Periodico di Mineralogia (2015), 84, 2, 233-246 DOI: 10.2451/2015PM0002

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on Environment, Archaeometry and Cultural Heritage

Thermal behaviour of alum-(Rb) $RbAl(SO_4)_2 \cdot 12H_2O$ from in-situ laboratory high-temperature X-ray powder diffraction data

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Abstract

The present work investigates *in-situ* the thermal behaviour of alum-(Rb), $RbAl(SO_4)_2 \cdot 12H_2O$, by high-temperature X-ray powder diffraction from 303 K to melting, which starts at 359 K and is completed, due to kinetics, at 363 K. The calculated a_0 linear thermal expansion coefficient is 10.33(12) x 10^{-6} K^{-1} within the investigated thermal range. The k order parameter, which is the measure of the extension of the orientational disorder of the sulphate group, decreases from ca. 0.80 at 303 K to ca. 0.75 just before melting. This behaviour has been shown to depend on the need to keep the bond valence sum of the Rb^+ cation, which coexists in both six- and seven-fold coordination, at a reasonable value of ca. 0.82 valence units.

Key words: X-ray powder diffraction; Rietveld method; thermal behaviour; alum-(Rb).

Introduction

The alum group is a broad group of minerals and synthetic compounds, crystallizing in space group *Pa*3, with the general formula $M^{I}M^{III}(SO_4)_2 \cdot 12H_2O$, where M^I and M^{III} represent a monovalent and a trivalent cation, respectively. Among those compounds, alum-(K) is a very common naturally occurring sulphate, which has been used for industrial purposes. It represents the archetypal member of the group and, as such, has been the object of several investigations aimed at analysing the peculiar orientational disorder of its sulphate group (Larson and Cromer, 1967). This feature is shared with several members of the group. At room temperature (RT) the sulphate group of alum-(K) is arranged between two orientations in a 70:30 proportion. They are characterized by having the oxygen atoms pointing toward the aluminium atom (more probable one, hereinafter labelled as SO, comprising oxygen atom sites O3 and O4), and the oxygen atoms pointing toward the potassium atom (less probable:

hereinafter labelled as SOA, comprising oxygen atom sites O3A and O4A), respectively (Larson and Cromer, 1967). The orientation of the two tetrahedra has been hypothesized to depend on the ionic radius of the monovalent M^{I} cation (Nyburg et al., 2000).

To date, only the thermal behaviour of alum-(K) has been investigated, predominantly by Raman spectroscopy (Eysel and Schumacher, 1977; Sood et al., 1981; Brooker and Eysel, 1990), and, only recently, by in-situ high-temperature X-ray powder diffraction (HT-XRPD) (Ballirano, 2015). Those studies indicate an increased ordering to the SO configuration as temperature is reduced.

The aim of this work is to investigate, from in-situ high-temperature laboratory parallel beam X-ray powder diffraction (HT-XRPD) the thermal expansion and the structural modifications of alum-(Rb) occurring from 303 K to melting. Larson and Cromer (1967) suggested the occurrence of a limited degree of orientational disorder of the sulphate group of alum-(Rb) from single crystal structure refinement (SCSR). However, owing to correlation among parameters, they were not able to refine at RT the *k* disorder parameter (fraction of tetrahedra in SO orientation: corresponds to the site occupancy factors (sof) of O3 = O4) that was estimated to be in the range 0.90-0.85. Suresh et al. (1996) subsequently confirmed the occurrence of limited disorder from single-crystal polarized Raman spectroscopy. The result was obtained from evaluation of the relative intensity of the two A_g components of the non-degenerate n1 mode of the SO and SOA tetrahedral located at, respectively, 990 and 975 cm^{-1}. The experimental set-up used in the present investigation, which is the same used for the recent investigation of alum-(K) stability (Ballirano, 2015), has been shown to produce high-quality diffraction data (Ballirano et al., 2010) substantially free from texture, and subjected to limited thermal gradients.

The results of this work, which is part of a wider, well-established study on the crystal chemistry and thermal stability of sulphates, are expected to provide additional information for devising a comprehensive model of the orientational disorder of alums.

Experimental

Alum-(Rb) was synthesised by precipitation in aqueous solution from a stoichiometric mixture of $Al_2(SO_4)_3 \cdot 18H_2O$ (alunogen: purum p.a. Fluka 06421) and Rb_2SO_4 (99.99% Aldrich 229830). Details of the instrumental set-up used for performing HT-XRPD may be found in Ballirano and Melis (2007). Diffraction patterns were collected in the 10-140° 2θ angular range with a step-size of 0.022° 2θ, and 2s of counting time. Data were measured isothermally in the 303-423 K thermal range at temperature steps of 4 K. No Bragg reflections were observed at T > 367 K indicating the complete melting of the compound as confirmed by a relevant increase of the background (Figure 1). This behaviour is in agreement with the melting T of alum-(Rb) of < 373 K reported by Haynes (2012).

Diffraction patterns were evaluated by the Rietveld method using TOPAS V.4.2 (Bruker AXS, 2009), using the Fundamental Parameters Approach FPA (Cheary and Coelho, 1992). The absorption was refined following the procedure described by Ballirano and Maras (2006). Starting structural data were taken from Larson and Cromer (1967) modified to take into account the orientational disorder of the sulphate group. Oxygen sites were labelled according to the recent works of Nyburg et al. (2000) and Ballirano (2015), renaming W(1) and W(2) as O2 and O1, and O(1) and O(2) as O3 and O4, respectively. Accordingly, the oxygen sites corresponding to the less probable orientation were identified as O3A and O4A. Managing of the strong correlation among absorption and displacement parameters and site occupancy was performed according to the procedure described by Ballirano (2015).

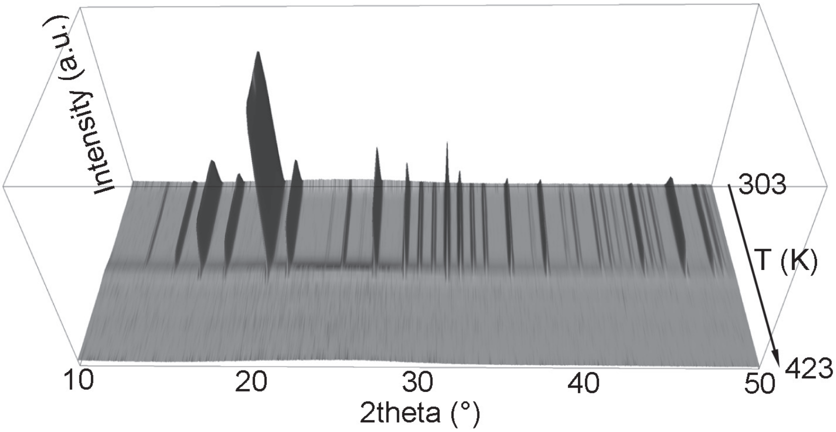

Figure 1. Magnified 3D-view of the full XRPD data set of the heating experiment of alum-(Rb).

Preferred orientation was modelled by means of spherical harmonics (Järvinen, 1993) and selecting the appropriate number of terms by the procedure devised by Ballirano (2003). Optimization of preferred orientation terms for multiple isothermal powder diffraction data was performed according to Ballirano (2011). The final average values of the spherical harmonics terms were: k41 = -0.060(5); k61 = 0.069(4); k62 = 0.058(8); k81 = 0.107(8). The hydrogen atoms position was kept fixed to calculated values throughout the refinements. In fact, inclusion of hydrogen atoms to the Rietveld refinement of structures containing a large number of water molecules has been proved to have beneficial effects on both agreement indices and structural parameters (Ballirano et al., 2003). Their starting position was calculated following a standard water molecule geometry and imposing the same hydrogen-bonding network reported by Nyburg et al. (2000), from SCSR, for several $M^{I}M^{III}(SO_4)_2 \cdot 12H_2O$ compounds. The hydrogen atoms fractional coordinates were not refined due to the minor displacement with temperature of both O1 and O2. In fact, in spite of keeping fixed the H atoms position, the largest difference in O-H bond distances, passing from 303 and 359 K, is of approximately 0.02 Å.

Refined structural parameters include fractional coordinates and isotropic displacement parameters of non-hydrogen atoms, and sof of the oxygen atoms of the SO (O3 and O4) and SOA (O3A and O4A) tetrahedra. The structure refined at a given temperature was used as input for the subsequent one. Experimental details and miscellaneous data of the refinements are reported in Table 1. A representative Rietveld plot of the diffraction pattern collected at 343 K is shown in Figure 2. Fractional coordinates, sof, and isosotropic displacement parameters of the structure of alum-(Rb) at 303 K is reported in Table 2. Full structural data are deposited under the form of CIF files as Supplemental Material.

Discussion

Table 3 lists the relevant bond distances of alum-(Rb) at 303 K. The geometry of the two sulphate groups is irregular, with the less probable configuration SOA being more regular than SO but characterized by very short bond distances. The <S-O> bond distances of the

Table 1. Experimental details and miscellaneous data of the refinements. Statistical indicators as defined by Young (1993).

Instrument	AXS Bruker D8 Advance
Optics	Multilayer graded (Göbel) mirrors
Slits	Soller x2 (incident: 2.3°; diffracted: radial)
Detector	PSD VÅNTEC-1D
Radiation	CuKα
2q range	10-140
Step size (°2q)	0.022
Counting time (s)	2
Thermal range (K)	303-423
Rwp	5.92-8.28
Rp	4.61-6.34
GoF	1.19-1.67
Durbin Watson “d”	0.82-1.52

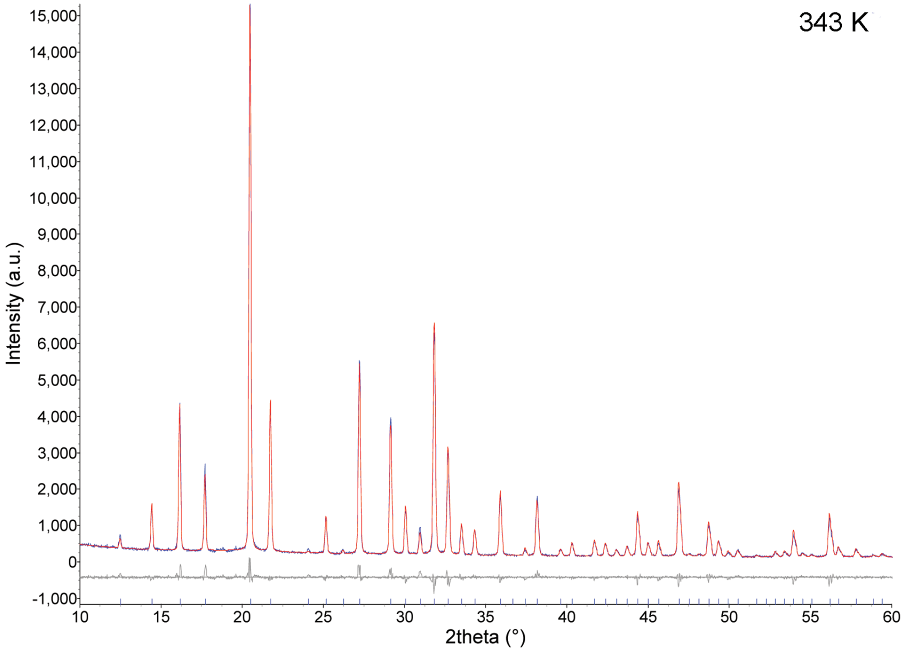

Figure 2. Conventional Rietveld plots of the angular range 10-60° 2θ, of the refinement of the diffraction data measured at 343 K. Experimental: blue; calculated: red; grey: difference. Vertical blue bars refer to Bragg reflections of alum-(Rb).

Table 2. Fractional coordinates, sof, and isosotropic displacement parameters of the structure of alum-(Rb) at 303 K. Reference data L&C67 of Larson and Cromer (1967), at RT, are reported in italic for comparison.

Site	*x*	*y*	*z*	U_{iso}	*sof*
S	0.3109(2)	0.3109(2)	0.3109(2)	0.0327(11)	1
	0.3127(4)	*0.3127(4)*	*0.3127(4)*	*0.021(2)*	
Al	0	0	0	0.0240(12)	1
	0	*0*	*0*	*0.019(4)*	
K	½	½	½	0.0541(8)	1
	½	½	½	*0.038(15)*	
O1	0.1493(3)	0.0178(4)	-0.0189(4)	0.044(2)	1
	0.1554(7)	*0.0173(10)*	*-0.0148(11)*	*0.017(8)*	
H11	0.200(0)	0.000(0)	0.040(0)	0.063(0)	1
	-	-	-	-	-
H12	0.190(0)	0.050(0)	-0.075(0)	0.063(0)	1
	-	-	-	-	-
O2	0.0481(4)	0.1396(4)	0.2974(4)	0.060(2)	1
	0.0451(10)	*0.1406(9)*	*0.2975(10)*	*0.022(8)*	
H21	0.010(0)	0.210(0)	0.300(0)	0.063(0)	1
	-	-	-	-	-
H22	0.115(0)	0.150(0)	0.260(0)	0.063(0)	1
	-	-	-	-	-
O3	0.2453(6)	0.2453(6)	0.2453(6)	0.043(3)	0.800(8)
	0.2471(17)	*0.2471(17)*	*0.2471(17)*	*0.089(12)*	*1*
O4	0.2702(5)	0.4226(5)	0.3220(5)	0.013(2)	0.800(8)
	0.2639(14)	*0.4237(10)*	*0.3172(11)*	*0.056(11)*	*1*
O3A	0.375(2)	0.375(2)	0.375(2)	0.043(3)	0.200(8)
	-	-	-	-	-
O4A	0.277(2)	0.227(2)	0.3703(19)	0.013(2)	0.200(8)
	-	-	-	-	-

two tetrahedra are 1.443 Å and 1.34 Å for SO and SOA, respectively. The former value is fairly close to the average S-O bond distance of 1.48 Å found in sulphate groups occurring within inorganic compounds (Bergerhoff and Brandenburg, 1995) and the corresponding grand <S-O> distance of 1.473 Å observed in minerals (Hawthorne et al. 2000). However, it is reasonably similar to both 1.452 Å and 1.459 Å reported, respectively, by Larson and Cromer

Table 3. Relevant bond distances of alum-(Rb) at RT. Reference data L&C67 of Larson and Cromer (1967) are reported for comparison.

	Present data	L&C67
S-O3	1.390(14)	1.39(4)
S-O4 x3	1.460(7)	1.485(12)
<S-O>	1.443	1.462
S-O3A	1.36(5)	-
S-O4A x3	1.33(2)	-
<S-OA>	1.34	-
Al-O1 x6	1.853(4)	1.923(9)
Rb-O2 x6	3.067(5)	3.068(12)
Rb-O3A x1	2.65(5)	-

(1967) for $RbAl(SO_4)_2 \cdot 12H_2O$ and by Figgis et al (2000) for $RbCr(SO_4)_2 \cdot 12H_2O$. Differently, the very short SOA-O bond distances, which have been similarly reported for a few SCSRs of $M^IM^{III}(SO_4)_2 \cdot 12H_2O$ (Nyburg et al., 2000) reflect the difficulty in accurately locate a very small electron density. The Al-O bond distance is of 1.853(4) Å, remarkably shorter than 1.923(9) Å reported by Larson and Cromer (1967). However, the latter seems to represent an anomalous value. In fact, it has to be noticed that those authors have systematically reported longer Al-O bond distances for both alum-(K) and -(NH_4) than those listed in more recent reference data (Abdeen et al., 1981; Nyburg et al., 2000; Ballirano, 2015) and to several Al-containing hydrated-sulfates (see for example halotrichite-group $M^{II}Al_2(SO_4)_4 \cdot 22H_2O$ members: Ballirano, 2006). This difference could be due to the fact that Larson and Cromer (1967) did not locate the H atoms. Therefore, the refined O2 position was possibly displaced toward the (missing) H atoms increasing the Al-O bond distance. The six Rb-O2 bond distances have been refined to 3.067(5) Å, almost identical with 3.068(12) Å of Larson and Cromer (1967). The additional two Rb-O3A bond distances, exclusively associated to the occurrence of the SOA orientation, were found to be 2.65(5) Å. The value of this distance is affected by the anomalously short S-O3A bond distance and should be, in effect, still shorter. Similarly to alum-(K), bond valence analysis (Breese and O'Keeffe, 1991) at the Rb site led to a bond valence sum of only 0.68 valence units (v.u.), significantly less than the ideal value of 1.00, from the contribution of the six M^I-O2 bond distances (0.113 x 6 v.u.). As explained in detail by Ballirano (2015) for alum-(K), the occurrence of the SOA orientation provides further 0.35 v.u. to Rb^+, due to an additional Rb-O3A bond, which results in a more conventional total of 1.03 v.u. for a seven-fold coordination. Owing to a *k* disorder parameter at 303 K of ca. 0.8 (see below), the Rb^+ ions coexist, in a statistically disordered distribution, in both six- and seven-fold coordination.

Isotropic displacement parameters are consistent with those reported at RT by Larson and Cromer (1967). The only exception is represented by the oxygen atoms of the sulphate group, which are moderately underestimated in the present study, following the same trend observed by Ballirano (2015) for alum-(K). In the present case, the larger displacement parameters of Larson and Cromer (1967) may be explained as arising from the sulphate group disorder that was not modelled.

The *k* disorder parameter has the value of 0.800(8) at 303 K. In the case of alum-(K), Ballirano (2015) hypothesized that a combined series of factors as the underestimation of the O4=O4A displacement parameters, their reported moderate anisotropy, as well as the imposition of the two O3=O3A and O4=O4A constraints, plus the more accentuated distortion of the SO tetrahedron, act to reduce the refined value of the *k* parameter. A similar effect could be invoked to explain the slightly smaller value obtained in the present work as compared to

Table 4. Dependence of the *a*-parameter of alum-(Rb) on temperature.

T (K)	*a*-parameter (Å)
303	12.23367(16)
307	12.23441(16)
311	12.23479(16)
315	12.23520(16)
319	12.23576(16)
323	12.23637(16)
327	12.23667(16)
331	12.23746(16)
335	12.23787(16)
339	12.23844(15)
343	12.23890(15)
347	12.23925(15)
351	12.23969(15)
355	12.24015(16)
359	12.24028(22)

0.85-0.90 estimated by Larson and Cromer (1967).

At 303 K, the *k* order parameter of 0.80 is consistent with 1.60 SOA tetrahedra per unit cell that may be bonded to four Rb^+ ions via O3A. Therefore, 40% of Rb^+ ions occurs in seven-fold and 60% in six-fold coordination. This cation population results in a bond valence sum of 0.82 v.u. for an "average" Rb^+ ion (40% six-fold and 60% seven-fold coordinated), a value that is meaningful from the crystal chemical point of view and justifiable by the ability of large monovalent cations to adapt their electronic ground state in response to the surroundings (Bosi et al., 2009).

The dependence on temperature of the *a*-parameter is listed in Table 4 and graphically shown in Figure 3. The linear thermal expansion coefficient has been calculated following the procedure described in Ballirano (2012) (Table 5). The a_0 linear thermal expansion coefficient of 10.33(12) x 10^{-6} K^{-1} is slightly smaller than 14.68(11) x 10^{-6} K^{-1} of alum-(K) (Ballirano, 2015).

Structure modifications are very small as temperature is raised. It is worth noting that the dependence from temperature of *a*-parameter, bond distances, and isotropic

Table 5. Linear thermal expansion coefficient a_0 of alum-(Rb).

		alum-(Rb) 303 K ≤ T ≤ 359 K
a-parameter	R^2	0.9925
	a_0 (x 10^{-6} K^{-1})	10.33(12)
	a_{Tr}	12.23367(16)

a_{Tr} is the *a*-parameter at reference temperature T_r = 303 K. R^2 = determination coefficients.

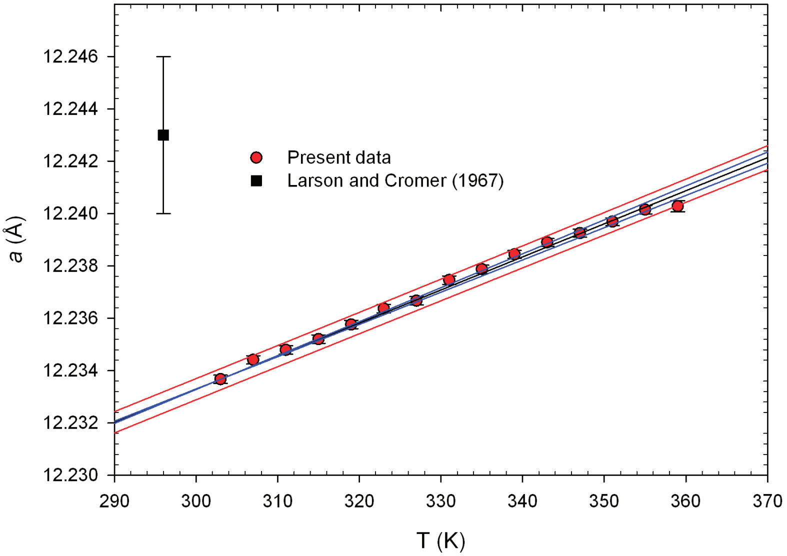

Figure 3. Dependence of the *a*-parameter of alum-(Rb) on temperature. Reference data at RT of Larson and Cromer (1967) are reported for comparison purpose. Linear regression (black), 95% confidence (blue), and 95% prediction (red) plots is reported.

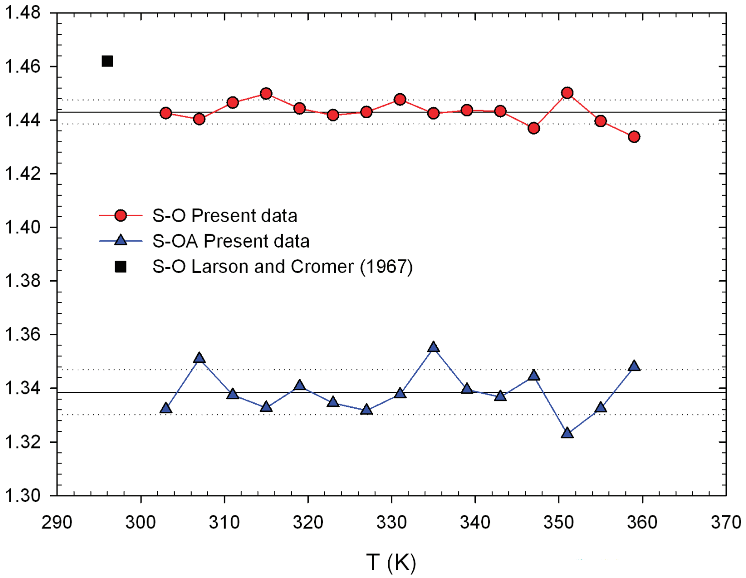

Figure 4. Dependence of the <S-O> bond distances on temperature. Reference data at RT of Larson and Cromer (1967) are reported for comparison purpose.

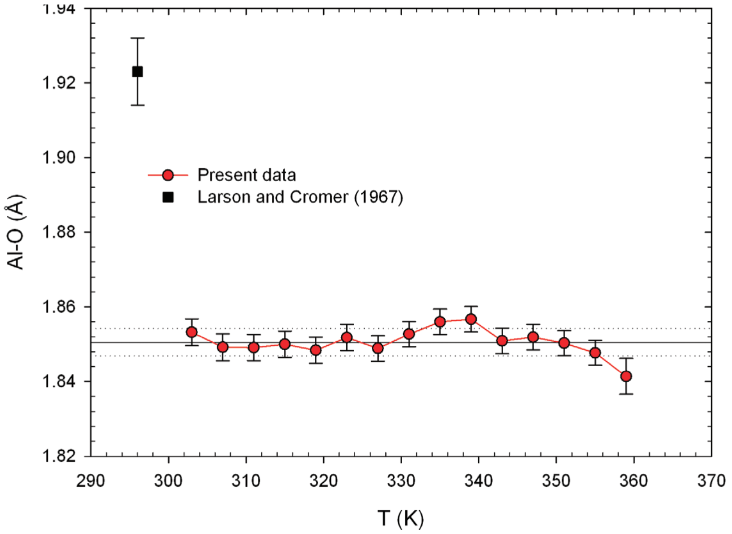

Figure 5. Dependence of the Al-O bond distance on temperature. Reference data at RT of Larson and Cromer (1967) are reported for comparison purpose.

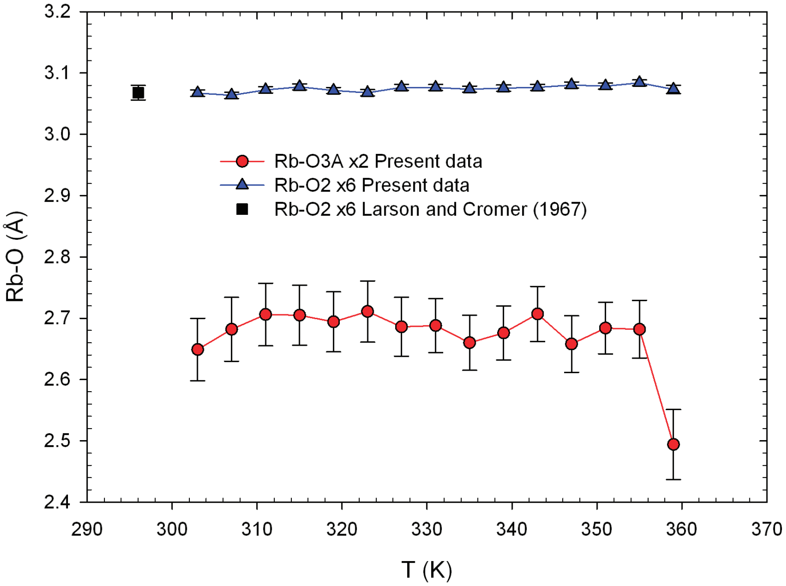

Figure 6. Dependence of the Rb-O bond distances on temperature. Reference data at RT of Larson and Cromer (1967) are reported for comparison purpose.

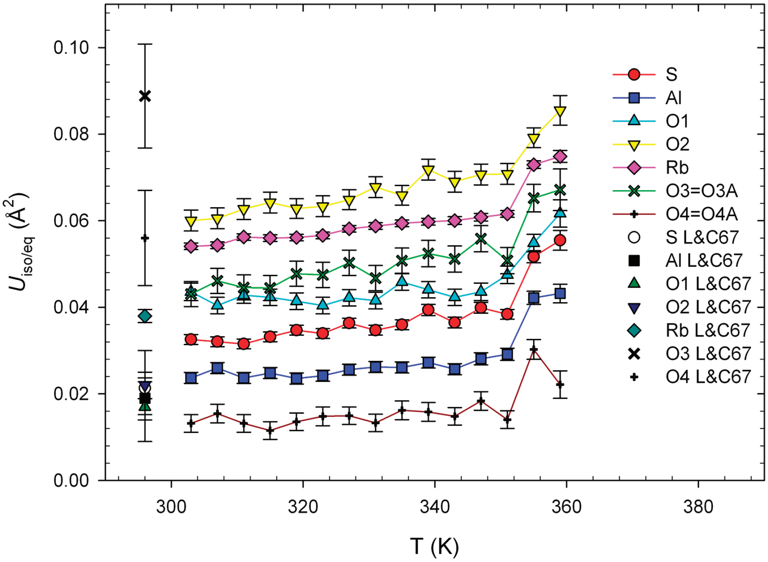

Figure 7. Dependence of the U_{iso} isotropic displacement parameters on temperature. Reference data (U_{eq}) at RT of Larson and Cromer (1967) (L&C67) are reported for comparison.

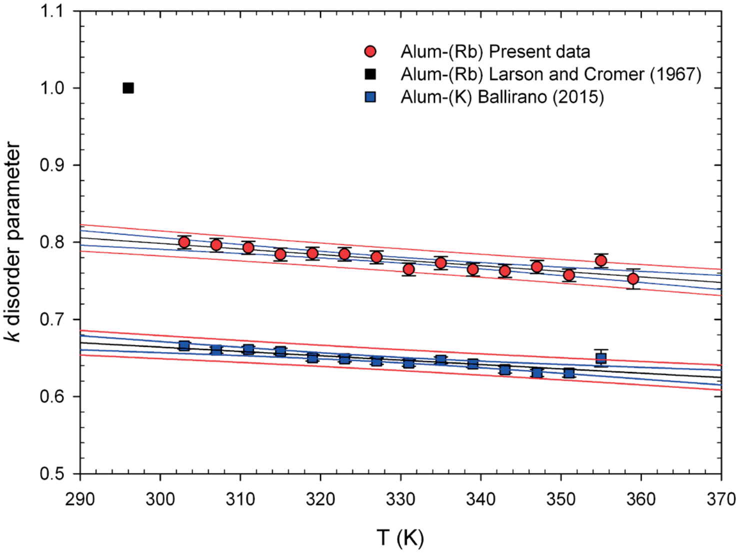

Figure 8. Dependence of the *k* disorder parameter on temperature. Linear regression (black), 95% confidence (blue), and 95% prediction (red) plots is reported. Reference data of alum-(K) (Ballirano, 2015) are reported for comparison purpose.

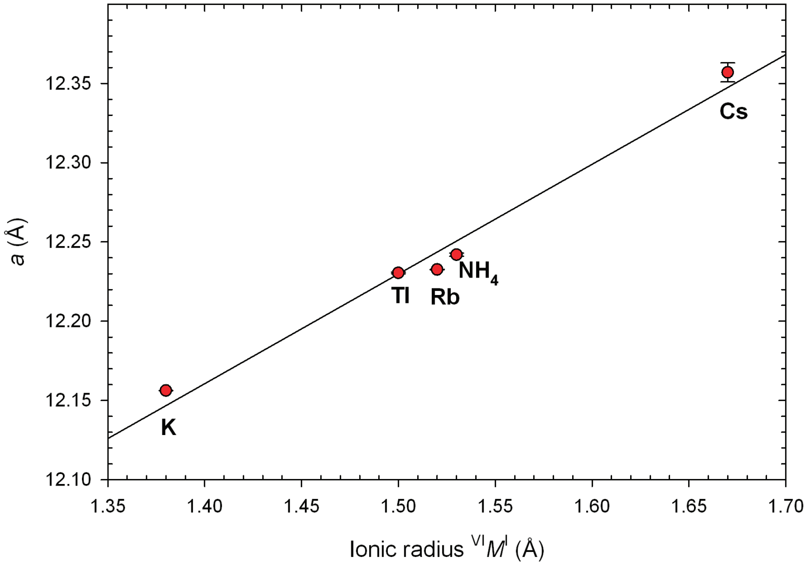

Figure 9. Dependence of the *a*-parameter of $M^{I}Al(SO_4)_2 \cdot 12H_2O$ on ionic radius of ${}^{VI}M^{I}$. Ionic radii from Shannon (1976). NH_4^+ ionic radius estimated from both *a*-parameter and *k* disorder parameter (see text for explanation). Reference data: alum-(K) = Ballirano (2015); alum-(Tl) = Nyburg et al. (2000); alum-(Rb) = present work; alum-(NH$_4$) = Abdeen et al. (1981); alum-(Cs) = Beattie et al. (1981).

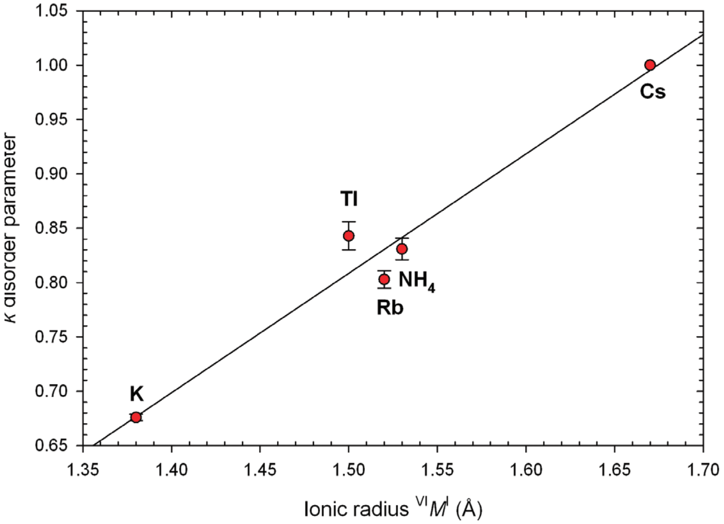

Figure 10. Dependence of the *k* disorder parameter of $M^{I}Al(SO_4)_2 \cdot 12H_2O$ on ionic radius of ${}^{VI}M^{I}$. Ionic radii from Shannon (1976). NH_4^+ ionic radius estimated from both *a*-parameter and *k* disorder parameter (see text for explanation). Reference data: alum-(K) = Ballirano (2015); alum-(Tl) = Nyburg et al. (2000); alum-(Rb) = present work; alum-(NH$_4$) = Abdeen et al. (1981); alum-(Cs) = Beattie et al. (1981).

displacement parameters is very regular up to 351 K. Instead, a deviation from this trend is observed at 355 K, possibly due to the effects of incipient melting, which becomes apparent as a broadening of the tails of the Bragg reflections coupled with a corresponding reduction of the intensity. The <S-O> bond distances of the SO and the SOA configuration are constant within the analysed thermal range, being 1.443(4) Å and 1.338(9) Å, respectively (Figure 4). Similarly, the Al-O bond distance is fairly constant throughout the analysed thermal range being 1.851(4) Å (Figure 5). The six Rb-O2 bond distances marginally increases from 3.067(5) Å to 3.084(5) Å (Figure 6), whereas, the dependence on T of the Rb-O3A bond distance cannot be properly evaluated due to the associated relatively large *esd*.

The displacement parameters regularly increase as a function of T up to 351 K, and with a greater rate at higher temperatures (Figure 7) with a behaviour similar to that reported for alum-(K).

The *k* disorder parameter dependence on T (Figure 8) is fairly linear in the 303-359 K thermal range ($R^2 = 0.804$; $k = 1.02(3) - 7.2(10) \times 10^{-4}\ K^{-1}\ T$). It is worth noting that the same slope has been reported for alum-(K) ($-7.2(5) \times 10^{-4}\ K^{-1}$: Ballirano, 2015).

Figure 9 and 10 show the linearity existing between the $^{VI}M^{I}$ ionic radius (Shannon, 1976) and both *a*- and *k* disorder parameter in $M^{I}Al(SO_4)_2 \cdot 12H_2O$. As can be seen, the best combined regression of the two plots, has been obtained for an ionic radius of ca. 1.53 Å for NH_4^+. This result agrees with the conclusion of Shannon (1976) that NH_4^+ is not significantly different in size from Rb^+. Finally, present data confirms the dependence of the extension of the sulphate group disorder from the ionic radius of the $^{VI}M^{I}$ cation (Nyburg et al., 2000).

Conclusions

The analysis of the thermal behaviour of alum-(Rb), from 303 K to melting, has revealed the occurrence of minimal structural modifications. The calculated a_0 linear thermal expansion coefficient is of $10.33(12) \times 10^{-6}\ K^{-1}$ only marginally smaller than that of isostructural alum-(K). The *k* order parameter, describing the population of the two orientationally disordered sulphate groups, has been found to decrease to ca. 0.75 before melting. Present data confirms that the *k* disorder parameter is a function of the ionic radius of the $^{VI}M^{I}$ cation (Nyburg et al., 2000) and that, in the analysed thermal range, the sulphate group ordering process has the same dependence from T than alum-(K).

Acknowledgments

This work was funded by Sapienza Università di Roma. The constructive review of David M. Jenkins and an anonymous reviewer is kindly acknowledged.

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Submitted, June 2014 - Accepted, January 2015