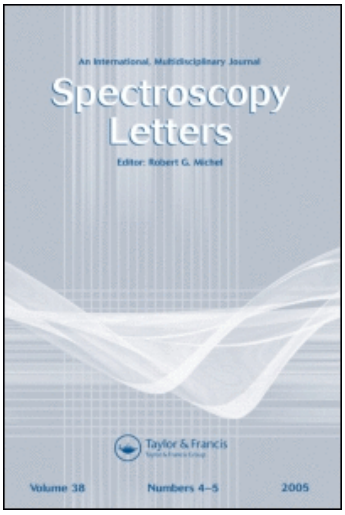

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Ft-Raman Study of Three Synthetic Solid Solutions Formed by Orthorhombic Sulfates: Celestite-Barytes, Barytes-Anglesite and Celestite-Anglesite

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FT-RAMAN STUDY OF THREE SYNTHETIC SOLID SOLUTIONS FORMED BY ORTHORHOMBIC SULFATES: CELESTITE-BARYTES, BARYTES-ANGLESITE AND CELESTITE-ANGLESITE

Key words: FT-Raman, solid solutions, celestite, barytes, anglesite

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ABSTRACT

In the present work, three different solid solutions whose end-members are the orthorhombic sulfates celestite ($SrSO_4$), barytes ($BaSO_4$) and anglesite ($PbSO_4$) are studied using FT-Raman spectroscopy. Sulfate anion symmetric internal modes have been examined in detail by means of band-shape analysis and component fitting procedures. The symmetric stretching mode $\nu_1(A_1)$ changes its wavenumber position linearly with the cationic composition of the samples which further confirms the ideal character of the solid solutions studied. The

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corresponding full-width at half-height is strongly increased in the central components of the different solid solutions which can be understood as an effect of the positional disorder induced by random cationic substitution. Similar results are observed in the symmetric bending mode, $\nu_2(E)$. The study of the low frequency spectral region permits one to differentiate traslational modes of the sulfate anion, which changes its wavenumber position when the alkali-earth metal ion changes from rotational modes. This permits the tentative band assignment of the anglesite rotational Raman bands at 134 and 152 cm^{-1}, which were previously not assigned.

INTRODUCTION

The study of those solid solutions formed by sparingly soluble orthorhombic sulfates (namely $BaSO_4$ barytes, $SrSO_4$ celestite, and $PbSO_4$ anglesite) has received considerable attention in recent years[1-4]. Geochemical, mineralogical, industrial and environmental reasons justify this interest (*see* [5-6] *and references therein*).

Although mechanistic[7], kinetic[8] and structural[9] studies dealing with the three binary solid solutions formed in the system $BaSO_4$-$SrSO_4$-$PbSO_4$ have been published, the vibrational dynamics of such solid solutions has not been studied, to the best of our knowledge. This lack of data contrasts with the numerous available references on Raman and infrared studies of the corresponding simple sulfates[10].

The present work reports the analysis of the three binary solid solutions formed in the system $BaSO_4$-$SrSO_4$-$PbSO_4$. The samples obtained by precipitation are studied by means of powder X-ray diffraction and FT-Raman spectroscopy. The experimental results allow the calculation of the unit cell dimensions of the samples and to study the ideality of the solid solutions obtained. The FT-Raman spectra are analyzed in detail, including band-fitting of the low frequency spectral region.

EXPERIMENTAL

Samples were prepared by the method of Kornicker et al.[1], adding dropwise an aqueous solution with the appropriate quantities of the cations (as nitrates, 0.25 M) to 6 M sulfuric acid at 60-65 °C with vigorous stirring. The stoichiometry of the precipitates was determined by dissolution of ca. 0.1 g (accurately weighed to ±0.1 mg) in 100 mL of 0.02 M Na_2EDTA at pH 10.8. The excess of chelating agent was subsequently determined with Ca^{2+}. Triplicate analyses were run for each sample. The observed stoichiometries of the cations were always within ±2% of their nominal value.

X-ray diffraction was carried out using a Philips PW 1710 automatic diffractometer with Cu K_α radiation (wavelength = 1.54056 Å), automatic divergence slit and graphite monochromator. Scanning rate (from $2\theta = 5°$ to 70°) was 0.5 ° min^{-1} using Si as an external standard.

FT-Raman spectra were excited at 1064 nm using an Nd:YAG laser and a Bruker IFS66 optical bench with a FRA 106 Raman accessory. Laser power was set at ca. 100 mW and 1000 scans were accumulated with a resolution of 2 cm^{-1}. Powdered samples were lightly pressed in the Bruker powder holder and mounted with 180° scattering geometry. The mathematical (curve fitting) treatment of the spectra was carried out using the commercial software GRAMS/32® (Galactic Industries). Smoothing procedures or baseline correction routines were not applied in this work. All the figures in the paper are produced from integrated intensity-normalized spectra.

RESULTS

Figure 1 shows the evolution of the unit-cell parameters against the chemical composition of the samples. Well-fitted linear plots are obtained in all the cases (see Table 1), which demonstrates that the solid solutions studied obey Vegard's law. This observation can be understood as a first index of ideality. Table 2 summarizes the unit-cell dimensions in the end-members of the solid solutions (pure phases). As can be observed, these are very close to the last reported

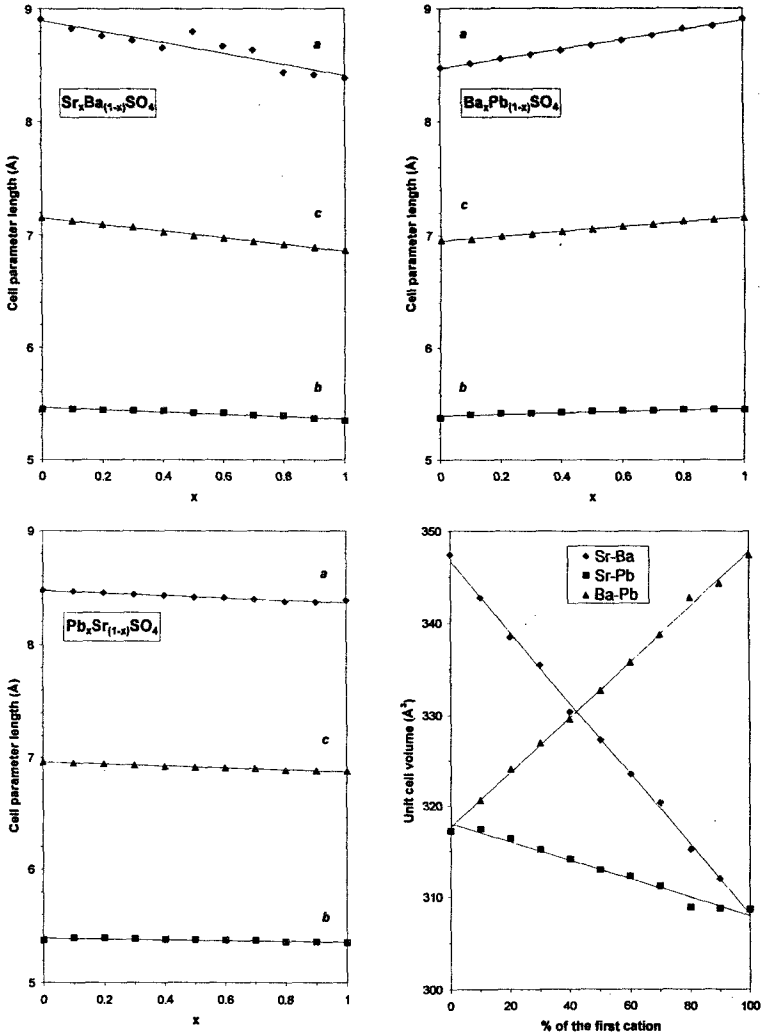

FIG. 1. Evolution of the unit-cell parameters against the chemical composition of the samples.

TABLE 1

Linear Fitting of the Unit Cell Parameters (*a, b, c*: Å ; V: Å^3) against the Mole Fraction *x*. s.e. = standard error; s.e.e. = standard error of the estimate.

			$Sr_xBa_{(1-x)}SO_4$			
Parameter	*Intercept*	*s.e.*	*Slope*	*s.e.*	r^2	*s.e.e.*
a	8.8991	0.0396	-0.4871	0.0669	-0.9245	0.0702
b	5.4642	0.0060	-0.0958	0.0101	-0.9534	0.0106
c	7.1505	0.0045	-0.2856	0.0075	-0.9969	0.0079
V	346.68	0.32	-38.608	0.538	-0.9991	0.56
			$Ba_xPb_{(1-x)}SO_4$			
Parameter	*Intercept*	*s.e.*	*Slope*	*s.e.*	r^2	*s.e.e.*
a	8.4664	0.0043	0.4311	0.0073	0.9987	0.0076
b	5.3970	0.0055	0.0651	0.0093	0.9192	0.0098
c	6.9542	0.0025	0.2051	0.0042	0.9981	0.0044
V	317.66	0.25	30.156	0.424	0.9991	0.44
			$Sr_xPb_{(1-x)}SO_4$			
Parameter	*Intercept*	*s.e.*	*Slope*	*s.e.*	r^2	*s.e.e.*
a	8.4720	0.0050	-0.1028	0.0085	-0.9708	0.0089
b	5.3942	0.0044	-0.0380	0.0075	-0.8596	0.0079
c	6.9584	0.0017	-0.0886	0.0029	-0.9952	0.0031
V	317.98	0.32	-10.032	0.536	-0.9874	0.5626

TABLE 2

Unit-cell Parameters of the End-members. All data in Angstrom (Å).

	$BaSO_4$		$SrSO_4$		$PbSO_4$	
	Observed	*Ref.[11]*	*Observed*	*Ref.[11]*	*Observed*	*Ref.[11]*
a	8.909	8.879	8.390	8.354	8.475	8.472
b	5.449	5.454	5.351	5.346	5.376	5.397
c	7.156	7.154	6.874	6.867	6.962	6.955
V	347.4	346.4	308.6	306.7	317.2	318.0

structure refinement[11] which is remarkable taking into account the nature of the precipitation of the solid solutions studied here.

Figure 2 shows the FT-Raman spectral region corresponding to the sulfate ion symmetric stretching $\nu_1(A_1)$ fundamental in several samples of the solid solutions. These are fairly symmetric bands whose Raman wavenumbers change linearly with the chemical composition of the samples (Figure 3, left).

The behavior of the corresponding half-widths (measured as the full-width at half-height, FWHH) (Figure 3, right) deserves some comments. The solid solutions which contain lead ($Ba_xPb_{1-x}SO_4$ and $Sr_xPb_{1-x}SO_4$) have a bimodal tendency with a maximum near the central points being observed, similar to that reported in other solid solutions[12,13]. However, the system barytes/celestite ($Ba_xSr_{1-x}SO_4$) shifts from this behavior and the FWHH changes linearly between both extremes. This observation could result from the geochemical similarity between barium and strontium ions; furthermore, their influence on the sulfate anion vibrational dynamics is very close, as can be deduced from the reported stretching and bending force constants of sulfate in barytes, celestite, and anglesite[14].

Figure 4 shows the symmetric bending mode $\nu_2(E)$ in samples of the different solid solutions. As in the $\nu_1(A_1)$ fundamental, the difference between the celestite/barytes solid solution and those which contain lead is evident. In Figure 5, left, the evolution of the band group center of mass is plotted against the chemical composition. As can be observed, this parameter does not change along the range of substitution in the celestite/barytes solid solution. However, the shift between the components of this doubly degenerate fundamental is very sensitive to the changes in the chemical composition, as shown in Figure 5, right. As already reported for other solid solutions[12,13], the shift between the components of a degenerate fundamental tends to decrease in the central members of a solid solution as an effect of the local disorder. Thus, the observed shift decreases abruptly in the first members of the series, increasing later, because anglesite shows the greatest shift between the components (11.4 cm^{-1}). A similar, although attenuated, effect can be observed in the celestite/barytes solid solution.

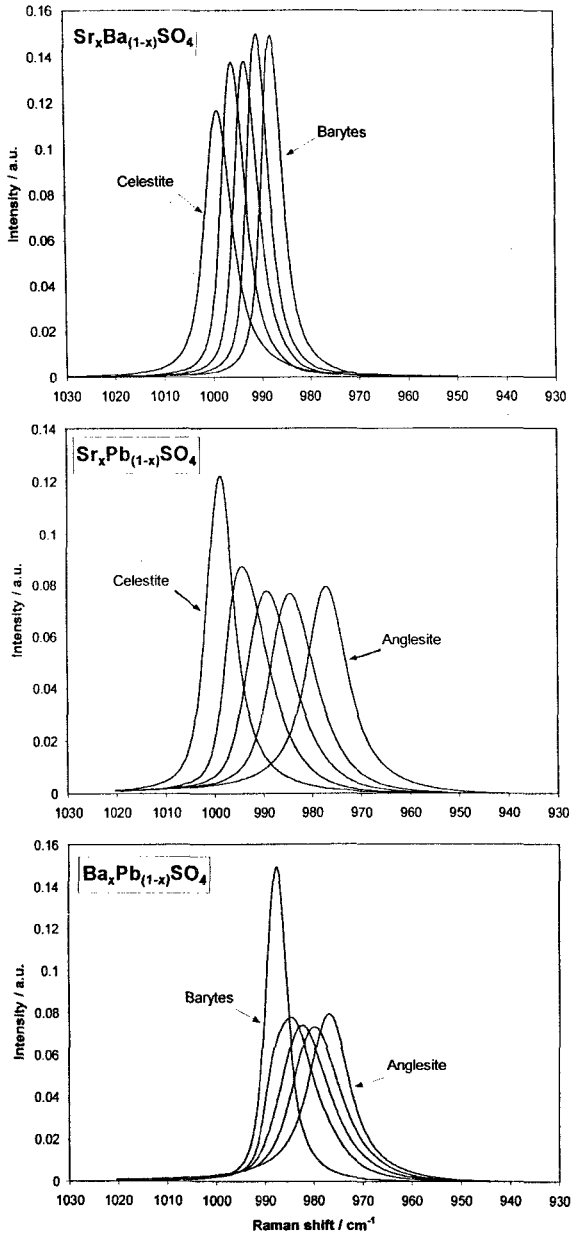

FIG. 2. Sulfate anion symmetric stretching $\nu_1(A_1)$ spectral region in the end-members and several samples of the solid solutions. The mole fractions, x, of the corresponding cation are 0.3, 0.5 and 0.7.

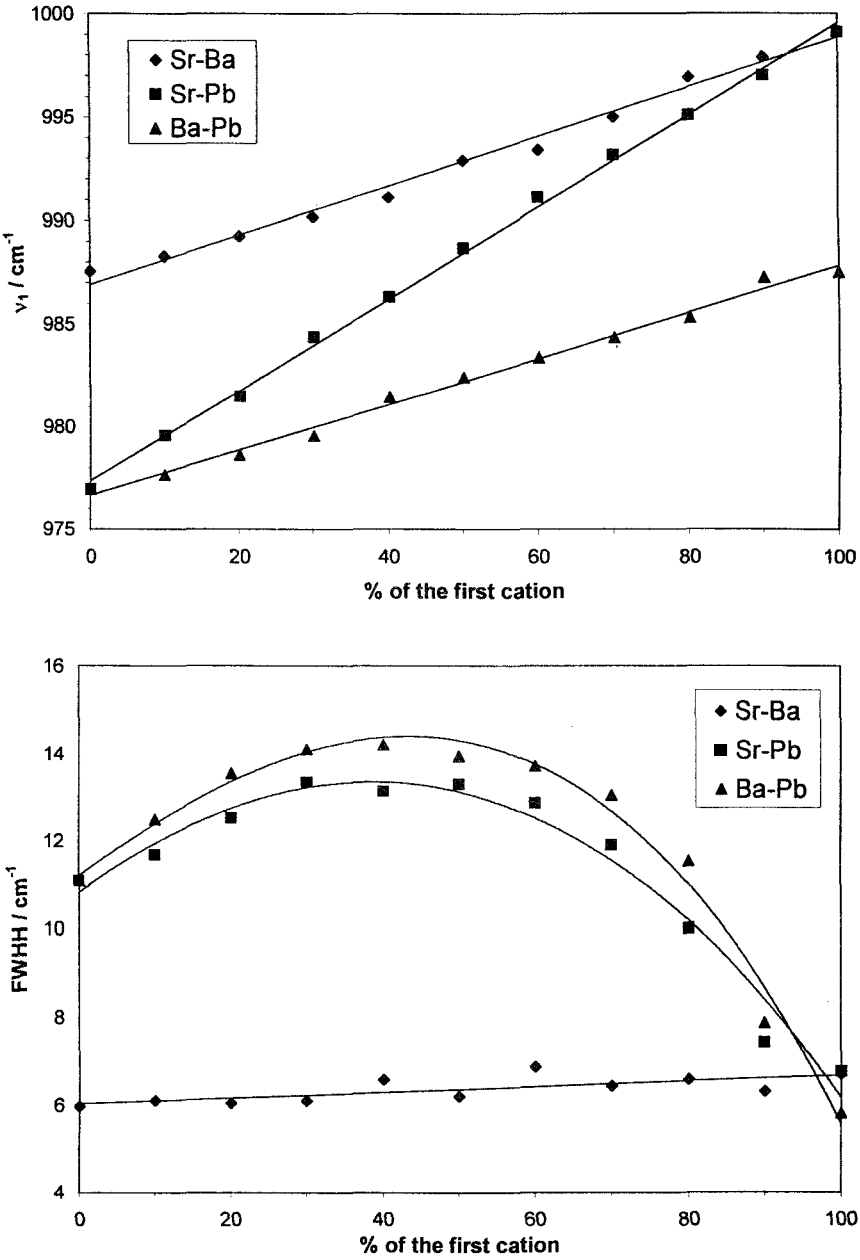

FIG. 3. (Top) Wavenumber of the sulfate anion symmetric stretching band against the chemical composition of the samples. (Bottom) Band full-width at half-height.

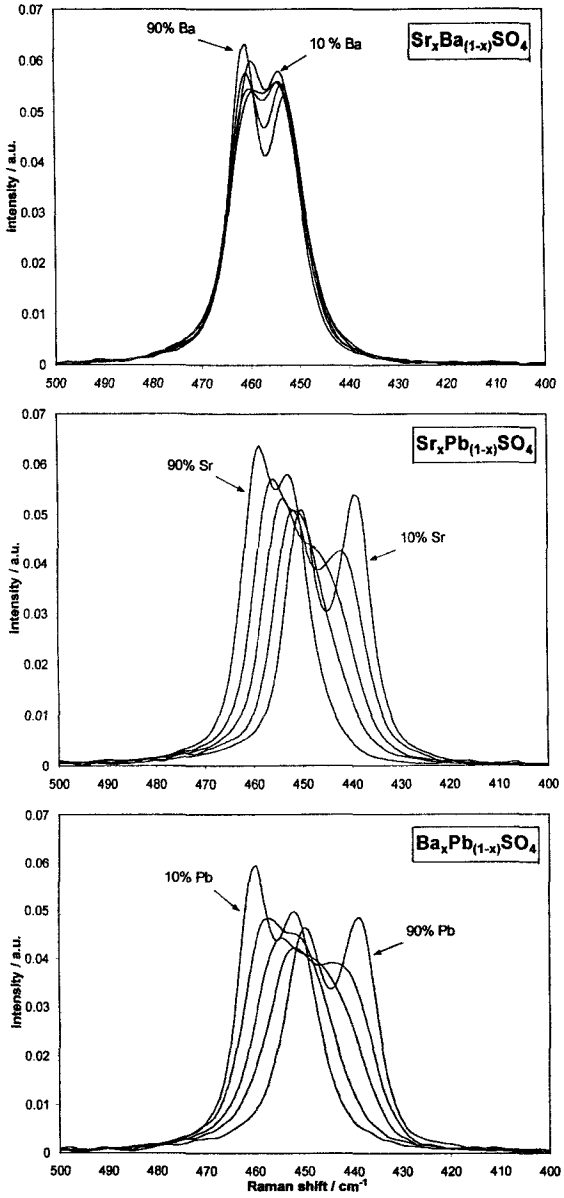

FIG. 4. Sulfate anion symmetric bending $\nu_2(E)$ spectral region in the end-members and several samples of the solid solutions. The mole fractions, x, of the corresponding cation are 0.3, 0.5 and 0.7.

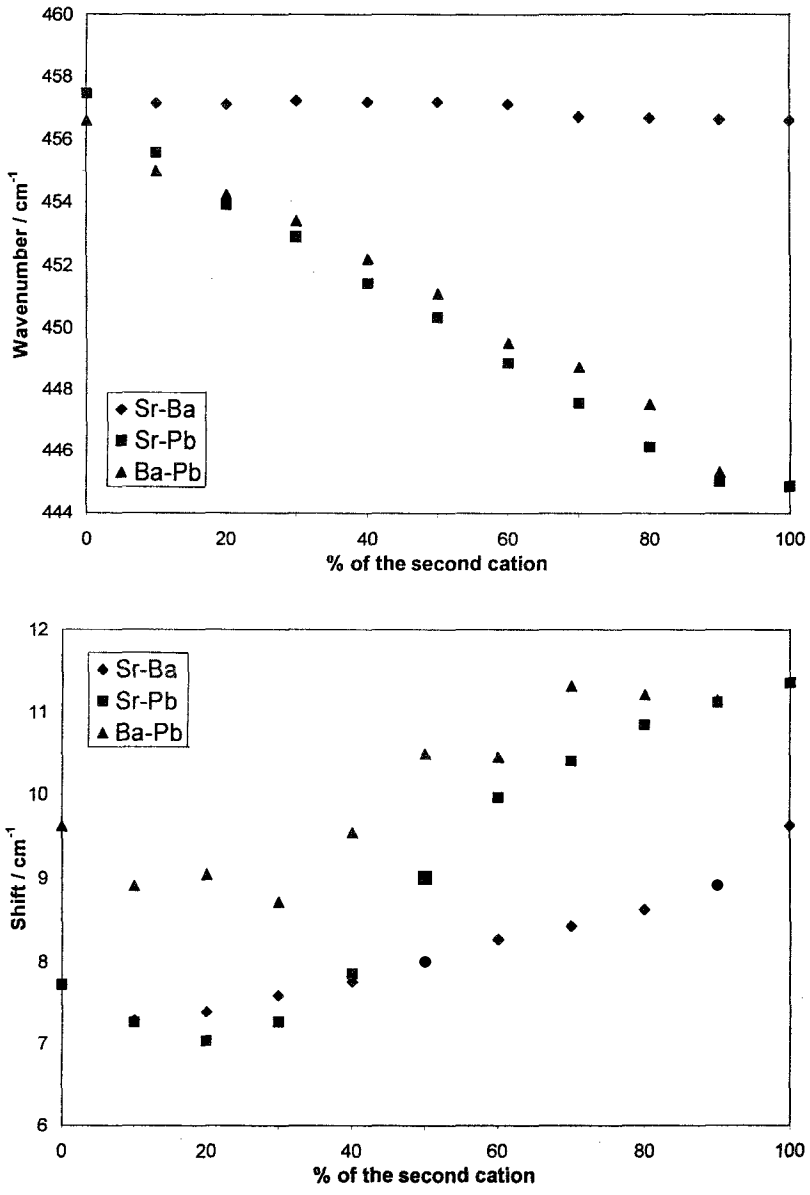

FIG. 5. (Top) Wavenumber of the sulfate anion symmetric bending band against the chemical composition of the samples. (Bottom) Band full-width at half-height.

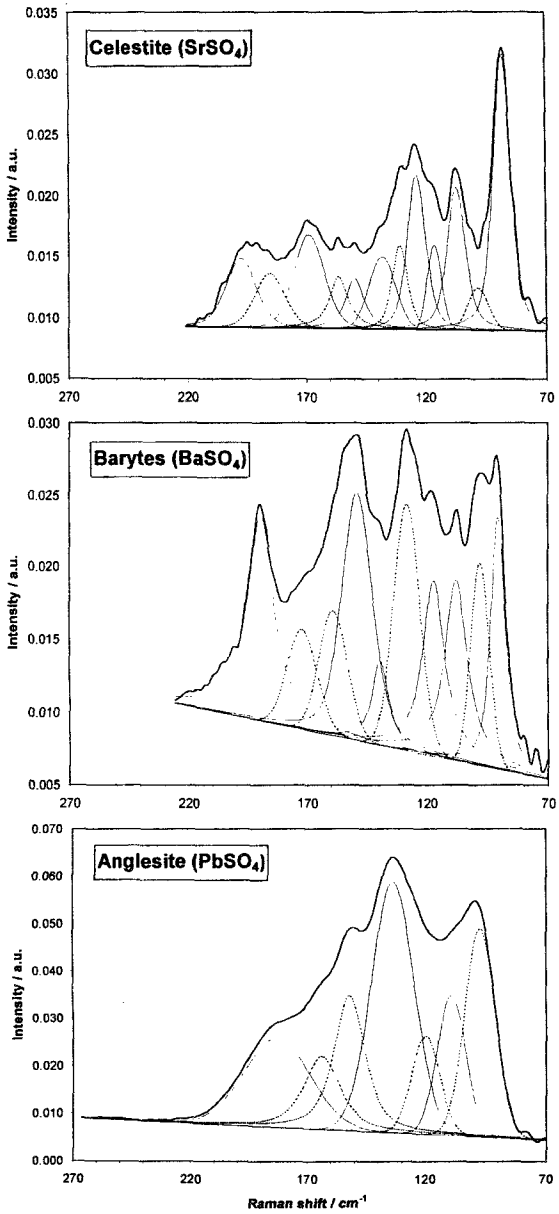

FIG. 6. Band-fitted low frequency spectral region down to the experimental limit of 70 cm^{-1} in the end-members (single phases) of the solid solutions studied. Components represented in broken line correspond to rotational (R) modes.

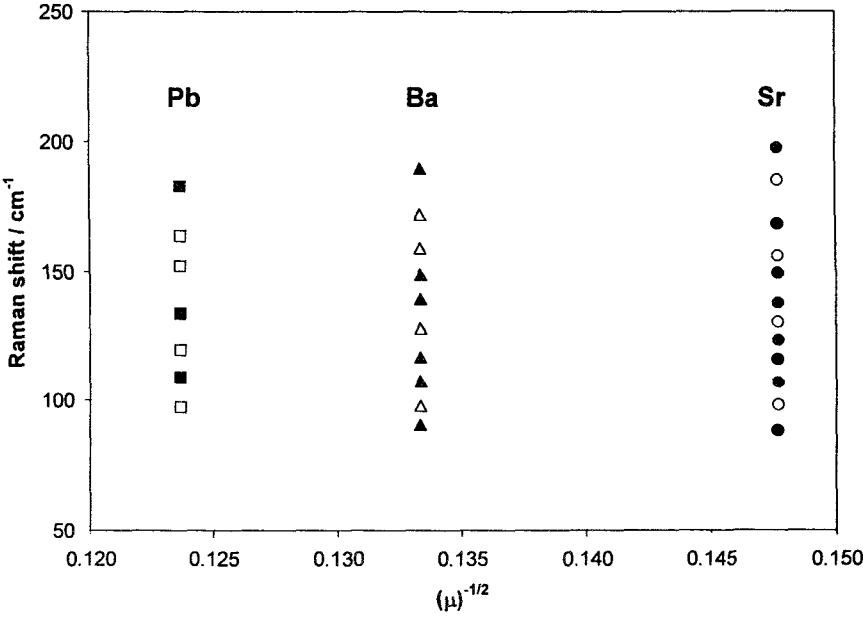

FIG. 7. Wavenumber of the low frequency fitted components against the square root of the inverse cationic mass. Open symbols correspond to rotational (R) modes.

Figure 6 shows the low frequency spectral region down to the experimental limit of 70 cm^{-1} in the end-members (single phases) of the solid solutions studied. External modes can be conveniently divided into translations (T) and rotations (R). The former imply mainly the cation/anion interactions whereas the rotations are characteristic librations of the anion. The R modes appear at wavenumbers which are nearly independent of the cation present in the structure (see Figure 7). The decrease in the number of components observed in barytes and, more clearly, in anglesite is due to the experimental limit (70 cm^{-1}) of the FT-Raman spectrometer which precludes the observation of the lower wavenumber spectrum.

As the T modes decrease their frequency when the mass of the cation increases, observed in Figures 6 and 7, several external modes of the samples

studied, mainly in anglesite, must appear below the limit of observation. In any case, all these external modes are very weak in the FT-Raman spectra[13,15,16]. The cationic substitution promotes the broadening of the T components which further hinders the rigorous analysis of this spectral region. However, the spectral study of those solid solutions which contain lead has enabled us to assign as rotations the anglesite Raman bands at 134 and 152 cm^{-1}, which were previously not assigned[15], since their wavenumber position and half-widths remain very approximately constant despite the cationic substitution.

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