# Strutural study of Lanthanum oxysulfate $(LaO)_2SO_4$

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## INTRODUCTION

Lanthanum oxysulfate belongs to the family of rare-erth oxysulfate compounds $(LaO)_2SO_4$, that are the subject of interest because of its application on preparation of magnetic gigante resistance compounds (manganites) and oxide fuel cell [1]. For manganites, polycrystalline samples of $La_{0.86}Sr_{0.14}Mn_{1-x}Cu_xO_3$ with x = 0, 0.05, 0.10, 0.15 and 0.20 ban be synthesized by usual solid-state reaction technique, starting from stoichiometric mixtures of $(LaO)_2SO_4$, $SrCO_3$, $MnO_2$ and $CuO$ powders, and the final sintering was performed in oxygen atmosphere at 1400°C for 30 min followed by a period of 24 h at 1300°C. The structure of $(LaO)_2SO_4$ had been determined as tetragonal [2], but subsequently Ball and Mareschal [3] claimed the crystal to be orthorhombic with separate layers of $(LaO)_2^{+2}$ and $SO_4^{-2}$ groups, normal to the $c$ axis. This work has been understaken to reexamine the structure of lanthanum oxysulphate by high intensity and resolution syncrotron X-ray diffraction. The results presented here can be used for futher investigation of energy level schemes of $Ln^{+3}$ ion in the $(LnO)_2SO_4$.

## EXPERIMENT

High-resolution and -intensity synchrotron X-ray diffraction data were collected at the XPD beamline, placed after the D10B dipolar source of LNLS [5]. X-rays of wavelength 1.19197(3) were selected by a double-bounce Si(111) monochromator, with water-refrigeration in the first crystal, while the second one is bent for sagittal focusing. The beam is vertically focused or collimated by a bent Rh-coated ultra low expansion glass mirror placed before the monochromator, which also provides filtering of high-energy photons (third- and higher-order harmonics). The experiments were performed in the vertical scattering plane, i.e., perpendicular to the linear polarization of the incident photons. Wavelength and the zero point were determined from several well-defined reflections of the NIST SRM640c silicon standard. The diffracted beam was detected with an Na(Tl)I scintillation counter with a pulse-height discriminator in the counting chain. The incoming beam was also monitored by a scintillation counter for normalization of the decay of the primary beam. In this parallel-beam configuration, the resolution is determined by the slits in front of the detector. The powder diffraction pattern was analyzed by the Rietveld method using the General Structure Analysis System (GSAS) [6] program and its graphical user interface, EXPGUI [7]. The background was fit using a 14-terms shifted Chebyschev function. The peak profile was modelled by a pseudo-Voigt profile function as parameterized by [8] with asymmetry corrections by [9] and microstrain anisotropic broadening terms by [10].

## RESULTS AND DISCUSSION

We summarize our refinement results below.

**Crystal data**

| | |
|---|---|
| **Formula sum** | $La_2O_2S$ |
| **Formula weight** | **341.87** |
| **Crystal system** | **trigonal** |
| **Space group** | **P-3 m (nr. 164)** |
| **Unit cell dimensions** | $a = 4.0512(0)$ **Å** |
| | $c = 6.9453(1)$ **Å** |
| **Cell volume** | **98.71(0) Å$^3$** |
| **Z** | **1** |
| **Density, calculated** | **5.750 g/cm$^3$** |
| **Pearson code** | **hP5** |
| **Formula type** | **NO2P2** |
| **Wyckoff sequence** | **d$^3$b** |

**Atomic coordinates and isotropic displacemente**

| Atom | Wyck. | x | y | z | U |
|---|---|---|---|---|---|
| La1 | 2d | 1/3 | 2/3 | 0.22018(19) | 0.0053(3) |
| S1 | 4e | 0 | 0 | 1/2 | 0.0015 |
| O1 | 4e | 1/3 | 2/3 | -0.1342(13) | 0.0047 |

**Symmetry codes: (i)** $1+x,y,z$**; (ii)** $-x,-y,-z$**; (iii)** $1-x,-y,-z$**; (iv)** $x,0.5-y,-0.5+z$**.**

**Rietveld Analysis.**

| Fitted | | -Bknd | |
|---|---|---|---|
| wRp | Rp | wRp | Rp |
| 0.2705 | 0.1798 | 0.3430 | 0.1597 |
| | | DWd | 1.782 |

**Cycle 239 There were 12483 observations.**

**$X^2$ = 1.233 for 26 variables RF2 = 0.2284 Phase/element fractions for phase no. 1 (La2O2S) Fraction : 1.87669 Sigmas : 0.971436E-02 Wt. Frac.: 0.83127 Sigmas : 0.726035E-03 Phase/element fractions for phase no. 2 (La2O2)SO4 Fraction : 0.802159E- Sigmas : 0.122398E-02 Wt. Frac.: 0.16873 Sigmas : 0.214018E-02**

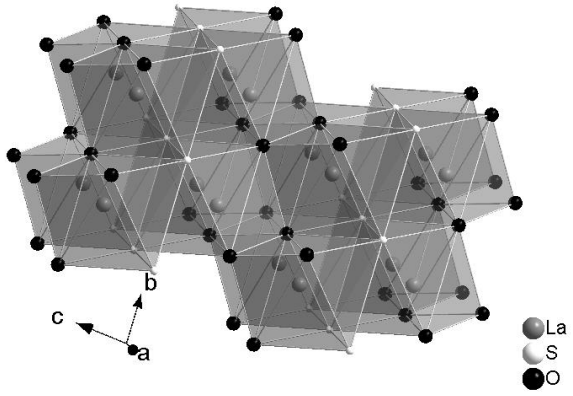


FIG. 1: Figure 1 - Structure of $(LaO)_2SO_4$

## CONCLUSION

**In conclusion, we would like to emphasize the effectiveness of the high resolution X-ray diffraction to determined the structure of $(LnO)_2SO_4$.**

## ACKNOWLEDGEMENTS

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[1] **S. Zhukov, *et al.*, Materials Research Bulletin, 32, (1997), 43.**
[2] **G. Pannetier, and A. Dereigner, Bull. Soc. Chim. Fr, (1963), 1850.**
[3] **R. ballestracci and J. Mareshal, Materials Research Bulletin, 2, (1967), 993.**
[4] **K Kishio *et al.*, J. Low Temp. Phys. 105, (1995), 1359.**
[5] **F. F. Ferreira *et al.*. J. Synchrotron Rad. 13, (2006), 46-53.**
[6] **A. C. Larson, and R. B. Von Dreele, Los Alamos National Laboratory Report LAUR, (2001), 86-748.**
[7] **B. H. Toby, J. Appl. Cryst. 34, (2001), 210-213.**
[8] **P. Thompson, D. E. Cox, and J. B. Hasting, (1987). J. Appl. Cryst, 20, (1987), 79-83.**
[9] **L. W. Finger, D. E. Cox, and A. P. Jephcoat, (1994). J. Appl. Cryst., 27, (1994), 892-900.**
[10] **P. W. Stephens. J. Appl. Cryst., 32, (1999), 281-289.**