA respectively.

The XRD profiles of all the samples were recorded in the angular range of $20-100^{\circ}$ with a step size of 0.02 and a dwell time of 4 s. The temperature behavior of FeBO₃ microstructure have been determined in the temperature range from 25°C to 600°C.

The unit cell parameters of $InBO_3$, $GaBO_3$ and $FeBO_3$ calculated on the program [5] are shown at table 1.



Figure 1. Observed X-ray powder diffraction pattern for GaBO₃

3. Analysis and discussion

The microstructure can be calculated from the broadening of X-ray diffraction peaks by considering the integral breadth β of the all individual peaks:

$$\beta = \frac{\int f(\theta) \, d\theta}{f_{max}},\tag{1}$$

where $f(\Theta)$ – function of the peak shape, f_{max} – peak intensity.

The two most commonly assumed line shapes are the Lorentzian and Gaussian [6]:

$$l(\theta) = A \cdot \exp\left[-\frac{(\theta - \theta_0)^2}{2\theta_L^2}\right]$$
(2)

and

$$g(\theta) = A \cdot \left[1 + \frac{(\theta - \theta_0)^2}{\theta_G^2}\right]^{-1}$$
(3)

We used the Pseudo-Voigt function, which is defined as the sum of a Gaussian peak G(x) and a Lorentzian peak L(x), weighted by a fourth parameter η (values between 0 and 1) which shifts the profile more towards pure Gaussian or pure Lorentzian when approaching 1 or 0 respectively:

$$V(\theta) = \eta \cdot l(\theta) + (1 - \eta) \cdot g(\theta) \tag{4}$$

and

$$V(\theta) = \eta \cdot A \cdot \exp\left[-\frac{(\theta - \theta_0)^2}{2\theta_L^2}\right] + (1 - \eta) \cdot A \cdot \left[1 + \frac{(\theta - \theta_0)^2}{\theta_G^2}\right]^{-1}$$
(5)

where $\theta_L \bowtie \theta_G$ – parameters of the Lorentzian and Gaussian, A – normalizing factor.

The particle-size broadening is suggested to be described by a Lorentzian, while the instrumental contributions can roughly be approximated by a Gaussian, and strain broadening may also possess a Gaussian form. Therefore, the Voigt profile is a theoretically natural description of diffraction peak shape [7].

Subtracting the instrumental effect from the obtained peak broadening, two main properties; crystallite size and lattice strain are extracted from peak width analysis. If the observed X-ray peak has broadening of width B_o and the width due to instrumental effect is B_i , then the remaining broadening of the peak due to crystallite size and lattice strain is B_r , which can be expressed considering pseudo-Voigt profile as [6]:

$$\beta_r = \left((\beta_o - \beta_i) \sqrt{\beta_o^2 - \beta_i^2} \right)^{\frac{1}{2}}$$
(6)

We have estimated the coherent crystallite size (D) on the Debye–Scherrer equation [8]:

$$D = K\lambda/B_r \cos\theta$$

were K - constant equal to 0.94, λ - wave length of the incident X-ray, B_r – the integral breadth, θ - Bragg's angle.

This formula can be used only if strain and other sources of broadening are small. If considerable strain broadening is expected, then the Williamson & Hall method can be used.



Figure 2. Debye–Sherrer plot of FeBO₃ at 25 °C (**a**), 400 °C (**b**), 500°C (**c**) and 600°C (**d**). Fit to the data, the crystallite size D is extracted from the slope of the fit.

(7)



Figure 3. Debye–Sherrer plot of $InBO_3$ (a) and $GaBO_3$ (b). Fit to the data, the crystallite size D is extracted from the slope of the fit.

This Williamson-Hall method is attributed to G.K. Williamson and his student, W.H. Hall [5]. It relies on the principle that the approximate formulae for size (Scherrer) broadening, βL , and strain broadening, βe , vary quite differently with respect to Bragg angle, θ :

$$\varepsilon = \rho_{\varepsilon}/4 \tan \theta \tag{6}$$

$$D = K\lambda/\beta_D \cos\theta \tag{9}$$

their combined effect should be determined by convolution. The simplification of Williamson and Hall is to assume the convolution is either a simple sum. Using the former of these then one gets:

$$\beta_{tot} = \beta_{\varepsilon} + \beta_D = 4\varepsilon \tan \theta + K\lambda/D \cos \theta \tag{10}$$

If one multiplies this equation by $cos(\theta)$ one gets:

$$\beta_{tot} \cos \theta = 4\varepsilon \sin \theta + K\lambda/D \tag{11}$$

where D is the grain size as determined from the Williamson-Hall plot. Comparing this to the standard equation for a straight line (m = slope; c = intercept), y = mx + c, one sees that by plotting $\beta_{tot}cos\theta$ versus sin θ we obtain the strain component from the slope (4 ε) and the size component from the intercept (K λ /D). Such a plot is known as a Williamson-Hall plot [9].



Figure 4. The Williamson-Hall analysis of InBO₃ (**a**) and GaBO₃ (**b**). Fit to the data, the strain is extracted from the slope and the crystallite size is extracted from the y-intercept of the fit.

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Figure 5. The Williamson-Hall analysis of FeBO₃ at 25 °C (**a**), 400 °C (**b**), 500°C (**c**) and 600°C (**d**). Fit to the data, the strain is extracted from the slope and the crystallite size is extracted from the y-intercept of the fit.

The crystallite size and strain is calculated by Debye–Sherrer and Williamson-Hall methods for three different samples are presented in Table 2.

Sample	Temperature, °C	Debye–Sherrer method	Williamson-Hall method	
			D,nm	ε, no unit
		D, nm		10^{-5}
InBO ₃	25	92.5±8.2	333.4±13.7	77.25±3.18
GaBO ₃	25	56.9±3.4	54.4±3.1	0.65 ± 0.04
FeBO ₃	25	159±8.4	167.6±6.5	3.23±0.13
	400	186.3±8.1	195.7±9.2	5.15±0.24
	500	192.5±14.9	208.9±13.1	6.04 ± 0.38
	600	194.1±16.1	196.5±18	6.597±0.6

Table 2. The crystallite size and strain is calculated by Debye–Sherrer and Williamson-Hall methods for InBO₃, GaBO₃ and FeBO₃.



Figure 6. The temperature dependence of the crystallite size and strain is calculated by Debye–Sherrer and Williamson-Hall methods for FeBO₃.

4. Conclusion

Microstructure has been studied for the samples of the calcite-type borates ABO3 (A=Fe, In, Ga). The crystallite size and lattice strain of GaBO₃ and FeBO₃ estimated from the two models show very negligible variations. There is a considerable difference between crystallite size of InBO₃ obtained from Debye–Scherrer equation and from Williamson-Hall models. This difference can be explained: the microstrain can induce a greater broadening in the diffraction peak while in the Debye–Scherrer equation, the integral breadth is considered in the calculation. The Williamson-Hall procedure presents a correction for this problem. Deviations from the straight line in the Williamson-Hall plotting indicates dispersion in particle size and strain suggesting that the sample has anisotropic particle size distribution and strain.

Heat treatment of $FeBO_3$ causes particles to anneal and form larger grains, thereby increasing the degree of crystallinity of the sample. On the other hand, the strain increases gradually with increasing temperature, as indicated in figure 6. This variation may be due to the increase of ordering and the increase of the structural defects among which the grain boundary.

The results of the work can be useful in the synthesis of metal borates nanopowders.

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