

# Metastability of atomic ordering in lead–strontium nitrate solid solutions

A.G. Shtukenberg\*

*Crystallography Department, St. Petersburg State University, Universitetskaya emb., 7/9, 199034, St. Petersburg, Russia*

Received 11 March 2005; received in revised form 28 April 2005; accepted 15 May 2005

Available online 11 July 2005

## Abstract

A decrease in the anomalous birefringence of ostensibly cubic crystals of  $(\text{Pb,Sr})(\text{NO}_3)_2$  during annealing between 280–450 °C shows first-order reaction kinetics with Arrhenius-like temperature dependence. The activation energies associated with this process were 111(5) and 359(17) kJ/mol below 370 °C and above 400 °C, respectively. Such behavior agrees with theoretical predictions and confirms that the ordering of cations is the primary cause of the anomalous birefringence.

© 2005 Elsevier Inc. All rights reserved.

**Keywords:** Kinetic phase transition; Lead nitrate; Strontium nitrate; Desymmetrization; Solid solution; Optical anomalies; Diffusion

## 1. Introduction

Kinetic ordering of atoms, ions, or molecules in crystals, sometimes referred to as “growth ordering” or “growth desymmetrization”, is a type of order–disorder phase transformation. This non-equilibrium process can arise when crystallographic sites related by symmetry in the bulk are geometrically and energetically distinct on the surfaces of a growing crystal. Such sites express different activities for adsorbing chemical species, thereby reducing the symmetry of the surface layer that subsequently becomes buried in the bulk. Metastable distributions of crystal components of this kind can persist for very long times due to the low diffusion rates in solids. The differential site occupancies result in distortions of the crystal structure giving physical properties that are excluded by symmetry in the corresponding structure at equilibrium.

Desymmetrization due to kinetic ordering is often apparent in optical measurements. Crystals showing lower optical symmetries than might be expected on the

basis of their morphology or X-ray analysis are called *optically anomalous*. Optical anomalies have been discovered and studied in many substances including [1] quartz, alums [2,3], garnets [4,5], topaz [6],  $\text{Na}(\text{ClO}_3, \text{BrO}_3)$  [7,8].

One of the main features of kinetic growth ordering is metastability. At high temperatures ( $T/T_{\text{melt}} > 0.6$ ) the degree of ordering decreases rapidly with a corresponding decrease of anomalous birefringence. This phenomenon was found to occur in topaz [6], analcite [9],  $(\text{Y}_{0.53}\text{Nd}_{0.47})_3\text{Ga}_5\text{O}_{12}$  garnets [10] and some other compounds. For the sodium chlorate–bromate isomorphs [7] and grandite garnets [11] the crystal structure refinement carried out before and after high-temperature annealing has shown equalization of occupancies and return to the ideal cubic symmetry. Quantitatively annealing kinetics was studied for quartz [1], alums [2,5] and grandite garnets [5], for which decreasing in birefringence was found to follow the first-order kinetics with a temperature dependence in agreement with the Arrhenius Law.

Anomalous birefringence in the lead–strontium–barium nitrates  $(\text{Pb,Sr,Ba})(\text{NO}_3)_2$  has been known since the 19th century [12]. While the earliest researchers

\*Fax: +7 812 328 4418.

E-mail address: [sasha@as3607.spb.edu](mailto:sasha@as3607.spb.edu).

attributed the anomalous birefringence to strain (Spannung), it was previously suggested that the birefringence was due to growth desymmetrization [13]. Here, we study the temperature dependence of the anomalous birefringence while annealing the mixed crystals. We aim to focus our understanding of the mechanisms of growth desymmetrization and self-diffusion in crystals.

## 2. Experimental

The lead–strontium nitrate  $(\text{Pb,Sr})(\text{NO}_3)_2$  crystals were grown to sizes of 5–15 mm from unstirred aqueous solutions supercooled by 1–5 °C by self-nucleation in 300–500 mL vessels or by solvent evaporation at the temperature of 29–32 °C. The principal facets expressed were  $\{111\}$ . Smaller  $\{100\}$  were evident. Seldom, very small  $\{210\}$  faces were also observed. Crystal sections (0.6–2 mm) were cut parallel to  $\{110\}$  planes (at the same time normal to  $\{111\}$  growth faces). The values of birefringence  $\Delta n$  were measured with a conventional polarizing microscope equipped with a Berek compensator accurate to within 5–10%. According to the data of electron probe microanalysis Sr/Pb distribution within each growth sector is relatively homogeneous (the difference in Sr content does not exceed 0.03 at.fr.). On the other hand,  $\{111\}$  growth sectors are slightly enriched by Sr with respect to  $\{100\}$  ones, the differences in composition increase to the middle of the series and attains 0.06 at.fr. The birefringence was measured at several points within each section before and after annealing in a muffle furnace at a temperature between 280 and 450 °C for times as short as 7 min and as long as 12 h.

### 2.1. Anomalous birefringence and ordering of cations

Lead nitrate  $\text{Pb}(\text{NO}_3)_2$  and strontium nitrate  $\text{Sr}(\text{NO}_3)_2$  belong to the cubic system (space group  $P\bar{a}3$  [14,15] or  $P2_13$  [16,17]); they are optically isotropic as required by symmetry. The compounds form a continuous series of solid solutions well known for their anomalous birefringence [12].

The  $\{111\}$  growth sectors are optically uniaxial negative with the optical axis  $X_{(e)}$  directed normal or nearly normal (deviations with a few degrees) to the respective growth face. The value  $\Delta n$  can be as high as  $1.6 \times 10^{-3}$  in the middle of the series, but it decreases towards the end members. Usually the birefringence is distributed uniformly throughout the growth sector; however, thin zones with gradually or even sharply changing birefringence were frequently observed. Assuming that the crystal symmetry after desymmetrization is a subgroup of the cubic group of the pure materials—symmetry is

destroyed but not created—then the mixed crystals are presumably trigonal. The similar optical patterns were also observed for the  $(\text{Pb,Ba})(\text{NO}_3)_2$  solid solutions [13].

In contrast to the  $\{111\}$  growth sectors, the  $\{100\}$  sectors display a much smaller value of  $\Delta n$  (typically less than  $5 \times 10^{-5}$ ) and are inhomogeneous with respect to the distribution of birefringent areas. The optical indicatrix orientation as well as the value of birefringence reveals a complicated or even oscillatory thin zoning, also typical for  $\{100\}$  growth sectors of alum mixed crystals [3]. This birefringence is stable during annealing and is probably related to intrinsic stress. Therefore, only the  $\{111\}$  growth sectors were further analyzed.

Although the experimental data on the  $(\text{Pb,Sr})(\text{NO}_3)_2$  crystal structures are lacking, some assumptions can be based on the results obtained for the  $(\text{Pb,Ba})(\text{NO}_3)_2$  isomorphs. Crystal structure refinement of two  $(\text{Pb}_{0.1}\text{Ba}_{0.9})(\text{NO}_3)_2$  birefringent samples cut out from  $\{111\}$  growth sectors showed symmetry reduced to either of the trigonal groups  $R\bar{3}$  or  $R3$  [13]. The single (0,0,0) cation site was found to split into two sites with different Pb/Ba ratios: a general site <sup>[1]</sup> with fractional atomic coordinates  $(x,y,z)$  and multiplicity 3 and a special site <sup>[2]</sup> with fractional coordinates  $(0,0,z)$  and multiplicity 1 [18]. This model, matching the observed uniaxial optical indicatrix, will be extended to  $(\text{Pb,Sr})(\text{NO}_3)_2$ .

### 2.2. Metastability of growth ordering: theory

We presume that diffusion assisted redistribution of Sr and Pb follows the vacancy mechanism [19]. Assume  $P$  to be the probability of cation (vacancy) jumps between neighboring sites. The cations form the face-centered lattice and in the cubic crystal structure have the same surrounding by oxygen atoms. Since the desymmetrization usually has a negligible effect on the geometry of the crystal structure, it would be reasonable to suggest that the jump probability  $P$  is nearly the same for the cations located at sites <sup>[1]</sup> and <sup>[2]</sup>. In the trigonal structure each <sup>[1]</sup> site is surrounded by four <sup>[2]</sup> sites and eight <sup>[1]</sup> sites, whereas each <sup>[2]</sup> site is surrounded by twelve <sup>[1]</sup> sites. Keeping in mind the expression for the average atomic fraction of strontium  $\bar{x} = (3x^{[1]} + x^{[2]})/4$ , we can write two rate equations that describe the equalization of occupancies:

$$\frac{dx^{[1]}}{dt} = \frac{4}{12} P x^{[2]} + \frac{8}{12} P x^{[1]} - P x^{[1]} = \frac{4}{3} P (\bar{x} - x^{[1]}), \quad (1)$$

$$\frac{dx^{[2]}}{dt} = \frac{0}{12} P x^{[2]} + \frac{12}{12} P x^{[1]} - P x^{[2]} = \frac{4}{3} P (\bar{x} - x^{[2]}). \quad (2)$$

Download English Version:

<https://daneshyari.com/en/article/1330191>

Download Persian Version:

<https://daneshyari.com/article/1330191>

[Daneshyari.com](https://daneshyari.com)