New Triclinic Modification of Lead Iodate Pb(IO$_3$)$_2$: Synthesis and Crystal Structure

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Abstract—A new triclinic modification of lead iodate Pb(IO$_3$)$_2$ (space group $C\bar{1}$) is obtained under hydrothermal conditions. The crystal structure is determined without preliminary knowledge of the chemical formula. [IO$_3$]$^-$ groups, which are characteristic of pentavalent iodine, have a typical umbrella-like configuration. The new phase has a more complex structure than the known orthorhombic modification. The arrangement of heavy Pb and I atoms follows $a' = a/3$ pseudoperiodicity. In the layers of two types that form sheets parallel to the $ab$ plane, Pb and I atoms have different coordinations. A polytypic nature of the new modification is responsible for the one-dimensional disordering along the $a$ axis as well as different variants of layer alternation. It is possible to obtain crystals of acentric and polar derivatives of the centrosymmetric phase that will be promising for application.

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INTRODUCTION

Iodates are compounds with pyramidal or umbrella-like (IO$_3$)$^-$ structural groups formed by pentavalent I atoms. These compounds are rare in nature [1, 2]. The position at a vertex of a pyramid at short distances from three O atoms lying in the base allows $I^+$ ion to direct its lone electron pairs outward from the base, that is, to form a polar distribution of electron density. This arouses interest in the synthesis of iodates, which can be obtained in the form of crystals exhibiting pyroelectric, ferroelectric, nonlinear-optical, or piezoelectric properties. Pyroelectric properties of the $\alpha$-LiIO$_3$ crystals with polar group $P6_3$ studied earlier are directly associated with the polar structure of IO$_3$ groups [3]. In the last few years, the search is targeted to new promising compounds whose crystals comprise different structural fragments contributing to predicted properties. Combining iodate groups with easily polarizable heavy elements, such as Pb, Hg, or Bi, is a promising direction. In Hg(IO$_3$)$_2$ crystals, which were obtained recently and have a polar structure, both the IO$_3$ groups and the difference in Hg–O bonds contribute to the properties analogous to those of LiIO$_3$ [4]. Recently prepared crystals of BiO(IO$_3$)$_2$ exhibit high optical nonlinearity which is associated mainly with the polar orientation of iodate groups in the structure [5], but the presence of bismuth atoms is also of great importance. The Ti element, which is able to form a short double titanyl bond, is combined with iodate groups in compounds both with and without alkali metals with much success. Thus, titanium iodate TiO(IO$_3$)$_2$, whose structure is close to that of potassium titanyl phosphate, also shows high nonlinearity [6].

In this paper the results of synthesis and a structural study of the new centrosymmetric triclinic lead iodate Pb(IO$_3$)$_2$ are presented and its specific structural features are compared with those of the orthorhombic centrosymmetric modification studied earlier.

EXPERIMENTAL

Synthesis of crystals. Crystals of Pb(IO$_3$)$_2$ (I) were obtained in the course of studies of phase formation in a complex system approaching the conditions in nature, where SiO$_2$ is available as a rule. For this reason, the starting composition contained an essential amount of silica, which enhanced the viscosity of the solution. New lead iodate crystallized at the mass ratios of the starting oxides of PbCO$_3$ : Bi$_2$O$_3$ : LiIO$_3$ : B$_2$O$_3$ : SiO$_2$ = 1 : 1 : 2 : 3 : 1. The ratio of the solid and liquid phases was 1 : 5. The synthesis was performed at $T = 270^\circ$C and $p \approx 70$ atm in standard autoclaves 5–6 cm$^3$ in volume protected with a fluoroplastic coating. The duration of the reaction between the ingredients to its completion required 18–20 days.

Owing to the complexity of the system, five phases were formed. The phases were identified based on the morphology, determination of the composition, the data of X-ray powder and single crystal diffraction, and the measurement of nonlinear-optical properties. All the products of crystallization were colorless.
Scanning electron microscope studies (Leo 1420 VP + INCA350 device) of a white pearlized crystalline powder revealed Bi and I atoms. A test for the second harmonic generation by a quantity of nacreous crystals in the shape of fine flakes that were selected from the product performed using a pulsed YAG : Nd laser [7] showed an intense signal. The powder diffraction pattern indicated that this phase is compound BiO(IO\(_3\))\(_2\), which was synthesized earlier in the form of a powder and single crystals. It was characterized structurally and exhibits very high optical nonlinearity [5]. Massive colorless aggregates obtained in the experiment in a considerable amount are sassoline H\(_2\)BO\(_3\) crystals, as follows from the determination of unit-cell parameters and composition. The experiment afforded a number of small well-faceted crystals in the shape of a trigonal prism. The determination of composition showed that this phase, like massive aggregates, does not contain heavy elements. Its structure corresponds to the new acentric polyborate Li\(_3\)[B\(_8\)O\(_{12}\)(OH)\(_3\)] [8]. In addition to the three phases described above, a large number of crystals containing Pb and I were obtained. These crystals were isometric in shape, and many of them had rhombic or prismatic faceting. After the determination of unit-cell parameters and composition, the crystals were divided into two groups: crystals of one group were triclinic with the unit cell that had no crystals were divided into two groups: crystals of one group were triclinic with the unit cell that had no crystals were divided into two groups: crystals of one group were triclinic with the unit cell that had no crystals were divided into two groups: crystals of one group were triclinic with the unit cell that had no crystals were divided into two groups: crystals of one group were triclinic with the unit cell that had no

**X-ray diffraction study.** The unit-cell parameters were determined and refined on an Xcalibur S diffractometer equipped with a CCD detector. Transparent crystals of the known orthorhombic phase I were of good quality. Their parameters were determined unambiguously. At the same time, crystals of new phase II, which were not visually dissimilar to crystals of phase II, were worse in quality; their diffraction patterns contained diffuse reflections. A triclinic cell was determined; for some samples, the \(c\) parameter was twice as long or even longer. The most perfect transparent crystal of new phase I in the shape of a prism was chosen for data collection. The unit-cell parameters with angles close to the right angle were chosen in order to bring phase I closer to the known orthorhombic modification II; however, no direct relation between the cell axes of phases I and II was found. A pseudoperiod \(d' = a/3 = 3.985\) \(\text{Å}\) was found for the \(a\) parameter, and some disturbance of the regular repetition of reflections was observed along the \(c\) axis. This provided an explanation for the doubling or greater increase of the \(c\) parameter found for other samples and indicated that the sample chosen was to some extent disordered. A three-dimensional set of experimental data for structure determination was obtained for the full sphere of the reciprocal space. The data set was processed with the CrysAlis program. The extinction of the reflections other than \(hkl: h + k = 2n\) corresponded to the lattice with \(C\) centering, that is, a nonstandard setting of the triclinic cell. At first the structure was solved in the acentric space group \(C1\).

The Pb(IO\(_3\))\(_2\) formula was introduced to calculate the direct method with the SHELXS program, which revealed four basis Pb atoms at general sites and eight I atoms. The positions of 24 lacking O atoms, which form the umbrella-like coordination of I atoms at characteristic distances of \(~1.8\) \(\text{Å}\) and in addition coordinate Pb atoms, were step by step determined on difference Fourier maps. The analysis of the model clearly showed that it is centrosymmetric, and a center of inversion was chosen as the origin. In the new centrosymmetric space group \(\overline{C1}\), the number of basis atoms decreased to two Pb, four I, and twelve O atoms. This composition actually corresponds to the Pb(IO\(_3\))\(_2\) formula for the number of formula units \(Z = 8\). The atomic coordinates and displacement parameters, anisotropic for all atoms but O5, whose thermal motion is relatively free because of a small number of bonds with cations, were refined by the least-squares procedure using the SHELXL program, which accounts for the anomalous scattering. The correction for absorption based on crystal faces did not improve the result, because the crystal shape was determined inaccurately and disagreed with the real crystal shape. Such discrepancy introduces an error that exceeds the effect of correction, especially at high absorption. The high pseudosymmetry of the structure owing to the arrangement of heavy atoms of two sorts also gives rise to spurious peaks of electron density; however, the estimates of the refinement, in particular, the \(S\) value, bear witness to the reliability of the model of phase I, which is characterized by disordering (as was concluded based on the analysis of the diffraction data and specific features of crystal chemistry). The crystal data, characteristics of data collection, and results of the refinement of the structure are given in Table 1. The atomic coordinates and thermal displacement parameters are listed in Table 2. Interatomic distances are presented in Table 3. The structural data are available in the ICSD database (deposit no. 426226).