

Crystal structure, vibrational properties and luminescence of $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ crystal doped with Cr^{3+} ions

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Abstract

Crystals of $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ doped with 0.5% Cr^{3+} ions have been synthesized and characterized by a single-crystal X-ray structure analysis and IR, Raman, electron absorption and luminescence spectroscopic studies. It has been shown that $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ crystallizes in the $P\bar{1}$ structure, with $a = 6.8744(8)$ Å, $b = 6.9342(7)$ Å, $c = 17.605(2)$ Å, $\alpha = 87.788(8)^\circ$, $\beta = 87.727(9)^\circ$, $\gamma = 78.501(9)^\circ$, $Z = 2$. The characteristic feature of the structure is its enormously large thermal displacement parameter for sodium, even at 105 K. The IR and Raman spectra indicate significant interactions between the MoO_4^{2-} ions in the structure. The electron absorption, excitation and luminescence studies have shown that there are at least two different sites of incorporated Cr^{3+} ions in the $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ crystal structure. They differ themselves by strength of crystalline field. One of them is characterized by Cr^{3+} in low ligand field and ${}^4T_2 \rightarrow {}^4A_2$ emission whereas the second is characterized by higher strength of the crystal field and dominant ${}^2E \rightarrow {}^4A_2$ emission. Temperature-dependent studies show that the compound does not exhibit any phase transition.

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1. Introduction

Molybdates have found many applications, for example as catalysts, laser materials, solid-state electrolytes [1–5]. Recently, a new group of ternary molybdates with general formula $\text{NaM}_3^{\text{II}}M^{\text{III}}(\text{MoO}_4)_5$, where $M^{\text{II}} = \text{Mg, Ni, Co, Mn, Fe}$; $M^{\text{III}} = \text{Al, In, Fe, Cr}$; has drawn attention since these molybdates may find application as solid-state electrolytes with sodium cation conductivity [6–8]. The iron containing molybdates are also suitable model systems for magnetic interactions because in this structure FeO_6 octahedra are separated from each other by MoO_4 tetrahedra and sodium ions [9]. These molybdates may also find application as catalysts in oxidation reactions

since both magnesium, iron, nickel, cobalt and chromium molybdates are well-known catalysts [10–13].

The synthesis of the title $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ crystals was described for the first time in Ref. [14]. It was shown that the crystals grow at high temperature and crystallize in triclinic system. Lattice parameters of $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ were determined from powder diffraction data and schematic structure was suggested. However, the crystal structure was not solved and the atomic coordinates were not given. Later on, the isomorphous structure of $\text{NaMg}_3\text{In}(\text{MoO}_4)_5$ was solved [15]. Its triclinic unit cell dimensions are: $a = 7.0476(7)$ Å, $b = 17.935(2)$ Å, $c = 6.9849(7)$ Å, $\alpha = 87.650(9)^\circ$, $\beta = 100.980(8)^\circ$, $\gamma = 92.510(9)^\circ$; $Z = 2$ and space group $P\bar{1}$. The framework of this structure is similar to that observed for the $M_2^{\text{III}}(\text{MoO}_4)_3$ type of compounds ($M^{\text{III}} = \text{Fe, In, Sc, Al}$), which are well known to exhibit many important properties

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due to flexibility of the structure: high-ionic conductivity of trivalent ions, amorphization at low pressures, negative thermal expansion and ferroelastic phase transitions [16–20]. However, in the case of ternary molybdate some large cavities formed by MoO_4 tetrahedra and $(\text{Mg,In})\text{O}_6$ octahedra, which are empty in the $M_2^{\text{III}}(\text{MoO}_4)_3$ structure, are occupied by Na^+ ions. It was also shown that Mg and In atoms occupy common positions with occupation 0.75 Mg + 0.25 In and that the sodium atom has an extremely large thermal displacement parameter which inclined the authors to split its positions into two, placed in a very short distance of 0.618 Å one from another.

Another isomorphous structure, $\text{NaFe}_4(\text{MoO}_4)_5$, was solved recently [9] as one of four new structures within Na–Fe–Mo–O system. Its lattice parameters are the following: $a = 6.9337(3)$ Å, $b = 7.0196(4)$ Å, $c = 17.8033(8)$ Å, $\alpha = 87.468(4)^\circ$, $\beta = 87.615(4)^\circ$, $\gamma = 79.090(4)^\circ$; $Z = 2$ and space group $P\bar{1}$. Also here, thermal displacement parameter for sodium is enormously large and anisotropic. Moreover, anomalous thermal displacement parameters of Na atoms were observed in many molybdates, e.g. $\text{NaIn}(\text{MoO}_4)_2$ [21], $\text{Na}_5\text{Sc}(\text{MoO}_4)_4$ [22], $\text{Na}_2\text{Zr}(\text{MoO}_4)_3$ [23], $\text{Na}_2\text{Mg}_5(\text{MoO}_4)_6$ [24] but without more detailed analysis of this phenomenon.

In the present paper we report on temperature-dependent X-ray diffraction, Raman, IR, luminescence and electron absorption studies of $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ crystal, which belongs to this family of ternary molybdates, in order to get information about structure at different temperatures, in particular the behavior of sodium in the crystal structure and possible phase transitions. Our aim was also to characterize the vibrational properties of this material since such information is necessary to explain luminescence properties. We would like to emphasize that vibrational properties of this family of ternary molybdates have not yet been studied.

$\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ compound was chosen for these studies for a few reasons. Firstly, the structure of this material has not yet been reported. Secondly, whereas in the previously studied $\text{NaMg}_3\text{In}(\text{MoO}_4)_5$ the Mg^{2+} and In^{3+} ions are disordered among the same crystallographic positions due to similarity of ionic radii, we expected to observe ordering of Al^{3+} and Mg^{2+} ions due to significantly different ionic radii of these ions. Thirdly, we expected to observe more efficient luminescence of Cr^{3+} ions doped in this material, when compared with the indium analog, due to the small ionic size of Al^{3+} ions and, consequently, stronger crystal field.

2. Experiment

Single crystals of $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$: 0.5% Cr^{3+} were grown by cooling of the molten mixture containing MgO (99.99%), Na_2CO_3 (99.5%), Al_2O_3 (99.99%), Cr_2O_3 (99.995%) and MoO_3 (99.95%). The amount of chemicals used corresponded to composition $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$:

0.5% Cr^{3+} and $\text{Na}_2\text{Mo}_2\text{O}_7$ in a ratio of 1:2. The mixture was kept at 950 °C for 20 h, cooled with a 2 °C/h rate to 600 °C and 10 °C/h rate down to room temperature (RT). The obtained good quality, not twinned crystals were separated from the $\text{Na}_2\text{Mo}_2\text{O}_7$ solvent by washing with hot water. Dimensions of the crystals were up to $3 \times 2 \times 2$ mm.

Single crystal of $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ was measured twice, at RT (293 K) and at 105 K, on Oxford Diffraction X'Calibur four-circle single-crystal diffractometer equipped with CCD detector using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). Oxford Cryosystem liquid nitrogen attachment was applied to the measurement at 105 K. The intensities of the reflections were corrected for Lorentz and polarization factors. Analytical absorption correction was applied.

The crystal structure was solved by Patterson methods and refined by full matrix least-squares method using SHELX-97 program [25]. Refinement was performed on F^2 against all reflections. The weighted R factor (wR) and goodness of fit (S) are based on F^2 , conventional R factors (R) are based on F , with F set to zero for negative

Table 1
Crystal data and structure refinement for $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$

| | | |
|------------------------------------|---|--|
| Empirical formula | $\text{NaMg}_3\text{Al}(\text{MoO}_4)_5$ | |
| Formula weight | 922.60 | |
| Z | 2 | |
| Crystal system, space group | Triclinic, $P\bar{1}$ (No. 2) | |
| Temperature | 105 (0.5) K | 293(1) K |
| Unit cell dimensions | $a = 6.8742(8)$ Å $b = 6.9305(7)$ Å $c = 17.575(2)$ Å $\alpha = 87.902(8)^\circ$ $\beta = 87.648(9)^\circ$ $\gamma = 78.942(15)^\circ$ | $a = 6.8744(8)$ Å $b = 6.9342(7)$ Å $c = 17.605(2)$ Å $\alpha = 87.788(8)^\circ$ $\beta = 87.727(9)^\circ$ $\gamma = 78.501(9)^\circ$ |
| Volume | $820.73(15)$ Å ³ | $821.28(15)$ Å ³ |
| Calculated density | 3.733 mg/m ³ | 3.731 mg/m ³ |
| Absorption coefficient | 4.018 mm ⁻¹ | 4.016 mm ⁻¹ |
| $F(000)$ | 860 | 860 |
| Crystal size | $0.375 \times 0.175 \times 0.008$ mm | $0.375 \times 0.175 \times 0.008$ mm |
| θ range for data collection | 4.38 – 33.10° | 3.20 – 33.00° |
| Limiting indices | $-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $0 \leq l \leq 26$ | $-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $0 \leq l \leq 26$ |
| Reflections collected/unique | 10978 | 11369 |
| Independent reflections | 5209 | 5207 |
| R_{int} | 0.0343 | 0.0355 |
| Completeness to $\theta = 25.25$ | 99.6% | 99.4% |
| Data/parameters | 5209/272 | 5207/272 |
| Goodness-of-fit on F^2 | 1.568 | 1.465 |
| Final R indices | $R_1 = 0.0292$, [$I > 2\sigma(I)$] $wR_2 = 0.0749$ | $R_1 = 0.0255$, $wR_2 = 0.0703$ |
| R indices (all data) | $R_1 = 0.0303$, $wR_2 = 0.0753$ | $R_1 = 0.0262$, $wR_2 = 0.0706$ |
| Extinction coefficient | 0.0039(3) | 0.0040(2) |
| Largest diff. peak and hole | 3.320 and -1.868 e/Å ⁻³ | 2.287 and -1.708 e/Å ⁻³ |

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